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The use of Green's Functions in Quantum Chemistry

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Abstract

Modern quantum chemical calculations commonly use wave function based models or densitry functional theory (DFT). Using Green's functions is an approach that has not been explored much, and is one that has only been explored relatively recently, with older examples being useful, but limited in scope. The use of Green's functions in literature, historically and contemporary, is outlined and explored, with a focus on the self-consistent second order Green's function (GF2), as well as the GW-approximation.

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1 Introduction

When creating models of molecules, there is a balance to be made between computability and accuracy. As such, finding computationally intensive tasks that can approximated or simplified was an important part of early quantum chemistry. One of the early approximations found was the Born-Oppenheimer approximation; briefly, it states that as the motion of the nuclei is in a different order of magnitude than that of the electrons, they can be treated separately. Under this assumption, the total wave function can be multiplicatively separated into two parts; an electronic wave function, ψ_e, which depends on the positions of the electrons, and where the positions of the nuclei are constant, and a nuclear wave function, ψ_n, which solely depends on the position of the nuclei.

This leads to electronic structure theory. As excitation energies are for many systems not significantly affected by the wave function of the nucleus, finding observables only requires looking at the electronic wave function. This is the domain of electronic structure theory; a collection of models describing the motion and states of electrons in compounds.

Obtaining the electronic wave function is not simple, as there is no analytical solution beyond the one-electron case. Further approximations are thus necessary, the most widely used and most basic of which being the Hartree-Fock approximation. Hartree-Fock is very non-intensive, computationally, and gives relatively good results. It is also the basis for many other methods, collectively referred to as post-Hartree-Fock methods.

Although the Hartree-Fock approximation can be made more accurate by adding more basis functions, it has a limit, known as the Hartree-Fock limit. This is the energy obtained when using an infinite set of basis functions. It is not equal to the exact energy of the system, and the difference between these two values is known as the correlation energy. Minimising this correlation energy is the goal of many post-Hartree-Fock methods, while others seek to eliminate it entirely.

Correlation energy can be divided into two broad categories - in other words, the deficiency of the Hartree-Fock approximation can be split twofold. These categories are static and dynamic correlation. Where dynamic correlation concerns itself with the motion of electrons and how Hartree-Fock does not properly describe it, static correlation covers the rest - correlation that can be described without referring to the motion of electrons. Post-Hartree-Fock methods usually differentiate themselves from basic Hartree-Fock by using static and/or dynamic correlation to make accurate and computationally easy calculations on a specific subset of systems - sometimes at the cost of lowering accuracy in other circumstances. Møller-Plesset perturbation theory, for instance, is known to diverge when energy levels lie close to the ground state for a given geometry.

Density functional theory (DFT) is a quantum chemical method that is not based on the Hartree-Fock approximation, but has some similar errors. Instead of using a set of spin-orbitals, it uses an average electron density. While it is not computationally expensive, especially compared to Hartree-Fock and its derivatives, it suffers from inaccuracies in exchange and correlation energies. This can be rectified by using DFT corrections, but they increase the computational cost.

All of these methods have a common objective, as described earlier: finding the electronic wave function, using it to find properties of the molecule using operators. However, there is an alternative to the wave

function itself; Green's functions. One large advantage of the Green's function over the wave function is that it contains a lot more information of the system, and thus has access to a different amount of observables, and different areas of mathematics can be taken advantage of. As the Green's function often depends on time - or rather, the difference between two points in time - using a Fourier transform to move into frequency-space is natural. Fourier transforms can be performed to switch between observables. However, this comes with a major issue; finding an analytic Green's function is, as with the wave function of most systems, not possible. In addition, finding an approximate Green's function is also difficult - not only does it require a significant amount of storage space, but many of the devised methods capable of creating an approximate Green's function are unsatisfactory.

Despite these faults, a number of methods have been explored successfully, and finding an appropriately accurate approximate Green's function is no longer prohibitively expensive. The usage of Green's functions in quantum chemistry is increasing for select problems, and select examples will be described and explored in this paper, with use cases and drawbacks highlighted.

2 Theory

2.1 Quantum Chemistry

Quantum chemistry, as a field, has developed to meet the need for modelling chemical events - including reactions, spectroscopy, thermodynamical properties, and more. It involves using quantum mechanical properties to create models that can be used to get a description of the state, from which observables can be attained. The wave function version of this is the application of operators to the wave function of the state;

$$\hat{\Omega}\,\Psi = \omega\,\Psi \tag{2.1}$$

where $\hat{\Omega}$ is the operator for a given observable, Ψ is the wave function and ω is the eigenvalue of the operator. In computing, the operator is commonly replaced by a matrix, and the eigenvalue by a list of eigenvalues. An example of this is obtained by replacing the general operator with the Hamiltonian; this gives eigenvalues in terms of energy, and is how energy levels are obtained from wave functions.

As any system beyond a one-electron state is not analytically solvable, approximate solutions are required. This can be simplified by using the Born-Oppenheimer approximation. It states that since the mass of the nucleus and the electrons are orders of magnitude apart - and thus momentum, giving a large difference in velocity - they can be treated separately; the nucleus does not react to any individual movement of the electrons, only the average, and it does not need the position of the electrons as variables. The electrons, moving quickly and not observing a significant change in position of the nucleus, can treat the position of the nucleus as a parameter and not a variable. This approximation has shown itself to significantly ease the cost of computing systems, without a significant reduction in the accuracy of results [1]. As quantum chemical calculations generally require a high degree of accuracy due to the differences even a few percentage points can make to the properties of a system, it is a very successful approximation, and is used in most quantum chemical methods [2].

2.2 Modelling systems

The core of modern quantum chemistry is, of course, its models and their variations. Historically, wave function based methods have dominated, of which a large subset are post-Hartree-Fock methods. The basic Hartree-Fock method, being a cheap and somewhat precise method in the right circumstances, fails to account for some electron-electron interactions. This has the consequence that it . At its core, it uses two approximations: the Born-Oppenheimer approximation, and the approximation that the wavefunction can be represented by a linear combination of constituent one-electron spin orbitals. The second assumption does not include Coulomb correlation, a form of electron correlation. This is the main disadvantage of Hartree-Fock, as it is not solvable by adding more basis orbitals, and corrections are required for more accurate results [3].

2.2.1 Full Configuration Interaction

Full configuration interaction (FCI) is, simply put, a post-Hartree-Fock method that uses a linear combination of Slater determinants - "configurations" - to describe a system. It is an exact method, but runs into the problem of being prohibitively expensive for anything but small systems. However, it is still an excellent tool for benchmarking other systems, and is used on very small molecules to great effect.

2.2.2 Coupled Cluster

While Hartree-Fock only takes into account the ground state and single-excitations (as outlined by Brillouin's theorem [4]), and FCI uses a linear combination of all excitations, coupled cluster uses exponential operators to create a linear combination without using the variational principle on other excitations than the first. This means that the method only needs to variationally find the solution of each excitation, and not the combination, which is predetermined. This is still a more expensive method than Hartree-Fock, but when compared to similarly advanced methods, it is relatively cheap and useful for many systems. There are three main categories of coupled cluster models; single-double, triple, and quadruple. Single-double, being the cheapest and least accurate, only adds single and double excitations, whereas triple and quadruple add triple and quadruple excitations, respectively. Computationally, each step leads to a large jump in computational cost, but with an increase in accuracy [5] [6].

2.3 Methods not based on Hartree-Fock theory

The starting point for most models include Hartree-Fock or similar theory, but there are many that use different starting points. The most widely used of these, after it became feasible for quantum chemical purposes in the 90s, is density functional theory. It is not a many-body model, and uses electron density instead of wave functions of individual electrons and orbitals to find energy levels and results. This has the effect of sometimes having simpler calculations, with a whole different realm of methods becoming available that are not available to Hartree-Fock based theories, among them the GW-approximation.

DFT is also well suited for oxides and systems where conduction is relevant, as it describes insulating and conducting behaviour somewhat well, especially with corrections. Among these corrections is GW-theory, which is based on Green's theory.

2.4 Green's functions

Green's functions are similar to wave functions, in that both contain a lot of information about the system, including position, momentum, energy, et cetera. However, Green's functions also contain more information about the system at different points in time, as well as direct access to thermodynamic properties without needing to calculate and apply Boltzmann factors in parallel - increasing computational complexity. Whereas wave functions are probability amplitudes, the equivalent Green's functions are not as easily physically related to physical concepts. On the other hand, Green's function still includes a lot of easily extractable information about the system it describes - including time-dependent information. In fact, it contains so much information that one of the primary problems in using Green's function to model system accurately is its immense storage space requirements. The different levels of information about the system, as well as the natural inclusion of temperature in Green's functions, lead to some important consequences for the usage of the two functions; for instance, while temperature dependence has often been added ad hoc to preexisting models, it arises naturally from the language of Green's functions. As temperature is intimately related to thermodynamic concepts, this provides some context as to why Green's functions are especially useful for thermodynamics.

On a more practical level, using Green's functions to obtain information about the system has some important drawbacks. For instance, you need perfect information of the system to form a perfect Green's function, which creates something of a chicken or the egg situation. However, like with wavefunctions, there are plenty of approximations available - however these add another layer of complexity

Mathematically, a Green's function is any function that is a solution to an inhomogeneous differential equation,

$$[z - L(r)]\, G(r, r'; z) = \delta(r - r'), \tag{2.2}$$

where $z \in \mathbb{C}$, L(r) is any linear, Hermitian differential operator, $\delta(r - r')$ is the Dirac delta function and $G(r, r'; z)$ is a Green's function, with r and r' as positional variables and z as a parameter [7]. For instance, by replacing L(r) with the Hamiltonian and z with the complex parameter E (for energy) [8] [9], the following equation is obtained:

$$[E - H(r)]\, G(r, r'; E) = \delta(r - r'). \tag{2.3}$$

This is similar to the Schrödinger equation,

$$[E - H(r)]\, \psi(r) = 0 \tag{2.4}$$

and, indeed, equation (2.3) is related. In an analysis of energy levels, the energies are represented by the position of poles, which are all positioned along the real axis in the complex plane. As Green's function exists in a Hilbert space, Fourier transforms can be used to change between different observables; energy, momentum, position, et cetera [10]. In other words, where observables from wavefunctions come from finding the eigenvalues of an operator, the observables from Green's function comes from complex analysis of the function in the relevant Fourier space.

2.5 GW approximation

The GW approximation is an approximation used to calculate the self-energy of many-body systems, being especially useful for improving results in the realm of electronic structure and in better predicting insulating, conducting and semiconducting properties of systems [11] [12] [13]. The G stands for Green's function, which is the system on which it is based, while the W represents screened coulomb interaction. It is essentially a truncated series containing only first element,

$$\Sigma \approx iGW, \tag{2.5}$$

hence the name [13] [14] [15]. It is useful for determining quasiparticle excitations [16], allowing for quantum chemical calculations to more accurately describe spectroscopic qualities [17].

3 Discussion

Early work in quantum chemistry using Green's functions mostly focused on electron gases and theoretical developments, with few real cases, like Hartree-Fock and its derivatives saw. The GW approximation started being used around the time DFT rose in usage around the 90s, while ab initio methods based on Green's functions weren't developed until a few decades later.

Electron gases were actively studied in the 50s and 60s, and it was found that Green's functions could be used to great effect [18]. As a specific example, Green's function helped provide perspective on the electron gas problem, which was a failure of models to predict the behaviour of electrons in the metallic density region [19]. Other methods failed for various reasons; for instance, Hartree-Fock predicts the wrong asymptotic behaviour for the integral of the pair correlation function; in short, this means that for areas where the pair correlation function is relevant to what observables are being observed, the result is wrong. This happens, in this case, around the metallic density region [20] [21].

However, in the 20-year period following 1970, there were few papers published. While the field of quantum chemistry was growing, Green's functions were not utilized to a great extent. As Green's functions are powerful and useful in other fields, and have been useful in some recent areas of quantum chemistry, this indicates that Green's functions are potentially underused compared to its potential.

Some potential reasons as to why Green's functions remained underused and not utilised for decades is its storage requirements, how computationally expensive it is, and a lack of contemporary, relevant literature - a vicious circle. Computationally, Green's functions are not expensive relative to modern methods, like the post-Hartree-Fock methods in wide use today. However, it is expensive compared to Hartree-Fock and other methods in use around the birth of computational quantum chemistry in the 50s and 60s. When combined with the large amounts of storage space required - often being the bottleneck of computations of large systems, even today - leads to it being disregarded in favour of other models, like the Hartree-Fock family and DFT. Major advances in the use of Green's functions often revolve around

saving storage space[22], which is reflective of its disadvantages and how they are still relevant, even if they are mitigated by the advancement of technology and general development of Green's functions.

In a 1999 article on electron propagator theory[23], which is based on Green's functions, the author summarises the theory behind the method, as well as some advantages and disadvantages. Among them, one that stands out include the ease at which spectroscopic quantities can be obtained. This is an important part of quantum chemistry, as spectroscopy is a bridge between the quantum scale and larger scale chemistry. Spectroscopy gives insights into the structures of solids, as well as better tools for analysing compounds; and having quantum chemical models that can predict structures is immensely useful to the chemistry community.

One of the more recent developments in creating new models is the Zgid group's efforts; in a 2019 paper, Shee and Zigd uses a CCSD method as a solver for for Green's function embedding methods[24]. The paper focuses on benchmarking the Green's function CCSD solver in comparison to ordinary CCSD, as well as comparing different base models, namely GF2 and HF. They found that GF2 outperformed HF, but as the thrust of the paper was benchmarking CCSD, the main conclusion of the paper is that the CCSD Green's function solver results align well with that of FCI for the 1D Hubbard model[25]. They do point out, however, that this is a perfect case for CCSD, which suggests that it is not indicative of most use cases of CCSD.

3.1 GF2

As for the actual use of Green's function, among the most prominent work recently is that of the Zgid-group. In a 2015 paper, they use perturbation theory to create a new method they call GF2, or 2nd order perturbed Green's function[26], and compare it to a method based on second-order Møller-Plesset perturbation theory (MP2). It is a method that is broadly similar to GF2, and is comparable in most areas. They show that, when it comes to the divergence of MP2 - which is a known problem for the method - GF2 performs better, avoiding it altogether. They also show that it adequately describes insulators, metals and Mott insulators - simultaneously. This is something of a trademark for the Zgid group; finding areas where Green's function has potential, and then using it to great effect.

The same group also examined the errors of the method. Using H_2 as a sample molecule, they found fractional charge error and fractional spin error, comparing it to other methods. It performed well consistently, having relatively low fractional spin and fractional charge error. They again point out MP2, as it seems comparable to GF2[27] [26], and indicate that while GF2 greatly improves upon the chronic divergences of MP2, it also keeps the excellent behaviour of MP2 in the areas where it is known for performing well. For instance, while MP2 has very low fractional charge errors compared to other similarly expensive methods, it suffers from high fractional spin errors. GF2 has similar fractional charge errors, *and* does not share the high fractional spin errors.

Of course, it is hard to examine Green's function and its use in quantum chemistry without touching on temperature dependence and the use of Matsubara Green's functions. Again returning to the Zgid group, a 2016 paper on storage space saving for Matsubara Green's functions[22] [22]. developed a method for lowering the amount of data needed to be saved. As one of the major drawbacks of the Green's function is the large amount of storage space required, this indicates that future calculations using Matsubara

Green's functions can be greatly simplified. As quantum chemical modelling requires a high degree of accuracy - small variations in energy levels and energy level differences can lead to very different chemical processes happening - the number of grid points is immense, and running out of computer memory is a real concern. However, the authors recognised that while you need two different Green's functions for finite-temperature calculations, the Matsubara Green's function is a smooth, slowly changing function; in other words, a given point can be interpolated from surrounding grid points. Using cubic spline interpolation - a form of polynomial interpolation that avoids excessive oscillation - the authors removed 95% of grid points without losing the accuracy required for quantum chemical calculations.

GF2 has gone through further study; in a 2016 paper [28], Rusakov and Zgid describe Green's function and its relation to Mott insulators. As a test structure, the model is used on a one-dimensional hydrogen lattice. Again comparing to MP2, they show that GF2 does not diverge where MP2 does in the same situation. Running the simulation with a range of interatomic distances, they found that it effectively described the transition from metallic to insulating behaviour, including both band and Mott insulation. However, they point out that the convergent behaviour of GF2 is not necessarily true for dimensions above the first, as it was the only one they examined. They also use the model self-energy embedding theory (SEET) for some parts of the calculation.

Further developed in 2017 [29], the model is a QM/QM theory (meaning the system and its environments are treated by different quantum mechanical methods), and is a Green's function embedding method. Prior to the developments this paper provided, it had a functional form that had several drawbacks, including a loss of the self-energy matrix during the course of the method. It is used in many of the preceding papers described, especially the papers from the Zgid group, as a useful embedding tool based on Green's functions.

In a 2018 doctoral thesis [30], the author investigates the accuracy of GF2 in relation to thermodynamic properties. Using a second-order perturbative temperature-dependent Green's function, they show that the method is sufficiently accurate for quantum chemical purposes for high temperatures, and is adequate for lower temperatures. To benchmark the method, they compare it to FCI and Hartree-Fock over different temperatures, using HF as a sample molecule. Over the entire range of temperatures, ranging from 10^3 K to 10^8 K, GF2 performed well, surpassing Hartree-Fock for most temperature points. Importantly, it also overperformed compared to Hartree-Fock for entropy, suggesting that Green's functions are well suited for examining temperature dependence.

3.2 GW approximation

Green's functions also show promise in other areas of molecular modelling; in a 2015 paper, researchers from Chicago developed a method based on DFT and Green's functions, creating a model that successfully predicted properties of systems with numbers of electrons exceeding 1000 [17]. Using a non-self-consistent GW approximation, they were able to avoid matrix inversions and explicit calculations of virtual electronic states, significantly lowering computational cost while seemingly maintaining good results. In other words, they were able to run large scale calculations using a simple DFT calculation, followed by perturbation using a Green's function, finally obtaining usable results. This is another example of Green's functions being used in conjunction with other methods. Given that the strength of Green's functions in quantum chemistry is it not necessarily its speed, but rather the information it explicitly contains, and additional

factors like temperature dependence, this trend becomes understandable [31] [32].

Another paper, also using the GW-method, explores quasiparticles and their behaviour and energies [33]. As before, they used DFT as the base and GW many-body perturbation as a correction, creating a model that allows for GW-correction of large systems. While the model yields a distribution, rather than exact values, it also reduces the scaling from polynomial to near linear ($O(N^{1.06})$). As the GW-correction is normally expensive, this is a significant development, allowing for large-scale computations. In a provided example, they use the model on a nanocrystal of silicon, $Si_{705}H_{300}$. As there are 3120 valence electrons in this system, calculations on this system using normal GW-corrections would be highly expensive. Instead, the method developed seems to be usable on any DFT-made system, as the GW-correction was consistently cheaper than the system itself. Finally, the new method also saves on storage space, being proportional to the grid size.

4 Conclusion

Green's function is not widely used to represent systems and extract observables. As a consequence, it has not been as widely explored as many other quantum chemical methods, like Hartree-Fock, post-Hartree-Fock methods or DFT. A main reason for this seem to be that Green's functions are memory intensive, requiring large amounts of storage space. This is understandable, as one of the strengths of Green's functions is the amount of information they contain, however storage space has historically come at a premium. This has had the consequence that models based on Green's functions were infeasible.

With modern computing, Green's functions are becoming more manageable. This has lead to some research groups developing methods based on Green's functions, GF2 likely being the most developed example. Directly competing with MP2, it has many of the same advantages, but missing the characteristic disadvantages MP2 has, namely divergent behaviour for degenerate and near-degenerate energy levels. As such, it has seen success in modelling crystalline structures. As temperature naturally arises from the language of Green's functions, it has also performed well in finite temperature simulations.

An older, more developed method - the GW-approximation - has also been widely used for decades, and was one of the methods that lead to DFT being accurate enough for use in the 90s. It has historically been used to describe band structures and the properties of solids, with a focus on electronic structure, and recent developments has allowed faster methods to be used, including one that is almost linear - making it usable on nearly any system.

Among the most recent advances is the integration of Green's function into a CCSD method. This allows Green's function to be used on a wider variety of systems, and lets it compete directly with wave function based implementations of CCSD.

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