Ensemble Green's function theory for interacting electrons with degenerate ground states

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(Dated: July 19, 2019)

An ensemble Green's function formalism, based on the von Neumann density matrix approach, to calculate one-electron excitation spectra of a many-electron system with degenerate ground states is proposed. A set of iterative equations for the ensemble Green's function and self-energy is derived and a simplest approximation corresponding to an ensemble GW approximation is naturally obtained. The derivation is based on the Schwinger functional derivative technique and does not assume any adiabatic connection between a non-interacting and an interacting ground state.

PACS numbers: 71.20.-b, 71.27.+a

A wide range of electronic systems found in nature have degenerate ground states. Prominent examples are open-shell atoms and molecules, vacancy defects in solids, two-dimensional electronic systems, quantum dots under magnetic field, and frustrated magnets. The degeneracy often gives rise to many fascinating phenomena not observed in systems with well-defined non-degenerate ground state. For example, the Landau degeneracy in a two-dimensional electronic system leads to fractional quantum Hall effect[1] and the high degeneracy in frustrated magnets causes the system to fluctuate among the degenerate ground states even at temperature close to absolute zero, leading to emergent phenomena of fractional spin excitations and magnetic monopoles in spin ice [2, 3]. Apart from the fundamental interest, systems with degenerate ground states may find useful applications in, for example, quantum computing.

For systems with non-degenerate ground state, there are already well-established methods developed over many years. Density functional theory (DFT) is a widely used method to calculate ground-state properties [4, 5] and Green's function method within many-body perturbation theory (MBPT), such as the GW approximation (GWA), is routinely applied to study excited-state properties[6–9]. The situation is completely different in the case of systems with degenerate ground states. Although DFT has been extended to the degenerate case, it has not been applied extensively [10]. There is even less work in developing methods for computing excited-state properties of systems with degenerate ground states.

An early attempt to extend the Green's function method to the degenerate case, without any concrete computational procedure provided, is by Layzer in 1962 [11]. Later attempts of extending the method is the work of Cederbaum *et al* in 1970's, in which they considered open-shell atoms and molecules [12, 13]. Several works applying the GWA to systems with degenerate ground states have appeared recently in the literature. Attaccalite *et al* [14] and Ma *et al* [15] applied the GWA to defects in crystals but the problem with degeneracy associated with the open-shell was not explicitly considered. Lischner and co-workers assumed a certain form for the self-energy and a careful choice of the starting mean-field [16]. An earlier work by Shirley and Martin avoided the degeneracy problem by special selection of the reference state [17]. So far there is no general formulation based on the Green's function to treat systems with degenerate ground states. One of the main problems stems from MBPT that usually assumes an adiabatic connection between the true interacting ground state and a non-interacting ground state. This connection is no longer obvious for degenerate ground states. An alternative Green's function method for the degenerate case built upon the nonperturbative adiabatic approximation is by Brouder *et al* [18].

In this Letter, a Green's function theory based on the ensemble density matrix formalism in quantum mechanics pioneered by von Neumann in 1927 is proposed. An ensemble is characterized by the density matrix

$$\hat{D} = \sum_{i=1}^{M} w_i \left|\Phi_i\right\rangle \left\langle\Phi_i\right|, \quad \sum_{i=1}^{M} w_i = 1, \; 0 \leq w_i \leq 1, \tag{1}$$

containing the information needed to calculate physical properties of the ensemble [19]. M is arbitrary and each weight w_i determines the fraction of the ensemble in state $|\Phi_i\rangle$, with the states $\{|\Phi_i\rangle\}$ not necessarily being orthogonal. The ensemble average of any operator $\hat{O}$ is given by $\mathrm{Tr}(\hat{D}\hat{O})$. For example, for the density operator we find

$$\rho(r) = \mathrm{Tr}[\hat{D}\hat{\rho}(r)] = \sum_{i=1}^{M} w_i \left\langle\Phi_i|\hat{\rho}(r)|\Phi_i\right\rangle = \sum_{i=1}^{M} w_i \rho_i(r), \tag{2}$$

with $r = (\mathbf{r}, \sigma)$. This density is referred to as ensemble density.

Similarly, we define an ensemble Green's function as follows:

$$G(1,2) = \sum_{n=1}^{M} w_n G_n(1,2), \tag{3}$$

where a short-hand notation $1 = (r_1, t_1)$ etc. is used and auxiliary Green's functions G_n are defined in the

interaction picture according to

$$iG_n(1,2) = \frac{\left\langle \Psi_n | T[\hat{S}\hat{\psi}_D(1)\hat{\psi}_D^\dagger(2)] | \Psi_n \right\rangle}{\left\langle \Psi_n | \hat{S} | \Psi_n \right\rangle}, \quad (4)$$

where T is the time-ordering operator and

$$\hat{S} = T\exp\left[-i\int_{-\infty}^{\infty} d\tau \int dr \hat{\rho}(r,\tau)\varphi(r,\tau)\right]. \quad (5)$$

$\{|\Psi_n\rangle, n = 1, ...M\}$ are arbitrary many-electron states, chosen later as the set of degenerate ground states, with corresponding fractions w_n in which the system is prepared at some initial time point. The perturbing field $\varphi(r,t)$ is a virtual field that is used as a tool to derive the self-energy and it will be set to zero after taking functional derivatives of G_n. The choice of denominator in Eq. (4) is motivated later. The ensemble expectation value of any one-particle operator can be obtained from the ensemble Green's function as follows:

$$\begin{aligned}\left\langle \hat{O} \right\rangle &= \sum_{n=1}^{M} w_n \left\langle \Psi_n | \hat{O} | \Psi_n \right\rangle \\ &= -i\int dr \lim_{r'\to r} O(r)G(rt, r't^+). \end{aligned} \quad (6)$$

Each G_n fulfills the equation of motion similar to the one for a system with a non-degenerate ground state:

$$\begin{aligned}&\left(i\frac{\partial}{\partial t_1} - h(1)\right)G_n(1,2) - \int d3\Sigma_n(1,3)G_n(3,2) \\ &= \delta(1-2), \end{aligned} \quad (7)$$

with $h(1) = h_0(1) + V^H(1) + \varphi(1)$. Here, the ensemble Hartree potential V^H has been introduced:

$$V^H(1) \equiv \sum_{n=1}^{M} w_n V_n^H(1) \equiv \sum_{n=1}^{M} w_n \int d3v(1-3)\rho_n(3), \quad (8)$$

and a set of iterative equations for self-energies Σ_n can be expressed, analogues to the standard non-degenerate approach,

$$\begin{aligned}\Sigma_n(1,2) &= iG_n(1,2)v(1-2) \\ &+ i\int d3v(1-3)G_n(1,2)\frac{\delta V^H(2)}{\delta\varphi(3)} \\ &+ i\int d3d4v(1-3)G_n(1,4)\frac{\delta\Sigma_n(4,2)}{\delta\varphi(3)} \\ &+ \delta(1-2)\left(V_n^H(1) - V^H(1)\right). \end{aligned} \quad (9)$$

We now apply the above formalism to a system with degenerate ground states. The states $\{|\Psi_n\rangle, n = 1, ...M\}$ are chosen to be degenerate ground states with energy E_0. The corresponding weights $\{w_n\}$ are equal and given by $1/M$. For this choice, the ensemble Green's function contains the information for the ensemble average ground state energy, by the Galitskii-Migdal formula, and the one-particle excitation spectra. It is noteworthy that since the denominator in Eq. (4) is equal to unity, the definition of the ensemble Green's function for degenerate ground states is invariant under a unitary rotation within the degenerate subspace.

A key quantity in calculating the self-energy is the density response function, which in turns determines the screened interaction. Thus, within the ensemble analogue of the well-established GWA, which corresponds to setting $\delta\Sigma_n/\delta\varphi = 0$ in Eq. (9), the linear density response function is required in order to compute $\delta V^H/\delta\varphi$:

$$\frac{\delta V^H(1)}{\delta\varphi(2)} = \int d3v(1-3)R(3,2) \quad (10)$$

with the linear density response function:

$$R(1,2) \equiv \frac{1}{M}\sum_{n=1}^{M} R_n(1,2) \equiv \frac{1}{M}\sum_{n=1}^{M}\frac{\delta\rho_n(1)}{\delta\varphi(2)}. \quad (11)$$

Introducing the basis $b_\alpha(\mathbf{r}) = \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})$, where ϕ_i is the orbital associated with c_i, the spectral representation of R reads

$$R(\mathbf{r},\mathbf{r}';\omega) = \sum_{\alpha\beta} b_\alpha(\mathbf{r})R^{\alpha\beta}(\omega)b_\beta(\mathbf{r}'), \quad (12)$$

$$\begin{aligned}R^{\alpha\beta}(\omega) = \frac{1}{M}\sum_{n=1}^{M}\sum_{m\neq n}\Bigg[&\frac{\rho_{nm}^\alpha\rho_{mn}^\beta}{\omega - E_m + E_0 + i\delta} \\ &- \frac{\rho_{nm}^\beta\rho_{mn}^\alpha}{\omega + E_m - E_0 - i\delta}\Bigg], \end{aligned} \quad (13)$$

where $|\Psi_m\rangle$ is an eigenstate of the Hamiltonian with eigenvalue E_m, where $\rho_{nm}^\alpha = \langle\Psi_n|\hat{c}_i^\dagger\hat{c}_j|\Psi_m\rangle$, and where α, β are the collective indices of (i,j). For systems with degenerate ground states, m can specify other degenerate ground states, and the terms appearing in the degenerate subspace can thus diverge for $\omega \to 0$, which is an artefact of perturbation theory.

A diagonalization procedure is proposed to eliminate this divergence. Diagonalizing the non-zero matrices ρ^α, with $\rho_{nn}^\alpha = 0$ for all n as the sum is over $m \neq n$, in the subspace of the degenerate ground states for each α one obtains a new basis set of degenerate ground states which diagonalize $\hat{\rho}^\alpha = \hat{c}_i^\dagger\hat{c}_j$. The diverging terms vanish in this new basis set since $m \neq n$. The remaining non-vanishing terms are independent on the choice of the degenerate ground state basis and the response function can thus be rewritten as

$$\begin{aligned}R(\mathbf{r},\mathbf{r}';\omega) = \frac{1}{M}\sum_{n=1}^{M}\sum_{m}^{\text{exci}}\Bigg[&\frac{\langle\Psi_n|\hat{\rho}(\mathbf{r})|\Psi_m\rangle\langle\Psi_m|\hat{\rho}(\mathbf{r}')|\Psi_n\rangle}{\omega - E_m + E_0 + i\delta} \\ &- \frac{\langle\Psi_n|\hat{\rho}(\mathbf{r}')|\Psi_m\rangle\langle\Psi_m|\hat{\rho}(\mathbf{r})|\Psi_n\rangle}{\omega + E_m - E_0 - i\delta}\Bigg], \end{aligned} \quad (14)$$

where the sum over m is now strictly over excited states, such that no divergence occurs when $\omega = 0$. We note that the diagonalization procedure is not required to be done in practice, when all $\{w_n\}$ are equal to $1/M$.

We now return to the choice of denominator in Eq. (4). With this choice, the response function contains no terms in which the density operator couples a given ground state to itself, as can be seen in Eq. (13), where the state m must be different from the state n. After applying the diagonalization procedure, off diagonal elements of ρ^{σ}_{nm} in the new degenerate ground states vanish. On the other hand, the diagonalization procedure cannot be employed for each separate R_n since the nonphysical $\omega \to 0$ divergence would remain, further motivating the choice of the Hartree potential as the ensemble one.

Contained within the time-ordered response function is the physical retarded response function. By the Kubo formula [20], the retarded linear ensemble density response function can be constructed as:

$$iR^r(1,2) = \frac{1}{M}\sum_{n=1}^{M}\langle\Psi_n|[\Delta\hat{\rho}_n(1), \Delta\hat{\rho}_n(2)]|\Psi_n\rangle\theta(t_1 - t_2), \tag{15}$$

where $\Delta\hat{\rho}_n(1) = \hat{\rho}(1) - \rho_n(1)$. An equivalent and standard form in literature of retarded response, is obtained by exchanging $\Delta\hat{\rho}_n(1)$ with $\Delta\hat{\rho}(1) = \hat{\rho}(1) - \rho(1)$. In the spectral representation, peaks at $\omega = 0$ originating from the degenerate subspace do not appear in the retarded response function. A time-ordered response function is defined to satisfy the relations:

$$\mathrm{Re}R(\mathbf{r},\mathbf{r}';\omega) = \mathrm{Re}R^r(\mathbf{r},\mathbf{r}';\omega), \tag{16}$$

$$\mathrm{Im}R(\mathbf{r},\mathbf{r}';\omega)\mathrm{sgn}(\omega) = \mathrm{Im}R^r(\mathbf{r},\mathbf{r}';\omega). \tag{17}$$

Only the time-ordered response function defined in Eq. (15) satisfies relations (16) and (17). The proposed form in Eq. (13) is based on the form (15), where the diagonalization procedure can be employed.

A widely used approximation to compute the response function is the random-phase approximation (RPA), on which the GWA is based. As input, the non-interacting response function corresponding to some mean-field Hamiltonian is needed. If the mean-field ground state is degenerate, the same diagonalization procedure as described above can be employed.

As a proof of concept and an illustration on how the formalism works in practice, we consider a hydrogen-like system, occupied by six electrons, and a two-dimensional harmonic oscillator, occupied by four electrons. In the H-like system the 1s,2s,2p,3s orbitals are considered, with the interaction between the electrons given by $v(\mathbf{r}-\mathbf{r}') = 1/|\mathbf{r}-\mathbf{r}'|$. The non-interacting ground state is nine-fold degenerate, with the 1s,2s orbitals filled and two electrons occupying the 2p orbital, while the interacting ground states is non-degenerate. In the 2D harmonic oscillator, only the six lowest energy orbitals are considered, with the electron-electron interaction given by a point-interaction $v(\mathbf{r}-\mathbf{r}') = U\delta(\mathbf{r}-\mathbf{r}')$. The non-interacting ground state is four-fold degenerate, while the interacting ground state is non-degenerate. For both systems, the non-interacting problem is solved with a mean-field ensemble Hartree potential. A comparison of a one-shot ensemble G^0W^0 approach to the exact solutions as well as a one-shot non-ensemble G^0W^0 approach is made. In the non-ensemble approach the degeneracy is neglected by computing new sets of energies for each of the separate Hartree potentials of the non-interacting ground states, with the non-interacting system chosen to correspond to a non-degenerate non-interacting ground state with the lowest energy. The ensemble and non-ensemble Green's function and self-energy are computed within the GWA.

We first compute the non-interacting Green's functions G^0_n and non-interacting response function or the polarization P^0. Once the polarization P^0 is obtained the rest of the computation follows a routine procedure of first calculating the screened interaction $W = v + vP^0W$ and then the self-energies given by

$$\Sigma_n(\mathbf{r},\mathbf{r}';\omega) = i\int\frac{d\omega'}{2\pi}G_n(\mathbf{r},\mathbf{r}';\omega+\omega')W(\mathbf{r}',\mathbf{r};\omega') + \delta(1-2)\left(V^H_n(1) - V^H(1)\right), \tag{18}$$

which can be computed with a similar procedure as in the non-degenerate case. The ensemble Green's function G can be computed from the auxiliary Green's functions G_n , obtained from the set of Dyson's equations:

$$G_n(1,2) = G^0_n(1,2) + \int d3d4G^0_n(1,3)\Sigma_n(3,4)G_n(4,2). \tag{19}$$

In addition, we compute the spectral forms of the ensemble response function and ensemble Green's function S and A, respectively. Special care is required to include the occupied and unoccupied peaks with the correct sign in the computation of the ensemble spectral function A. A proposed scheme is computing the spectral functions A_n from the spin-polarized Green's functions G_n, as the poles are separated, and then computing A as the weighted sum over A_n.

In the H-like model the nuclear charge $Z = 6$ and $Z = 3$ is used for the initial one-electron energies and orbitals, respectively, as convergence issues appear in the non-interacting mean-field solution when the orbitals of the $Z = 6$ system are used. The trace of S and A are plotted against ω in the three cases in Fig. 1. In the ensemble case, the main exact peak structure of S is well captured, except for an absence of the low energy peak structure which the non-ensemble approach can partially capture. An excellent agreement of the peak structure and positions of A between the exact and ensemble G^0W^0 approach A is observed.

The low ω peak structure in S corresponds to transitions originating from the degenerate non-interacting ground state subspace, which vanishes in the diagonalization procedure, and which may appear in the degeneracy breaking going from the non-interacting to the interacting system. The degeneracy breaking is first included in

the self-energy, and thus the peaks are absent in the one-shot approach. A self-consistent approach is expected to be able to capture the absent peaks. In the one-shot approach, a mean-field Hamiltonian capturing the energy structure of the system better than the ensemble Hartree approach would be required to capture the absent peaks.

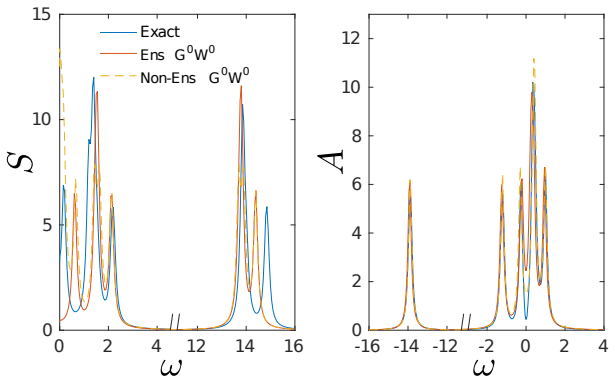

FIG. 1. The trace of the spectral response function S (left figure) and spectral function A (right figure) plotted against energy ω in the exact, and ensemble and non-ensemble G^0W^0 cases for the H-like system. Breaks in the x-axes are employed. Atomic units with $\hbar = m_e = 4\pi\epsilon_0/e^2 = 1$ are employed.

The trace of S and A are plotted against ω for the 2D harmonic oscillator, with $U = 1$, in the three cases in Fig. 2. The ensemble peak structure of S is in reasonable agreement with the exact one, and in better agreement then the non-ensemble approach. The non-ensemble approach incorrectly predicts a peak at low ω, while no low ω peak is present in the ensemble approach. A good agreement between the exact and ensemble G^0W^0 approach for the main peak structure of A is observed, however, some detailed peak structure is captured better by the non-ensemble approach, for example in the vicinity of $\omega = -1$.

An iterative self-consistent computational scheme for G_n can be constructed. The polarization can be computed from the set of G_n by the following ensemble analogue of one of the Hedin's equations within GWA:

$$P(1,2) = -\frac{i}{M}\sum_{n=1}^{M} G_n(1,2)G_n(2,1^+). \qquad (20)$$

The diagonalization procedure is employed for the computation of the polarization in each iteration. A conceptual issue is the degeneracy breaking in an iteration. We propose to employ the Galitskii-Migdal formula on the auxiliary Green's functions to identify degeneracy, choosing the ones giving the lowest ground state energy for the following iteration. A slight mixing between the auxiliary Green's functions and the ensemble Green's function can be employed.

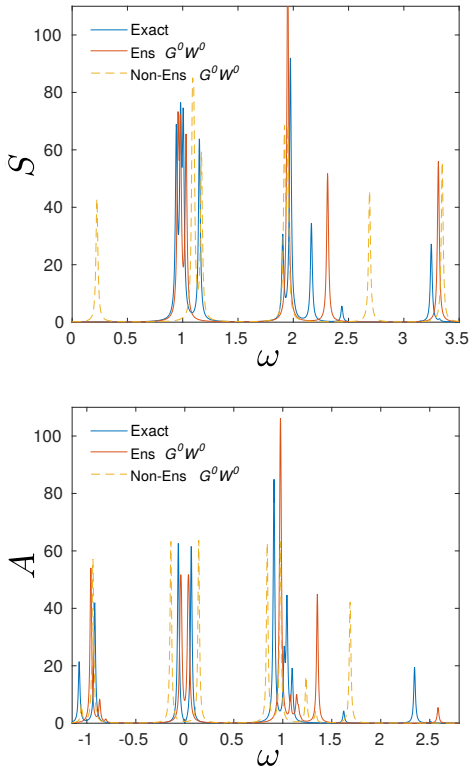

FIG. 2. The trace of the spectral response function S (upper figure) and spectral function A (lower figure) plotted against energy ω in the exact, and ensemble and non-ensemble G^0W^0 cases for the 2D harmonic oscillator. Small satellite features are not included in the plot. Atomic units with $\hbar = m_e = 1$ are employed.

We propose to extend the finite-temperature Green's function theory to include degenerate states by writing the Matsubara Green's function in the modified interaction picture as a weighted sum over auxiliary Matsubara Green's functions, with the weight given by the Boltzmann distribution. This choice leads to an ensemble real-time response function which satisfies the required properties of the time-ordered response function.

In summary, we have developed an ensemble Green's function formalism for treating many-electron systems with degenerate ground states in a well-defined way. An exact set of iterative equations, analogous to Hedin's equations for the non-degenerate case, is derived for the ensemble Green's function. An ensemble GWA is naturally obtained from the iterative equations. The formalism does not rely on an adiabatic connection between interacting and non-interacting ground states as commonly assumed in many-body perturbation approaches. Further application to realistic systems with degenerate ground states in the future would enlighten the strengths and weaknesses of the formalism. Most considerations were applicable for an arbitrary set of states $|\Psi_n\rangle$ and weights w_n, and studying other choices of ensembles cap-

turing non-equilibrium aspects would be of interest.

ACKNOWLEDGMENTS

We gratefully acknowledged financial support from the Swedish Research Council (VR).

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