Parquet approximation for molecules: spectrum and optical conductivity of the Pariser-Parr-Pople model

P. Pudleiner,1,2 P. Thunström,3 A. Valli,1 A. Kauch,1 G. Li,4 and K. Held1
1Institute for Solid State Physics, Vienna University of Technology, 1040 Vienna, Austria
2Institute of Theoretical and Computational Physics, Graz University of Technology, 8010 Graz, Austria
3Department of Physics and Astronomy, Materials Theory, Uppsala University, 751 20 Uppsala, Sweden
4School of Physical Science and Technology, ShanghaiTech University, Shanghai 200031, China

(Dated: December 13, 2018)

We study a simple model system for the conjugated π-bonds in benzene, the Pariser-Parr-Pople (PPP) model, within the parquet approximation (PA), exemplifying the prospects of the PA for molecules. Advantages are the polynomial scaling of the PA with the number of orbitals, and the natural calculation of one- and two-particle spectral functions as well as of response and correlation functions. We find large differences in the electronic correlations in the PPP model compared to a Hubbard model with only local interactions. The quasiparticle renormalization (or mass enhancement) is much weaker in the PPP than in the Hubbard model, but the static part of the self-energy enhances the band gap of the former. Furthermore, the vertex corrections to the optical conductivity are much more important in the PPP model. Because non-local interactions strongly alter the self-energy, we conclude that the PA is more suitable for calculating conjugated π-bonds in molecules than single site dynamical mean-field theory.

I. INTRODUCTION

The calculation of strongly correlated electron systems is particularly challenging since strong correlations imply that many body perturbation theory (MBPT), e.g., up to first or second order in the interaction \( V \), is not a reliable approximation. Even relatively small systems pose a problem. An exact diagonalization (ED) of the Hamiltonian, also coined full configuration interaction (CI) in chemistry, is still possible for \( N = O(20) \) states (orbitals times spins). Quantum Monte Carlo simulations (QMC) on the other hand, suffer from the Fermionic sign problem, restricting this method to \( N = O(100) \).

Against this background, the methods of choice in solid state physics, where (infinitely extended) periodic crystals are typically considered, are density matrix renormalization group (DMRG) and dynamical mean field theory (DMFT) which are favorable for one dimensional systems which can be typically described by matrix product states (MPS) with relatively small matrices. The latter becomes exact for infinite dimensions and is a good approximation for three dimensional problems, where a local DMFT self-energy often yields a good description. Recently, DMFT has been extended diagrammatically to account for non-local correlations beyond the local DMFT self-energy; this is done in the dynamical vertex approximation (DFA) which includes not only all diagrams up to third order in \( V \) (i.e. corrections are \( \sim V^3 \)) but in addition some diagrams up to infinite order in \( V \) (including all ladder diagrams). The parquet equations have been developed in the 60s and revisited in the 90s at a time when sufficiently powerful computers were not yet available. More recently we have seen a revival in the context of diagrammatic extensions of DMFT, specifically in the context of DFA, and for disordered problems.

In the (parquet) DFA \( \Lambda \) is approximated by a locally irreducible vertex \( \Lambda = \Lambda_{\text{loc}} \) supplemented by the bare non-local Coulomb interaction which can be calculated numerically by solving an Anderson impurity problem with continuous-time quantum Monte Carlo simulations. In this context it has also been recognized that the PA works quite well for weak-to-intermediate Coulomb interactions, i.e., when we are still quite far below the Mott transition. Hitherto these studies have been mainly focused on the Hubbard model with only a local Coulomb interaction both in one and two dimensions. Notwithstanding, a non-local interaction can be added to the Hamiltonian of the system without changing the form of the parquet equations.

In the present paper, we employ the PA for one of the simplest but nonetheless relevant models with local copies thereof. Taking single and double excitations into account goes under the name of CCSD, whereas also taking triple excitations into account is coined CCSDT. Another resummation of Feynman diagrams is better known in the field of physics: the parquet approximation (PA) It is based on an exact set of equations, the parquet equations (PE). The PE require as (only) input the two-particle fully irreducible vertex \( \Lambda \) and the non-interacting, one-particle Hamiltonian. If we approximate \( \Lambda \) by the bare interaction, \( \Lambda = V \), we obtain the PA which includes not only all diagrams up to third order in \( V \) (i.e. corrections are \( \sim V^3 \)) but in addition some diagrams up to infinite order in \( V \) (including all ladder diagrams). The parquet equations have been developed in the 60s and revisited in the 90s at a time when sufficiently powerful computers were not yet available. More recently we have seen a revival in the context of diagrammatic extensions of DMFT, specifically in the context of DFA, and for disordered problems.

In the (parquet) DFA \( \Lambda \) is approximated by a locally irreducible vertex \( \Lambda = \Lambda_{\text{loc}} \) supplemented by the bare non-local Coulomb interaction which can be calculated numerically by solving an Anderson impurity problem with continuous-time quantum Monte Carlo simulations. In this context it has also been recognized that the PA works quite well for weak-to-intermediate Coulomb interactions, i.e., when we are still quite far below the Mott transition. Hitherto these studies have been mainly focused on the Hubbard model with only a local Coulomb interaction both in one and two dimensions. Notwithstanding, a non-local interaction can be added to the Hamiltonian of the system without changing the form of the parquet equations.

In the present paper, we employ the PA for one of the simplest but nonetheless relevant models with local
(U) and non-local interactions (V): the Pariser-Parr-Pople (PPP) model \[39,40] for a benzene ring. It consists of six orbitals (one \( p_z \) orbital on each carbon site) or \( N = 6 \times 2 \) states with a nearest-neighbor hopping and both local and non-local Coulomb interactions. It has the advantage that an exact ED solution is still possible. For comparison, we show results for the six-site Hubbard model \[31] (U-only model) which has the same Hamiltonian except for neglecting all non-local Coulomb interactions \( V \), as well as for the intermediate case, the extended Hubbard model with only the nearest-neighbor interaction \( (U + V_1) \) model.

The paper is organized as follows: In Section II we introduce the PPP model including the values of the parameters used. In Section III the methods employed, i.e., the PE and the PA, are briefly discussed, as well as the necessary changes to the \( \text{victory}^{31} \) code solving the PE. The results obtained are presented in Section IV. We start in Section IV A with the structure of the two-particle vertex function and changes thereof when including non-local interaction in the PPP model. Further we discuss in Section IV B the leading instabilities (largest susceptibilities) on the basis of the largest eigenvalues in the corresponding channel. Section IV C is devoted to the self-energy and the one-particle spectral function; and Section IV D to the optical conductivity. Finally, Section V provides a brief summary and outlook.

II. PARISER-PARR-POPLE MODEL

The Pariser-Parr-Pople (PPP) model \[39,40] was developed as a realistic albeit simple one-band model of the conjugated \( \pi \)-bonds in carbon-based organic molecules. The model contains a \( p_z-p_z \) hopping term \( t \) between neighboring carbon sites and a long-range Coulomb interaction \( V_{ij} = U/\sqrt{\tau + \alpha |\mathbf{r}_i - \mathbf{r}_j|^2} \). Here, \( U \) is the local Coulomb interaction, \( \alpha = (U/(14.397eV))^2 \), and \( d_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \) the distance between carbon site \( i \) and \( j \). The resulting Hamiltonian has the form of an extended Hubbard model:

\[
\mathcal{H} = -t \sum_{i,\sigma} c_{i\sigma}^\dagger c_{i+1\sigma} + \frac{1}{2} \sum_{i,j,\sigma,\sigma'} V_{ij} (n_{i\sigma} - 1)(n_{j\sigma'} - 1),
\]

where \( n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \), and \( c_{i\sigma}^\dagger \) and \( c_{i\sigma} \) represent creation and annihilation operators for an electron with spin \( \sigma \) at carbon site \( i \), respectively. We restrict ourselves to the PPP model for a benzene molecule, i.e., Hamiltonian \( \mathcal{H} \) lives on a ring with six sites, which can also be considered as a one-dimensional extended Hubbard model with periodic boundary conditions.

The second term in Eq. 1 contains the effective interaction, modeled by a density-density interaction, combined with a chemical potential that makes the system particle-hole symmetric with \( n = 1 \) electrons per site. The geometry of the benzene ring gives \( d_{i,i+1} = 1.4\text{Å}, d_{i,i+2} = \sqrt{3} \times 1.4\text{Å}, d_{i,i+3} = 2 \times 1.4\text{Å} \), which together with \( t = 2.539\text{eV} \) and \( U = 3.962\text{eV} \) yields \( V_{ii} = 3.962t \), \( V_{i(i+1)} = 2.832t \), \( V_{i(i+2)} = 2.014t \), and \( V_{i(i+3)} = 1.803t \). In the following, we set our unit of energy to the hopping element, i.e., \( t \equiv 1 \).

Besides the PPP model, we also study the corresponding Hubbard model \( (U-only) \) model by setting \( V_{ij} = \delta_{ij}U \), and the extended Hubbard model \( (U + V_1) \) model with nearest-neighbor interaction with \( V_{ii} = 3.962t \), \( V_{i(i+1)} = 2.832t \) only.

The Fourier transformation to momentum \( (\mathbf{k}) \) space yields the one-particle energies \( e_{\mathbf{k}} = -2t \cos k_{\mathbf{k}} \), with \( k_{\mathbf{k}} \in \{0, \pi/3, 2\pi/3, \pi, 4\pi/3, 5\pi/3\} \); and interactions \( V_{\mathbf{q}} = \sum_{\mathbf{q} \neq 0} V_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \). Here we have excluded the local interaction \( U = V_{00} \) as it is treated separately in the following. In this work the temperature is set to \( T = 0.1t \).

III. METHOD: EXTENDING VICTORY TO TREAT NON-LOCAL INTERACTIONS

The physical quantities studied in this paper, such as transport properties or scattering rates, require the determination of both, one- and two-particle, Green’s functions. Hence, a theory that treats one- and two-particle Green’s functions on an equal footing and in a self-consistent way is preferable. To this end, we apply the parquet formalism \[41\] which is a set of self-consistently coupled equations, namely the Bethe-Salpeter equation, the parquet equation \[20,45,46\] and the Schwinger-Dyson equation. A state-of-the-art implementation is available in the recent \textit{victory} release \[22\]. This package is an efficient parquet solver for electron systems in one or two dimensions, which properly takes the high-frequency asymptotics into account via so-called kernel functions \[41,42\].

While the parquet equations are an exact set of equations, they require the fully irreducible two-particle vertex \( \Lambda \) as an input. But in general \( \Lambda \) is not known. It can be approximated by its local contribution (known as parquet-variant of the dynamical vertex approximation, DF \[12,13,31,12\]) which needs to be calculated by means of other methods, such as ED and QMC simulations. Or one can take the bare Coulomb interaction as \( \Lambda \), which is also known as parquet approximation \( (PA) \) \[23,27\].

The parquet equations are numerically quite involved, and require an iterative solution scheme. In particular, since the crossing relations between vertex functions in different channels involve combination of momentum and frequency indices, the range in which the knowledge of the vertex functions is required increases at each iteration of the parquet equation (see below). Due to translational invariance (periodic boundary conditions), the momenta can be restricted to the first Brillouin zone. The frequency, however, must be kept in an, in principle, infinite range. The so-called kernel approximations handle this issue, by taking care of the vertex asymptotics in the frequency space, see Ref. \[32\]. It is beyond the scope of the present article to introduce and derive the parquet equations in full, and we refer the reader to
Refs. [12] [24] [32] and [43] instead.

Hitherto only a local Hubbard interaction has been treated in victory. Dealing with non-local interactions requires a modification of the self-energy calculation by further contributions, i.e., the one-particle Fock term, a constant Hartree term \((U/2 + V_q = 0)/n\) (with the density fixed to \(n = 1\) electrons per site), and by a two-particle vertex contribution:

\[
\Sigma_k = (U/2 + V_q = 0)n - \frac{1}{N\beta} \sum_q V_q G_{q+k} - \frac{1}{(N\beta)^2} \sum_{k',q} G_{k'q} G_{q+k'q} + G_{q+kq} + V_q F_{q+kq}' \]  

Here, \(N\) (\(N = 6\) for the benzene molecule) corresponds to the total number of points in the discretized momentum-space in the first Brillouin zone, and \(\beta = 1/T\) is the inverse temperature. The one-particle Green’s function is labeled by \(G\), and the two-particle full vertex function by \(F\). The vertex function \(F\) is directly linked to the connected part of the two-particle Green’s function by cutting (“amputating”) four one-particle Green’s functions from the latter. We employ a combined four-vector notation \(k = (k, \nu)\) for the momentum \(k\) and the fermionic Matsubara frequency \(\nu = (2n + 1)\pi/\beta\), and \(q = (q, \omega)\) for the (one-dimensional) momentum \(q\) and the bosonic Matsubara frequencies as \(\omega_n = 2n\pi/\beta\), with \(n \in \mathbb{Z}\). Due to the \(SU(2)\)-symmetry of the Hamiltonian, the vertex function \(F\) can be written in a spin-diagonalized form, with a density \((d)\) and magnetic \((m)\) channel; cf. Refs. [12] and [39].

Beside the modification in the self-energy, the momentum-dependent first-order contribution \(V_q\) has to be added explicitly to the fully irreducible vertex function \(\Lambda\). This is obvious for the PA, but it is also used as an approximation in the \textit{ab initio} DΓA which only takes into account local vertex corrections besides the bare interaction in \(\Lambda\). Both cases are in our extension of the \textit{victory} code, by adding the bare non-local interaction to the local \(\Lambda\). In terms of formulas, we replace the bare interaction vertex \(U\) in the PA by

\[
\begin{align*}
U_d^{kk'q} &= U \rightarrow U + 2V_q - V_{k'k} \\
U_m^{kk'q} &= -U \rightarrow -U - V_{k'k} \\
U_s^{kk'q} &= 2U \rightarrow 2U + V_{q-k-k'} + V_{k-k} \\
U_t^{kk'q} &= 0 \rightarrow V_{q-k-k'} - V_{k-k} ,
\end{align*}
\]

where the subscripts \(s\) and \(t\) refer to the singlet and triplet channels which are conveniently introduced in the spin-diagonalized notation [52].

The parquet equation reads, e.g., in the density channel

\[
f_{d}^{kk'q} = \Lambda_{d}^{kk'q} + \Phi_{d}^{kk'q} = \frac{1}{2} \Phi_{d}^{k(k+q)(k'-k)} - \frac{3}{2} \Phi_{d}^{k(k+q)(k'-k)} \\
+ \frac{1}{2} \Phi_{s}^{kk'(k+k'+q)} + \frac{3}{2} \Phi_{t}^{kk'(k+k'+q)} ,
\]

where \(\Phi_r\) denotes the reducible vertex function in a given parquet channel \(r = d, m, s, t\). The evaluation of the parquet equations requires frequency and momenta outside the box for which \(\Phi\) is stored [52], due to frequency-momentum combinations such as \(k' - k\) and \(k + k' + q\) in Eq. (4). While the periodic boundary conditions resolve this issue for the momenta, there is no periodicity in frequency space. For the frequencies we hence calculate the asymptotic kernel functions by scanning the surface of the known frequency box as described in Ref. [32]. However, since the bare vertex now depends on \(k\), \(k'\), and \(q\), so does the high frequency asymptotics of the reducible vertex functions \(\Phi\). The reducible vertex function in a given channel \(\Phi_r\) \((r = d, m, s, t)\) is related through the Bethe-Salpeter equation to the full vertex \(F\) and the irreducible vertex in channel \(r\), \(\Gamma_r\). The asymptotics of \(\Phi\) can thus be obtained [52] by replacing \(F\) and \(\Gamma\) in the Bethe-Salpeter equation by \(U\), yielding

\[
\begin{align*}
\Phi_{d/m}^{kk'q} &= \frac{1}{N\beta} \sum_{k_1} \Gamma_{d/m}^{kk_1k_1} G_{k_1} G_{q+k_1} F_{d/m}^{k_1k'} \\
\Phi_{s/t}^{kk'q} &= \frac{1}{N\beta} \sum_{k_1} U_{d/m}^{kk_1k_1} G_{k_1} G_{q+k_1} U_{d/m}^{k_1k'} F_{s/t}^{k_1k'q} \quad (7)
\end{align*}
\]

We utilize this high-frequency behavior when solving the Bethe-Salpeter equations by extending the frequency sum over \(\nu\) (as part of the \(k_1\) sum) outside the box for which \(F\) and \(\Gamma\) are stored, i.e., using Eqs. (6) and (7) instead of Eqs. (5) and (7). These terms are actually evaluated as a difference and in imaginary time, see Ref. [11]. A similar regularization (extension to high frequencies) is employed for the Dyson-Schwinger equation (2).

With these changes we can employ \textit{victory} for studying non-local interactions, keeping in mind that a larger number of frequencies \(N_f\) are needed compared the case with local interactions only, due to the slower convergence to the asymptotic behavior.

### IV. RESULTS

#### A. Two-particle vertex function

Let us start by inspecting the two-particle full vertex functions which are obtained in the PA. Fig. [1] shows the
full vertex function $F_{d}^{kk'q}$ for the benzene ring, comparing the PPP and $U$-only model. Here, we concentrate on the density channel $(d)$ since it is the relevant channel for the optical conductivity. The magnetic channel gives a qualitatively similar analysis.

Comparing the upper and lower row of Fig. 1, we see that including a non-local interaction in the PPP model causes a strong momentum selectivity of the full vertex function. The main difference between the full vertex of the PPP and $U$-only model stems from the additional bare non-local interaction, i.e., from $\Lambda_d = U + 2V_0 - V_{k' - k}$ in Eq. [4]. This frequency-independent but non-local ($q$-dependent) interaction causes quite different background values for the different momentum patches (different colors in Fig. 1). For the $q = 0$ contribution shown in Fig. 1 this leads to a clear main diagonal structure $k = k'$ in the vertex of the PPP model.

On top of this, in the patches with $q - k \neq k' = \text{const.}$, we observe main and secondary diagonal structures also in the frequency subindex of Fig. 1 for both models. These stem from vertex diagrams where the external legs pairwise connect to the same interaction term, which also determine the asymptotics in the first kernel approximation, i.e., Eqs. [6] and [8]. Additionally, when $q \pm k^{(j)} = \text{const.}$, there is a hardly discernible plus structure which stems from vertex diagrams where only one pair of the external legs connect to the same interaction term (they constitute the second kernel).

Except for the constant background given by the bare interaction, it seems that the frequency structure of the vertex for the different models is quite comparable. Picking for instance the momentum patch $(k,k') = (\pi,0)$ for $q_0 = (0,0)$ in the third column of Fig. 1 where the constant background $U + V_0$ is already subtracted, the frequency structures shown look similar. On a quantitative level, the side diagonal $\nu_n = -\nu'_n$ is somewhat sharper for the $U$-only model than for the PPP model, which instead shows a broader structure. The latter characteristic is the reason why an accurate simulation of the PPP model requires large frequency boxes. This aspect is even more important for the bosonic frequency $\omega_n$, as the kernel functions are set to zero outside of the inner bosonic frequency box.

B. Eigenvalues of the BSE

Valuable insights on the physics of the benzene ring can be obtained by analyzing the eigenvalues of the Bethe-
Here, we have for each $q$, a characteristic equation for the eigenvalue $\lambda$, or more precisely three equations for the density and magnetic ($d/m$) channels, as well as for the particle-particle ($pp$) channel. For the latter the given combination of singlet and triplet ($s/t$) channels allows for a simultaneous study of all superconducting instabilities. In the following, we consider the value of $q_{\text{max}} = (q_{\text{max}}, \omega_{\text{max}})$, corresponding to the leading eigenvalue $\lambda_{\text{max}}$ in the respective channel. The leading eigenvalues are shown in Fig. 2. For all three models considered, the dominating instabilities are in the $d$ and $m$ channels, which display the largest eigenvalues at $q_{\text{max}} = (\pi, 0)$, while the leading eigenvalues in the $pp$ channels, at $q_{\text{max}} = (0, 0)$, are much smaller.

Within the $U$-only model, $\lambda_{m}$ is the largest among the leading eigenvalues in the different channels, thus revealing a strong tendency toward spin ordering, with an antiferromagnetic (AF) pattern associated to $q_{\text{max}} = \pi$. In contrast, within the $U + V$ model, the system is at the verge of a charge density wave (CDW) instability ($\lambda_{d} \approx 1$). The corresponding wave vector is again $q_{\text{max}} = \pi$, i.e., there is a strong tendency toward an alternating occupation of sites. Such an ordering is clearly favored by the nearest neighbor repulsive interaction $V_{ij}$. The PPP model is somewhat in between the previous scenarios, with a similarly large $\lambda$ in both the $m$ and $d$ channels, since the long-range tail of the Coulomb repulsion "frustrates" both the AF and CDW staggered order. Finally, for all three models, the eigenvalue $\lambda_{pp}$ indicates a pairing tendency at $q = 0$. This is slightly enhanced for the $U + V_{i}$ model, but very far from a superconducting instability for all models.

### C. Self-energy and spectra

Let us now turn to the self-energy shown in Fig. 3 for the PPP model and the $U$-only model. Here, the Fock (and Hartree) term is subtracted for a better comparison of the two models. As an exact diagonalization (ED) for a one-band Hamiltonian with six sites is still feasible, the ED results for the self-energy are displayed in Fig. 3 as well. Further we show the $(k$-independent) DMFT self-energy obtained by continuous time Monte Carlo simulations in the interaction expansion.

In the top panel of Fig. 3 we show the imaginary part of the self-energy for two $k$-points. In the case of the $U$-only model, the DMFT self-energy provides a good description of the system, as it roughly corresponds to a $k$-average of the ED data. The PA slightly underestimates the self-energy, but it nevertheless provides the correct tendency with respect to the momentum dependence, i.e., the self-energy is (in absolute terms) larger at $k = (\pi/3)$ than at $k = (0)$. This confirms previous calculations showing that the PA gives excellent results in the weak-to-intermediate coupling regime for the Anderson impurity model. Stronger deviations may instead be expected toward strong coupling. As long as the DMFT solution gives a reasonably correct description of the local physics, the parquet results can be improved by using the local vertex $\Lambda_{\text{loc}}$ instead of the bare $U$ as the starting point for the parquet equations, i.e., using the parquet DGA instead of the PA. However, as seen in Fig. 3, the DMFT self-energy is clearly inaccurate for the PPP model, and a DGA calculation starting from a DMFT solution without self-consistency can therefore not be expected to yield reliable results.

A similar good agreement with the exact ED result is also obtained for the real part of the PA self-energy, shown in the lower panel of Fig. 3. In contrast, the real part of the self-energy is identical zero in DMFT because of particle-hole symmetry, i.e., it is qualitatively and quantitatively very different from the ED and PA result.

When we include non-local interactions and consider the PPP model, the self-energy in Fig. 3 is dramatically suppressed within ED. This aspect is completely missing in the DMFT, which yields exactly the same self-energy for both models, as long as there is no CDW order, since non-local interactions are only included at the Hartree level. Instead, the PA provides an excellent description of the PPP model, and it is able to reproduce not only the overall suppression of the self-energy, but also the change of sign of $\text{Re} [\Sigma_{k=0} - \Sigma_{k=0}^{HF}]$. One can rationalize the smaller self-energy for the PPP model, by considering the extreme case that the non-local interaction $V_{ij}$ is independent of the distance $|i - j|$. For $V_{ij} = V_{00} = U$ and a fixed number of electrons, all configurations in the...
FIG. 3. (Color online) Imaginary part \( \text{Im}\Sigma_k \) (top panels) and real part \( \text{Re}\Sigma_k \) (bottom panels) of the self-energy at \( k = 0 \) (left) and \( k = \pi/3 \) (middle), comparing DMFT, ED, and PA results for the \( U \)-only and PPP models. In case of the PPP model, the Hartree-Fock contribution is subtracted in the main figures, but the Fock term is explicitly included in the inset. The inset also shows the convergence of the PA (circles) vs. frequency box size \( N_f \) (note that the x-axis ticks scale as \( 1/N_f^2 \)) up to \( N_f = 320 \) (used for the data in the main panels). The ED results (triangles) of Ref. 53 are shown for comparison at \( N_f = \infty \). Right panels: first (top) and second (bottom) moments of the high-frequency asymptotics of the self-energy for both models at \( k = 0 \) (top) and the \( U \)-only model at \( k = 0 \) and \( k = \pi/3 \) (bottom).

Occupation space compatible with the Pauli exclusion principle have the same interaction energy. Hence the system behaves more like the non-interacting system. In particular there is neither a renormalization (narrowing) effect (corresponding to the large linear part of \( \text{Im}\Sigma \) for small frequencies) nor a different \( \text{Re}\Sigma \) for each \( k \) points (however occupied/unoccupied states are shifted against each other). In the PPP model we do not yet have this extreme case, but the self-energy is already very much suppressed compared to the \( U \)-only model with the same \( U \). As the PPP model is less strongly correlated, it is maybe not surprising that the PA provides even better results than for the \( U \)-only model. This suggests that the PA is a good approximation to describe the conjugated \( \pi \)-bonds in carbon-based molecules where non-local interactions partially compensate the effect of the local interaction.

The insets of Fig. 3 show the convergence of our results with respect to the size of the frequency box used, now including the Fock term. We see that at \( N_f = 320 \) (total number of frequencies: positive and negative) deviations from the extrapolated \( N_f \to \infty \) result are very minor. Hence \( N_f = 320 \) has been employed for the main panel. Also shown in the inset is the ED result[53] (as a triangle at \( N_f = \infty \)), and we see that PA approaches the ED results for large frequency boxes \( N_f \) and high frequencies \( (\nu_0) \), whereas for smaller frequencies \( (\nu_5) \) there are deviations, as is also visible in the main panel. The right panel of Fig. 3 shows that PA not only correctly reproduces the frequency independent Fock (and Hartree) term but also captures the asymptotic \( 1/\nu \) behavior of the imaginary part of the self-energy (which is \( k \)-independent) and the \( 1/\nu^2 \) behavior of the real part of the self-energy.

Reproducing the high-frequency behavior correctly is an important non-trivial aspect of the PA and parquet variants of the DFA. In fact, within the ladder DΓA, the correct \( 1/\nu \) asymptotic is only recovered if a Moriya \( \lambda \)-correction is included[12,13] In dual fermion calculations ED the correct asymptotics is obtained if the theory is truncated at the level of the two-particle vertex, but not any longer if three-particle vertex terms are included[16,18]

Fig. 4 shows the \( k \)-integrated and \( k \)-resolved spectral function \( A_k(\nu) \), for which the PA and DMFT are obtained by an analytic continuation using the Padé method[59]. The discrete peaks of the ED have been broadened by a Lorentzian of width \( \delta = 0.05\nu \). Again we show results for the PPP (right) and \( U \)-only model (left).

For the top panel of Fig. 4, i.e., the \( k \)-integrated spectral function, we see that the (HOMO-LUMO) gap is considerably larger for the PPP model than for the \( U \)-only model. To get a better understanding of this difference let us start by looking at the self-energy, which within the band gap is accurately described by its leading order terms

\[
\Sigma_k(\nu) \approx \text{Re}\Sigma_k|_{\nu \to 0} + i\nu \frac{\partial \text{Im}\Sigma_k}{\partial \nu} \bigg|_{\nu \to 0}.
\]  (10)

The static term \( \text{Re}\Sigma_k(0) \), which here also includes the chemical potential, has opposite sign for the occupied part of the spectrum \( (k = 0, \pi/3) \) and the unoccupied one \( (k = 2\pi/3, \pi) \). It is added to the non-interacting energies \( \epsilon_k \), and contributes therefore directly to the band gap.

The linear term, given by the slope of \( \text{Im}\Sigma \) in Fig. 4, contributes instead indirectly to the band gap through...
the quasiparticle renormalization factor

\[ Z_k = \left[ 1 - \frac{\partial \text{Im} \Sigma_k(0)}{\partial \nu} \right]^{-1}. \tag{11} \]

The two terms together yield the following positions for the poles \( \epsilon_k^* \) of the one-particle Green’s function

\[ \epsilon_k^* = Z_k \left[ \epsilon_k + \text{Re} \Sigma_k(k, \nu = 0) \right]. \tag{12} \]

The effect of \( Z \) is to make the whole spectrum and hence also the band gap more narrow. Numerically, we determine the slope \( \partial \text{Im} \Sigma_k/\partial \nu \) for a finite \( T \) by fitting a second order polynomial in \( \nu \) to \( \text{Im} \Sigma_k(k, \nu) \). The quasiparticle excitation energies Eq. (12) nicely fit to the peak positions of the PA and ED data, as shown in the blue shaded fields of Tab. I.

Now, to understand why the gap increases for the PPP model compared to both, the \( U \)-only model and the non-interacting spectrum, we can analyze \( Z \) and \( \text{Re} \Sigma_k(0) \) in Tab. I. We find \( Z \approx 0.8 \) for the \( U \)-only model and \( Z \approx 0.95 \) in the PPP model. The narrowing effect of \( Z \) in the \( U \)-only model is almost completely canceled by the contribution from \( \text{Re} \Sigma_k(0) \), which brings the band gap very close to its non-interacting value. In the PPP model the effect of \( Z \) is instead almost negligible, and \( \text{Re} \Sigma_k(0) \) is dominated by a large Fock term, proportional to the non-local interaction strength, which strongly enhances the band gap. Since \( \text{Re} \Sigma_k \approx 1.3 \) is quite similar for \( k = 0 \) and \( k = \pi/3 \), the effect is like cutting the non-interacting spectrum at the Fermi level with a pair of scissors and shifting the occupied (unoccupied) down (up). This scissor operator is also a major effect of the GW approximation for semiconductor band gaps.

We can conclude that, despite the sometimes problematic analytic continuation procedure, the PA provides a very good description of the ED spectrum, with the spectral features being somewhat broadened. In particular, the PA predicts very accurately the spectral gap. In contrast, DMFT slightly underestimates the spectral gap for the \( U \)-only model, which is not surprising given the previous analysis of the self-energy.

However, the DMFT results are the same for the \( U \)-only and PPP model (not plotted again in the right panel of Fig. 3), and thus completely miss the enhancement of the spectral gap due to the \( k \)-dependence of \( \text{Re} \Sigma_k \) in case of the PPP model.

The good description of the PA is even more explicit when we inspect the \( k \)-dependent spectral function in the lower of the two plots of Fig. 4. The insets therein show a zoom of the respective main panels, and hence resolve all the spectral features. We observe that the binding energy of all the spectral features of the ED calculation are excellently reproduced by the \( k \)-resolved components within the PA. Please note that, the spectral function at \( k = \pi \) and \( k = \frac{2\pi}{3} \) (above the Fermi energy) can be obtained by mirroring (at the Fermi energy the spectrum of \( k = 0 \) and at \( k = \frac{2\pi}{3} \)). Overall, we can record that the PA provides an excellent approximation of the one-particle spectrum.

### D. Optical conductivity

We study the linear response of the benzene molecule to an electric field. The response is related to the perturbation by the relation \( J(\omega) = \alpha(\omega) E(\omega) \), where the optical conductivity \( \alpha(\omega) \) corresponds to the regular part of the current-current correlation function

\[ \sigma(\omega) = \epsilon^2 \frac{\chi_{jj, q=0}(\omega + i\delta) - \chi_{jj, q=0}(i\delta)}{i(\omega + i\delta)}. \tag{13} \]

Here, the current-current correlation function \( \chi_{jj, q} \) is defined as

\[ \chi_{jj, q} = \int_0^\beta d\tau \langle j_q(\tau) j_{-q}(0) \rangle e^{i\omega_\tau}, \tag{14} \]
FIG. 5. Optical conductivity in z-direction i.e., for a perpendicular electric field [case (i)], calculated with (dark color) and without (light color) vertex corrections for the different models. The insets display the corresponding current-current correlation function $\chi_{C,q=0}(\omega_n)$ (same color code) where the colorful dots correspond to the actual grid points used for the Padé analytic continuation.

where

$$j_q(\tau) = \sum_k \left[ e^{-i(k+q)} - e^{i\hat{k}q} \right] c_{k+q}(\tau) c_k(\tau).$$

(15)

The current-current correlation function $\chi_{jj,q}$ is evaluated in terms of the Green’s function and the full vertex as

$$\chi_{jj,q} = \chi_{jj,q}^{\text{bub}} + \chi_{jj,q}^{\text{ver}} = \frac{2}{\beta N} \sum_k [\gamma_k^q]^2 G_{q+k}G_k$$

$$+ \frac{2}{(\beta N)^2} \sum_{k,k'} \gamma_k^q \gamma_{-k'}^q G_{k'} G_{q+k} G_{k'k'}^* G_{q+k'} G_k,$$

where we have separated the contribution from the bare bubble $\chi_{jj,q}^{\text{bub}}$ and that from the vertex corrections $\chi_{jj,q}^{\text{ver}}$. The matrix elements $\gamma_k^q$ (not to be confused with the two-particle vertices of the parquet equation) depend on the applied perturbation. That is, it depends on the direction in which the electric field is applied and in which direction the current response is measured.

In the following, we consider the optical response for two cases: (i) The external field is a magnetic field applied in the direction perpendicular to the benzene ring. It generates a magnetic flux, and is equivalent to a circular electric field applied along the ring. In this case, the coupling with the electrons at small $q$ is approximately given by the Peierls contribution to the (current) vertex, $\gamma_k = \gamma_{q=0} = 2\tilde{F}(\omega_n) \beta \sin(k)$, where $\tilde{F}(\omega_n)$ is evaluated within density functional theory. Since it is $k$-independent, we can calculate however the optical conductivity up to an unknown prefactor which we set to one. For this second case we use the label $C$ (for constant $\gamma_k$), i.e., $\chi_C$ and $\sigma_C$.

Within victory, Eq. (16) can be easily evaluated. Let us stress that, in order to obtain reasonable results, especially for $\chi_{jj,q}^{\text{bub}}$, the kernel approximations are extensively exploited. For obtaining the optical conductivity $\sigma(\omega)$ we evaluate the Matsubara current-current correlation function and then perform a numerical analytic contin-
nation $\chi_{jj}(\omega_n) \to \chi_{jj}(\omega + i\delta)$ via the Padé method. The analytic continuation is a delicate procedure, and in order to obtain physical result, only a subset of the bosonic Matsubara frequencies has been used, as shown in the insets of Fig. 5. As the temperature considered ($\beta = 10/t$) is low enough, a sparse frequency grid can be used for the interpolation without qualitative changes in the outcome. Note, in fact, that a larger number of input points do not result in actual poles, as they are canceled by the numerator in the continued fraction.

Let us discuss first the case (ii), i.e., the optical response to a perpendicular electric field, with $\gamma_k \propto \text{const.}$ (labeled by $C$). The results for both $\sigma_C(\omega)$ and $\chi_{C,\mathbf{q}=0}(i\omega_n)$ are shown in the main panel and in the inset of Fig. 5, respectively. For $\chi_{C,\mathbf{q}=0}(i\omega_n)$, we show the full dataset as well as the actual subset used for the analytic continuation. The optical conductivity obtained by the analytic continuation displays a single peak. We analyze the evolution of the position of the peak at frequency $\omega_{\text{peak}}$ for the different interaction models and we observe two different effects, as discussed below. Taking into account just the bare bubble contribution $\chi_{\text{bub}}$, the peak if found at $\omega_{\text{peak}} \approx 4.9$ for the $U$-only model. It shifts to a higher frequency $\approx 7.6$ ($U + V_1$) and to $\approx 7.4$ (PPP) when increasing the range of the Coulomb interaction. This is in agreement with the larger gap in the spectral function Fig. 4.

The second effect is a reduction of $\omega_{\text{peak}}$ due to vertex corrections. While this effect is relatively weak in the $U$-only model and still within the uncertainties of the Padé fit ($\omega_{\text{peak}} \approx 4.8 \to 4.9$), it becomes significantly stronger both for the $U + V_1$ ($7.6 \to 6.7$) and the PPP models ($7.4 \to 5.2$). This behavior is consistent with the formation of excitons due to non-local interactions, which cause a shift of weight in the optical conductivity to lower frequencies. The fact that this effect is more pronounced in the PPP model than in the $U + V_1$ one is unexpected. It shows that, although the one-particle self-energy is suppressed by the non-local interactions in the PPP model, the system does not necessarily resemble an effective non-interacting limit. Electronic correlations induced by non-local interactions have a much stronger effect on the two-particle response than on the one-particle properties.

Unfortunately, a quantitative comparison of the results obtained for the PPP model to actual experimental data is difficult. The electron-impact spectra for benzene experience a rich structure of resonances. The low-energy excitations detected in the experiments in the range of $4.5 - 5.5$ eV and $6.2 - 6.5$ eV have been discussed to occur due to vibrational distortions of the benzene ring which are not included in our model. Our results for $\sigma_C(\omega)$ are instead compatible with the broad experimental spectrum observed at energies above $7.5$ eV. However, since the analytic continuation yields a single broad peak with a relatively large width, we do not have the resolution to identify any substructure.

For the bubble contribution, we can also compare the frequency structure of $\sigma_C(\omega)$ to the results obtained from the one-particle Green’s function for the local and the $\mathbf{k}$-resolved spectral function $A_k(\omega)$ in Fig. 4. Optical transitions must occur between occupied and unoccupied parts of $A_k(\omega)$ (i.e., between contributions below and above the Fermi level which is put to zero in Fig. 4). Further the optical transitions must occur between the same momentum $\mathbf{k}$ since the transferred momentum is $\mathbf{q} = 0$. The lowest-energy for transitions within the $U$-only and PPP models occur both for $\mathbf{k} = \frac{\pi}{2}$ (and symmetrically for $\mathbf{k} = \frac{3\pi}{2}$), at a transferred energy $\Delta \omega = 3.9$ and $\Delta \omega = 6.9$, respectively. These values are off by 7% and 20% for the PPP model and $U$-only model, respectively. But given the ambiguity of the Padé method the results are actually quite comparable.

Hence, we obtain a consistent picture between the bubble contribution to $\sigma_C(\omega)$ and the spectral function.

Finally, we can perform a similar analysis as the one above for the optical response to a perpendicular magnetic field, i.e., case (i) with $\gamma_k = \partial \epsilon_k / \partial \mathbf{k}$. The results are shown in Fig. 9. The peak positions of the bubble contribution to the conductivity nicely reproduce the optical gaps of the spectral function; and thus are not affected by the type of field either magnetic or electric. Also, the effect of vertex corrections on the position of the peak is qualitatively similar to the case of perpendicular electric field, for all models. The main difference is that the response is overall larger [taking a dipole element $\gamma_k = 1$ of the same magnitude in case (ii)]—even more so if vertex corrections are taken into account, and that the width of the main peak is substantially reduced.

V. CONCLUSION AND OUTLOOK

We have studied, within the PA, the PPP model and for comparison the six site Hubbard model with periodic boundary conditions ($U$-only model) as well as in-between–the $U + V_1$ model with local and next-nearest neighbor interactions. We find that the vertex is strongly enhanced in the PPP model compared to the $U$-only model, simply because the non-local interaction $V$ itself contributes to the vertex. Except for this effect, both (reducible) vertices are quite similar with the vertex for the PPP model being somewhat more smeared out over a larger frequency range than that of the $U$-only model. As for the leading instabilities, we find that antiferromagnetic fluctuations are dominant for the $U$-only (Hubbard) model, whereas charge fluctuations are so strongly enhanced for the $U+V_1$ model that this model is actually on the verge of a transition to a charge density wave. For the PPP model these charge fluctuations are again suppressed since also interactions to second and third nearest neighbors are included; antiferromagnetic and charge density wave fluctuations turn out to be on par for the PPP model.

Despite the larger vertex, we find that the imaginary part of the self-energy (and with this the quasiparticle
renormalization) of the PPP model is actually much smaller than that of the U-only model. In this respect electronic correlations are reduced. This can be understood as follows: If we consider two electrons, they are strongly correlated in the case of the Hubbard (U-only) model where finding both electrons on the same lattice site is largely suppressed. The non-local interactions, on the other hand, balance the local repulsion and therefore mitigate differences where the two electrons are located; and hence they reduce electronic correlations. However, the non-local interactions also lead to a large static contribution to the \( k \)-dependent self-energy, which in a scissors-like way enhances the splitting of the occupied and unoccupied states. For this reason the one-particle gap in the PPP model is considerably larger. For the optical conductivity, we find that for the PPP model (but not for the U-only model) vertex corrections result in a much smaller optical gap than the gap in the (one-particle) spectral function. In this respect electronic correlations have a large effect also in the PPP model.

Since the self-energies of the PPP and U-only model are so different, DMFT is certainly not a good approximation for the PPP model (or for the conjugated \( \pi \)-bonds in carbon based molecules) as it yields the same self-energy (with and without non-local interactions) as long as there is no symmetry breaking. This is mitigated to some extent when using density functional theory (DFT) as a staring point in the so-called DFT+DMFT approach, but for getting the scissors-like self-energy we observe even a more involved \( GW+\text{DMFT} \) is needed. This also implies that doing one-shot (\textit{ab-initio}) \( \text{DFA} \) calculations with the vertex taken from a DMFT impurity problem is not justified; DMFT is too far away from the correct solution. A self-consistent \( \text{DFA} \) calculation of the vertex is necessary.

Besides self-consistent \( \text{DFA} \), of course also QMC, ED (CI), CC, and (for the special geometry considered) DMRG are viable alternatives for calculating molecules. Our work shows that this list should be supplemented by the PA which has a similar scaling as the CCSD, i.e., the numerical effort scales by the PA which has a similar scaling as the CCSD, i.e.,

\[
\text{PA} \sim N_2^2 N_u^4 \quad \text{(PA)} \quad \text{number of unoccupied states/occupied states which are both in general } \sim N^{23} \quad \text{and the ED even scales exponentially with } N. \text{ The biggest bottleneck of the PA is the memory, vertices in terms of both, Matsubara frequencies and states (or } \textbf{k}\text{-points in case of corresponding symmetries) need to be stored.}
\]

The advantages of the PA are that all one and two-particle quantities are naturally calculated without any significant further efforts, including one-particle spectra measured experimentally in photoemission spectroscopy (PES), two-particle spectra measured e.g. through the optical conductivity, and response function as e.g. the magnetic susceptibility. For dynamical quantities (involving excited states) an analytic continuation is necessary which has some broadening effect. This broadening is more relevant for small molecules, where individual levels are smeared out because of the analytical continuation, than for large molecules, where the actual spectrum is already “smeared out” due to the large number of energy levels. Last but not least, an advantage of the PA is that a physical understanding is fostered: we have, among others, the self-energy and vertex corrections from various channels at hand, not only the total energy and the (in general way to complicated) wave function.

**ACKNOWLEDGMENT**

We would like to thank Felix Hörbinger for helping to set up the ED calculations and Tin Ribic for helpful discussions on the optical conductivity. PP, AK and KH were supported by European Research Council under the European Union’s Seventh Framework Program (FP/2007-2013) through ERC Grant No. 306447, and by the Austrian Science Fund (FWF) through SFB ViCoM F41 and project P 30997. PP has been further supported by the FWF Doctoral School W 1243 “Building Solids for Function”; and AV acknowledges financial support from the Austrian Science Fund (FWF) through the Erwin Schrödinger fellowships J3890-N36, and through project ‘LinReTraCe’ P 30213. Calculations have been done in part on the Vienna Scientific Cluster (VSC).

---

1. R. M. Martin, L. Reinig, D. M. Ceperley, Interacting Electrons: Theory and Computational Approaches, Cambridge University Press Cambridge, 2016.
2. A. Weiße, H. Fehske, Exact Diagonalization Techniques, in: H. Fehske, R. Schneider, A. Weiße (Eds.), Computational Many-Particle Physics, Vol. 739 of Lecture Notes in Physics, Berlin Springer Verlag, 2008, p. 529. doi: 10.1007/978-3-540-74686-7_18
3. P. Thunström, I. Di Marco, O. Eriksson, Electronic entanglement in late transition metal oxides, Phys. Rev. Lett. 109 (2012) 186401. doi:10.1103/PhysRevLett.109.186401
4. M. W. Haverkort, Quanty for core level spectroscopy - excitons, resonances and band excitations in time and frequency domain, Journal of Physics: Conference Series 712 (1) (2016) 012001. URL http://stacks.iop.org/1742-6596/712/i=1/a=012001
5. C. Sherrill, H. F. Schaefer, The Configuration Interaction Method: Advances in Highly Correlated Approaches,
Advances in Quantum Chemistry 34 (1999) 143–269. doi: 10.1016/S0065-3276(08)60532-8
6 W. M. C. Foulkes, L. Mitas, R. J. Needs, G. Rajagopal, Quantum monte carlo simulations of solids [Rev. Mod. Phys. 73 (2001) 33–83. doi:10.1103/RevModPhys.73.33 URL https://link.aps.org/doi/10.1103/RevModPhys.73.33]
7 S. R. White, Density matrix formulation for quantum renormalization groups [Phys. Rev. Lett. 69 (1992) 2863–2866. doi:10.1103/PhysRevLett.69.2863 URL https://link.aps.org/doi/10.1103/PhysRevLett.69.2863]
8 U. Schollwöck, The density matrix renormalization group in the age of matrix product states, Ann. of Phys. 326 (2011) 96.
9 W. Metzner, D. Vollhardt, Correlated lattice fermions in d = ∞ dimensions [Phys. Rev. Lett. 62 (1989) 324–327. doi:10.1103/PhysRevLett.62.324 URL http://link.aps.org/doi/10.1103/PhysRevLett.62.324]
10 A. Georges, G. Kotliar, Hubbard model in infinite dimensions [Phys. Rev. B 45 (1992) 6479–6483. doi:10.1103/PhysRevB.45.6479 URL http://link.aps.org/doi/10.1103/PhysRevB.45.6479]
11 A. Georges, G. Kotliar, W. Krauth, M. J. Rozenberg, Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions, Rev. Mod. Phys. 68 (1) (1996) 13. doi:10.1103/RevModPhys.68.13 URL http://dx.doi.org/10.1103/RevModPhys.68.13
12 G. Rohringer, H. Hafermann, A. Toschi, A. A. Katanin, A. E. Antipov, M. I. Katsnelson, A. I. Lichtenstein, A. N. Rubtsov, K. Held, Diagrammatic routes to nonlocal correlations beyond dynamical mean field theory [Rev. Mod. Phys. 90 (2018) 025003. doi:10.1103/RevModPhys.90.025003 URL https://link.aps.org/doi/10.1103/RevModPhys.90.025003]
13 A. Toschi, A. A. Katanin, K. Held, Dynamical vertex approximation; a step beyond dynamical mean-field theory, Phys Rev. B 75 (2007) 045118. doi:10.1103/PhysRevB.75.045118
14 H. Kusunose, Influence of spatial correlations in strongly correlated electron systems: Extension to dynamical mean field approximation [J. Phys. Soc. Jpn. 75 (5) (2006) 054713. doi:10.1143/JPSJ.75.054713 URL http://jpsj.ipap.jp/link?JPSJ/75/054713/]
15 A. A. Katanin, A. Toschi, K. Held, Comparing pertinent effects of antiferromagnetic fluctuations in the two- and three-dimensional hubbard model [Phys. Rev. B 80 (2009) 075104. doi:10.1103/PhysRevB.80.075104 URL http://link.aps.org/doi/10.1103/PhysRevB.80.075104]
16 A. N. Rubtsov, M. I. Katsnelson, A. I. Lichtenstein, Dual fermion approach to nonlocal correlations in the hubbard model, Phys. Rev. B 77 (2008) 033101. doi:10.1103/PhysRevB.77.033101
17 C. Taranto, S. Andersgassen, J. Bauer, K. Held, A. Katanin, W. Metzner, G. Rohringer, A. Toschi, From infinite to two dimensions through the functional renormalization group [Phys. Rev. Lett. 112 (2014) 196402. doi:10.1103/PhysRevLett.112.196402 URL http://link.aps.org/doi/10.1103/PhysRevLett.112.196402]
18 G. Rohringer, A. Toschi, H. Hafermann, K. Held, V. I. Anisimov, A. A. Katanin, One-particle irreducible functional approach: A route to diagrammatic extensions of the dynamical mean-field theory [Phys. Rev. B 88 (2013) 115112. doi:10.1103/PhysRevB.88.115112 URL http://link.aps.org/doi/10.1103/PhysRevB.88.115112]
19 G. Li, Hidden physics in the dual-fermion approach: A special case of a nonlocal expansion scheme [Phys. Rev. B 91 (2015) 165134. doi:10.1103/PhysRevB.91.165134 URL http://link.aps.org/doi/10.1103/PhysRevB.91.165134]
20 T. Ayral, O. Parcollet, Mott physics and spin fluctuations: a unified framework [Phys Rev. B 92 (2015) 115109. URL http://link.aps.org/doi/10.1103/PhysRevB.92.115109]
21 A. Gallet, P. Thunström, P. Gunacker, J. M. Tomczak, K. Held, Ab initio dynamical vertex approximation [Phys. Rev. B 95 (2017) 115107. doi:10.1103/PhysRevB.95.115107 URL http://link.aps.org/doi/10.1103/PhysRevB.95.115107]
22 F. Coester, H. Kümmler, Short-range correlations in nuclear wave functions [Nuclear Physics B 17 (1966) 477–485. doi:10.1016/0029-5582(66)90140-1 URL http://www.sciencedirect.com/science/article/pii/0029558266901401]
23 R. J. Bartlett, M. Musiał, Coupled-cluster theory in quantum chemistry [Rev. Mod. Phys. 79 (2007) 291–352. doi:10.1103/RevModPhys.79.291 URL https://link.aps.org/doi/10.1103/RevModPhys.79.291]
24 N. E. Bickers, Theoretical Methods for Strongly Correlated Electrons, Springer-Verlag New York Berlin Heidelberg, 2004, Ch. 6, pp. 237–296.
25 C. De Dominicis, Variational formulations of equilibrium statistical mechanics [J. Math. Phys. 3 (5) (1962) 983–1002. doi:10.1063/1.1724313 URL http://jmp.aip.org/resource/1/jmapaq/v3/i5/p983_s1]
26 C. De Dominicis, P. C. Martin, Stationary entropy principle and renormalization in normal and superfluid systems. I. Algebraic formulation [J. Math. Phys. 5 (1) (1964) 14–30. doi:10.1063/1.1704062 URL http://jmp.aip.org/resource/1/jmapaq/v5/i1/p14_s1]
27 N. E. Bickers, S. R. White, Conserving approximations for strongly fluctuating electron systems. ii. numerical results and parquet extension [Phys. Rev. B 43 (1991) 8044–8064. doi:10.1103/PhysRevB.43.8044 URL http://link.aps.org/doi/10.1103/PhysRevB.43.8044]
28 V. Janiš, Parquet approach to nonlocal vertex functions and electrical conductivity of disordered electrons [Phys. Rev. B 64 (2001) 115115. doi:10.1103/PhysRevB.64.115115 URL http://link.aps.org/doi/10.1103/PhysRevB.64.115115]
29 S. X. Yang, H. Fotso, J. Liu, T. A. Maier, K. Tomko, E. F. D’Azevedo, R. T. Scalettar, T. Pruschke, M. Jarrell, Parquet approximation for the 4×4 hubbard cluster [Phys. Rev. E 80 (2009) 046706. doi:10.1103/PhysRevE.80.046706 URL http://link.aps.org/doi/10.1103/PhysRevE.80.
of three-particle vertex within dual fermion calculations. Phys. Rev. B 96 (2017) 235127. doi:10.1103/PhysRevB.96.235127.
URL https://link.aps.org/doi/10.1103/PhysRevB.96.235127.

For the Padé interpolation, about 15 grid points equally spaced with respect to Matsubara frequency are utilized and chosen such that the high-frequency behavior is not included. The correct tail is anyway automatically obtained by the assumed continued fraction.

W. Godby, M. Schlüter, L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159–10175. doi:10.1103/PhysRevB.37.10159.
URL https://link.aps.org/doi/10.1103/PhysRevB.37.10159.

H. Assmann, P. Wissgott, J. Kuneš, A. Toschi, K. Held, Dipole matrix element approach versus peierls approximation for optical conductivity, Phys. Rev. B 85 (2012) 205133. doi:10.1103/PhysRevB.85.205133.
URL https://link.aps.org/doi/10.1103/PhysRevB.85.205133.

Note that the broadening of the PA spectral function in the top panel is larger than for each k-resolved component, since the Padé fit was performed after the k-summation.

W. Godby, M. Schlüter, L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159–10175. doi:10.1103/PhysRevB.37.10159.
URL https://link.aps.org/doi/10.1103/PhysRevB.37.10159.

P. Wissgott, J. Kuneš, A. Toschi, K. Held, Dopole matrix element approach versus peierls approximation for optical conductivity, Phys. Rev. B 85 (2012) 205133. doi:10.1103/PhysRevB.85.205133.
URL https://link.aps.org/doi/10.1103/PhysRevB.85.205133.

Note that the broadening of the PA spectral function in the top panel is larger than for each k-resolved component, since the Padé fit was performed after the k-summation.

W. Godby, M. Schlüter, L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159–10175. doi:10.1103/PhysRevB.37.10159.
URL https://link.aps.org/doi/10.1103/PhysRevB.37.10159.

K. Held, C. Taranto, G. Rohringer, A. Toschi, Hedini equations, gw, gw+dmft, and all that, Lecture Notes of the Autumn School 2011 Hands-on LDA+DMFT, Forschungszentrum Juelich GmbH (publisher). arXiv:1109.3972.
URL http://arxiv.org/abs/1109.3972.

Note that the broadening of the PA spectral function in the top panel is larger than for each k-resolved component, since the Padé fit was performed after the k-summation.

W. Godby, M. Schlüter, L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159–10175. doi:10.1103/PhysRevB.37.10159.
URL https://link.aps.org/doi/10.1103/PhysRevB.37.10159.

K. Held, C. Taranto, G. Rohringer, A. Toschi, Hedini equations, gw, gw+dmft, and all that, Lecture Notes of the Autumn School 2011 Hands-on LDA+DMFT, Forschungszentrum Juelich GmbH (publisher). arXiv:1109.3972.
URL http://arxiv.org/abs/1109.3972.

Note that the broadening of the PA spectral function in the top panel is larger than for each k-resolved component, since the Padé fit was performed after the k-summation.

W. Godby, M. Schlüter, L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159–10175. doi:10.1103/PhysRevB.37.10159.
URL https://link.aps.org/doi/10.1103/PhysRevB.37.10159.

K. Held, C. Taranto, G. Rohringer, A. Toschi, Hedini equations, gw, gw+dmft, and all that, Lecture Notes of the Autumn School 2011 Hands-on LDA+DMFT, Forschungszentrum Juelich GmbH (publisher). arXiv:1109.3972.
URL http://arxiv.org/abs/1109.3972.

Note that the broadening of the PA spectral function in the top panel is larger than for each k-resolved component, since the Padé fit was performed after the k-summation.

W. Godby, M. Schlüter, L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159–10175. doi:10.1103/PhysRevB.37.10159.
URL https://link.aps.org/doi/10.1103/PhysRevB.37.10159.

K. Held, C. Taranto, G. Rohringer, A. Toschi, Hedini equations, gw, gw+dmft, and all that, Lecture Notes of the Autumn School 2011 Hands-on LDA+DMFT, Forschungszentrum Juelich GmbH (publisher). arXiv:1109.3972.
URL http://arxiv.org/abs/1109.3972.

Note that the broadening of the PA spectral function in the top panel is larger than for each k-resolved component, since the Padé fit was performed after the k-summation.

W. Godby, M. Schlüter, L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159–10175. doi:10.1103/PhysRevB.37.10159.
URL https://link.aps.org/doi/10.1103/PhysRevB.37.10159.

K. Held, C. Taranto, G. Rohringer, A. Toschi, Hedini equations, gw, gw+dmft, and all that, Lecture Notes of the Autumn School 2011 Hands-on LDA+DMFT, Forschungszentrum Juelich GmbH (publisher). arXiv:1109.3972.
URL http://arxiv.org/abs/1109.3972.

Note that the broadening of the PA spectral function in the top panel is larger than for each k-resolved component, since the Padé fit was performed after the k-summation.

W. Godby, M. Schlüter, L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159–10175. doi:10.1103/PhysRevB.37.10159.
URL https://link.aps.org/doi/10.1103/PhysRevB.37.10159.

K. Held, C. Taranto, G. Rohringer, A. Toschi, Hedini equations, gw, gw+dmft, and all that, Lecture Notes of the Autumn School 2011 Hands-on LDA+DMFT, Forschungszentrum Juelich GmbH (publisher). arXiv:1109.3972.
URL http://arxiv.org/abs/1109.3972.

Note that the broadening of the PA spectral function in the top panel is larger than for each k-resolved component, since the Padé fit was performed after the k-summation.

W. Godby, M. Schlüter, L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159–10175. doi:10.1103/PhysRevB.37.10159.
URL https://link.aps.org/doi/10.1103/PhysRevB.37.10159.

K. Held, C. Taranto, G. Rohringer, A. Toschi, Hedini equations, gw, gw+dmft, and all that, Lecture Notes of the Autumn School 2011 Hands-on LDA+DMFT, Forschungszentrum Juelich GmbH (publisher). arXiv:1109.3972.
URL http://arxiv.org/abs/1109.3972.