Local Self–Energy Approach For Electronic Structure Calculations

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Using a novel self—consistent implementation of Hedin’s GW perturbation theory we calculate space and energy dependent self–energy for a number of materials. We find it to be local in real space and rapidly convergent on second— to third— nearest neighbors. Corrections beyond GW are evaluated and shown to be completely localized within a single unit cell. This can be viewed as a fully self consistent implementation of the dynamical mean field theory for electronic structure calculations of real solids using a perturbative impurity solver.

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The construction of a controlled practical approximation to the many body problem of solid state physics is a long sought goal. Controlled approximations are important because the accuracy of the results can be improved in a systematic way. This goal has been achieved in quantum chemistry by the configuration interaction (CI) method. CI can be thought as a controlled approximation that becomes more accurate as two factors are increased: a) the number of configurations (i.e. Slater determinants) kept and b) the size of the basis used to represent the one—particle orbitals which are used to represent the configurations. Dynamical mean field theory (DMFT) and its cluster extensions (C–DMFT) [1] [2] merge CI ideas with band structure methods. They allow us to tackle the problem of periodic infinite systems.

The central goal is the computation of the one–electron Greens function, (its Fourier transform can be measured via photoemission and inverse photoemission spectroscopy), \( G(\mathbf{r}, \mathbf{r}', \omega) \), and the self–energy \( \Sigma(\mathbf{r}, \mathbf{r}', \omega) \). At the same time, following Hedin [3], one introduces the effective or screened interaction \( \mathcal{W}(\mathbf{r}, \mathbf{r}', \omega) \). The solution of the full many–body problem can be formulated as the extremization of a functional \( \mathcal{L}[G, \mathcal{W}] = \text{Tr} \ln G + \text{Tr} \ln \mathcal{W} - \Sigma G - \Pi W + \Phi[G, \mathcal{W}] \). It is defined as the Legendre transform of thermodynamic potential with respect to non–interacting Green function and bare Coulomb interaction \( \Pi \). It strongly resembles the Luttinger–Ward functional \( \Phi \) but has extremum both in the self–energy \( \Sigma \) and polarizability \( \Pi \), which plays the role of the self–energy for \( \mathcal{W} \).

The interaction functional \( \Phi[G, \mathcal{W}] \) is then expanded in a perturbative series. The first few graphs are shown in Fig. 1(a) and corresponds to the Hartree, the GW, and the first correction beyond GW. Variations of \( \Phi \) over \( G \) and \( \mathcal{W} \) give us \( \Sigma \) and \( \Pi \). For the self–energy these diagrams are given in Fig. 1(b). To solve the corresponding Dyson equations numerically one introduces a basis set and corresponding expansions for the self energies polarizations and effective interactions. Cluster DMFT ideas truncate the functional \( \Phi \), \( \Sigma \) and \( \Pi \) by setting its variables, i.e. the Greens functions, equal to zero beyond a given range \( R \). When \( R \) is one lattice spacing we have the highly successful single site DMFT, as the range \( R \) increases the approximation converges to the solution of the full many–body problem. In this paper we address the central problem of determining the minimal range that is needed to obtain accurate results for various materials.

There are three different parameters that need to be increased to achieve convergence, a) the size of the basis set \( L_{\text{max}} \), b) the order of the perturbation theory kept \( n_{\text{max}} \), c) the range of the graphs \( R_{\text{max}} \) which needs to be kept to obtain accurate approximation. \( R_{\text{max}} \) depends on \( L \) and \( n \). We do not consider in this paper the important issue of convergence as a function of \( L_{\text{max}} \) as well as the dependence of the range of the type of basis set chosen. Instead we make the choice of a minimal basis set and focus on the issues of convergence as a function of \( n \) and \( R \).

FIG. 1: Diagrammatic representation of the interaction energy functional \( \Phi \) (a) leading to the so called Hedin perturbation series for the self–energy (b). First term in the expansion is the Hartree contribution, second represents GW diagram, third is the correction to GW.
Keeping $R_{\text{max}}$ equal to one lattice spacing and $n_{\text{max}} = \infty$ results in the $L_{\text{max}}$ orbitally degenerate single site DMFT approximation. Keeping $R_{\text{max}} = \infty$ and $n = 1$ corresponds to the famous GW approximation [3, 8, 9]. $R_{\text{max}} = 1$ and $n_{\text{max}} = 1$ is reduced to the local GW approximation introduced by Zein and Antropov [10], as an approximation to accelerate the convergence of the GW method. Keeping $R_{\text{max}}(n = 1) = \infty$, $R_{\text{max}}(n > 1) = 1$ and $n_{\text{max}} = \infty$ constitutes the GW+DMFT approximation [11, 12, 13]. Until now, this approximation has only been fully implemented in model Hamiltonians [12] and its more realistic implementations [12] still contain adjustable parameters such as the double counting correction.

In this work we present a real–space cluster implementation of the GW technique which allows us to monitor directly the locality of the self–energy in the real space. In addition, we evaluate corrections beyond the GW and answer the question of their convergency with respect to the cluster size. We show that the most non–local are the contributions from the diagrams with one loop. It was recognized early on [14] that the higher the order of the diagram, the more local it is because “crossing” integration over internal wavevectors increases the role of large momentum leading to the locality in real space. We show here that in many real solids, the truncation of diagrams beyond one loop to the range of one lattice constant is already very accurate.

We also investigate the smallest value of $R_{\text{max}}$ which is needed to obtain accurate results for each value of $L$. This allows us to obtain fully self consistent results, independent of the starting point where local density approximation (LDA) to density functional theory (DFT) serves in many cases [6, 7, 8, 9]. We establish that even in case of semiconductors when the Coulomb interactions have an infinite range due to lack of screening, a reasonable small cluster produces very accurate results. The size of the cluster needed to obtain accurate results is reduced as the order in perturbation theory increases.

For weakly correlated systems our approach can be regarded as a trick to simplify and accelerate the solution of the GW equations and further perturbation corrections to it. Alternatively, our approach should be viewed as the first fully self–consistent implementation of an ab initio cluster DMFT method for solids (with second order perturbation theory playing the role of impurity solver).

We discuss the results of our calculations for a number of materials such as simple and transition metals as well as semiconductors. Especially the latter class represents a hard case scenario for methodologies based on local self–energy approximations due to the long range nature of its statically screened Coulomb interaction. We focus on the electronic structure of Si, a benchmark in the past GW studies. Some aspects of this problem are still debated, such as the effect of higher lying energy states, core exchange, pseudopotential vs. all–electron approximations [10, 13]. We focus on the convergence of the electronic structure as a function of the cluster size used for determination of the self–energy for a given basis set. We also evaluate several diagrams beyond GW to examine the issue of convergency of the whole perturbation theory with respect to the Coulomb interaction.

Our implementation is based on the linear muffin–tin orbital (LMTO) method for electronic structure calculations using the atomic sphere approximation (ASA) [13] which has been already used in realizations of GW [6, 9, 13]. The LMTO basis functions separate the wavevector and radial dependences

$$\chi^{\mathbf{k}}(\mathbf{r}) = \Phi^{H}(\mathbf{r}) + \sum_{L} \Phi^{J}_{L}(\mathbf{r}) S^{L}_{\mathbf{k}}. \quad (1)$$

Here $S^{L}_{\mathbf{k}}$ are the LMTO structure constants while $\Phi^{H, J}_{L}$ are linear combinations of the solutions of the radial Schrödinger equation as well as their energy derivatives taken at some fixed set of energies $\epsilon_{\nu}$ at the center of interest which are matched continuously and differentiably to spherical Hankel (H) and Bessel (J) functions at the muffin–tin sphere boundaries.

In order to find the matrix elements $\Sigma_{\alpha\beta}(\mathbf{k}, \omega_{\nu})$ of the self–energy operator $\Sigma(\mathbf{r}, \mathbf{r}', \omega_{\nu})$ in brackets of the LMTOs (1) for a set of imaginary Matsubara frequencies $\omega_{\nu} = (2n + 1)\pi T$ it is useful to represent real space vectors $\mathbf{r} = \rho + \mathbf{R}$, $\mathbf{r}' = \rho' + \mathbf{R}'$, where $\rho, \rho'$ are restricted by the unit–cell, $\mathbf{R}, \mathbf{R}'$ are the lattice translations, and re–denote $\Sigma(\mathbf{r}, \mathbf{r}', \omega_{\nu}) = \Sigma_{R}(\rho, \rho', \omega_{\nu})$ (due to translational invariance we can always set $\mathbf{R}' = 0$). Then, $\Sigma_{\alpha\beta}(\mathbf{k}, \omega_{\nu})$ has the following structure

$$\Sigma_{\alpha\beta}(\mathbf{k}, \omega_{\nu}) = \Sigma^{(HH)}_{\alpha\beta}(\mathbf{k}, \omega_{\nu}) + \sum_{L} \Sigma^{(HJ)}_{\alpha L}(\mathbf{k}, \omega_{\nu}) S^{L}_{\mathbf{k}} + \sum_{L} S^{k}_{L \alpha} \Sigma^{(JJ)}_{L \beta}(\mathbf{k}, \omega_{\nu}) S^{L}_{\mathbf{k}} + \sum_{L} S^{L}_{L \alpha} \Sigma^{(JJ)}_{L L}(\mathbf{k}, \omega_{\nu}) S^{L}_{\mathbf{k}} \quad (2)$$

where $\Sigma_{LL'}^{(\mu\nu)}(\mathbf{k}, \omega_{\nu}) = \sum_{R} e^{i \mathbf{k} \mathbf{R}} \Sigma_{LL'}^{(\mu\nu)}(\mathbf{R}, \omega_{\nu})$ and the cluster self–energy is given by the matrix element

$$\Sigma_{LL'}^{(\mu\nu)}(\mathbf{R}, \omega_{\nu}) = \int \Phi^{(\mu\nu)*}_{L'}(\rho) \Sigma_{R}(\rho, \rho', \omega_{\nu}) \Phi^{(\mu\nu)*}_{L'}(\rho') d\rho d\rho'. \quad (3)$$

As we see, even if $\Sigma(\mathbf{r}, \mathbf{r}', \omega_{\nu})$ can be local (i.e. non–zero only when both $\mathbf{r}$ and $\mathbf{r}'$ are in the same cell), the
The Green function is proportional to

\[ G(\rho, \rho', \omega_n) = \sum_{\mu \nu = HJ} \Phi_\mu^{(i)}(\rho) G^{(\mu \nu)}(\mathbf{r}, \omega_n) \Phi_\nu^{(i)}(\rho') \]

and, as a result, the polarization operator \( \Pi(\mathbf{r}, \mathbf{r'}, \omega_n) \),

| Table I: Correlational contribution to the self-energy matrix element, \( \Sigma_{c,LL}(\mathbf{r}, \omega_0) \), in eV as a function of \( \mathbf{R} \) for Fe, Ni, Na, Al, and Si. \( \mathbf{R}_1 = a/\sqrt{2}, \mathbf{R}_2 = a, \mathbf{R}_3 = a\sqrt{3}/2 \) in fcc structure, \( \mathbf{R}_1 = a\sqrt{3}/2, \mathbf{R}_2 = a, \mathbf{R}_3 = a\sqrt{3}/2 \) in bcc structure, \( \mathbf{R}_1 = 0.5a, \mathbf{R}_2 = 0.83a \) \( \mathbf{R}_3 = a \) in diamond structure. |
|---|---|---|---|---|---|
| \( \mathbf{R} = 0 \) | \( \mathbf{R}_1 \) | \( \mathbf{R}_2 \) | \( \mathbf{R}_3 \) |
| Fe: \( \Sigma_{ss}(\mathbf{R}) \) | 0.70 | 0.35 | 0.16 | 0.00 |
| Fe: \( \Sigma_{dd}(\mathbf{R}) \) | 6.53 | 0.05 | 0.08 | 0.00 |
| Ni: \( \Sigma_{ss}(\mathbf{R}) \) | -0.54 | 0.05 | 0.03 | 0.00 |
| Ni: \( \Sigma_{dd}(\mathbf{R}) \) | 7.34 | 0.38 | -0.03 | 0.00 |
| Na: \( \Sigma_{ss}(\mathbf{R}) \) | -1.36 | 0.52 | 0.30 | 0.05 |
| Al: \( \Sigma_{pp}(\mathbf{R}) \) | 0.46 | 0.16 | -0.08 | 0.00 |
| Si: \( \Sigma_{ss}(\mathbf{R}) \) | 0.95 | 0.30 | 0.14 | 0.03 |
| Si: \( \Sigma_{pp}(\mathbf{R}) \) | -1.06 | 0.05 | -0.27 | -0.03 |

| Table II: Polarizability \( \Pi_{ij}(\mathbf{R}, \omega = 0) \) as a function of cluster size \( \mathbf{R} \) as well as \( \Pi_{ij}(\mathbf{k} = 0, \omega = 0) \) for Si (\( ij = 3 \) numerates empty spheres). \( \Sigma \Pi \) shows how the sum rule \( \Pi(k \to 0, \omega \equiv 0) \to 0 \) is fulfilled in both \( \mathbf{R} \)-space and \( \mathbf{k} \)-space calculations. |
|---|---|---|---|---|---|
| \( \mathbf{R} = 0 \) | \( \Pi_{11} \) | \( \Pi_{12} \) | \( \Pi_{13} \) | \( \Pi_{14} \) | \( \Sigma \Pi \) |
| \( \mathbf{R}_1 \) | 5.34 | 0 | 0 | 0 | 14.78 |
| \( \mathbf{R}_2 \) | 4.98 | -2.60 | -0.55 | 0.21 | 6.76 |
| \( \mathbf{R}_3 \) | 4.98 | -2.67 | -1.00 | -0.09 | 3.45 |
| \( \mathbf{k} \)-space | 4.96 | -3.36 | -1.159 | -0.21 | 0.81 |
| \( \mathbf{k} \)-space | 4.96 | -3.36 | -1.14 | -0.23 | 0.41 |
in Si approximately extends up to a third coordination sphere.

We have evaluated the first self–energy correction beyond GW, \( \Delta \Sigma(\mathbf{R}) \), for Si as a function of the cluster size. Our obtained on-site values for s and p electrons are as follows: \( \Delta \Sigma_{s}(0) = 0.22 \, \text{eV} \) and \( \Delta \Sigma_{p}(0) = -0.14 \, \text{eV} \). The self–energies at first and second coordination sphere are given by: \( \Delta \Sigma_{s}(\mathbf{R}_{1}) = 0.002 \, \text{eV} \), \( \Delta \Sigma_{p}(\mathbf{R}_{1}) = -0.002 \, \text{eV} \), \( \Delta \Sigma_{s}(\mathbf{R}_{2}) = 0.0003 \, \text{eV} \), \( \Delta \Sigma_{p}(\mathbf{R}_{2}) = -0.0005 \, \text{eV} \). We see that the correction to GW is completely local and permits us to calculate it in the real space which much less time–consuming. It is also interesting to note that the energy dependence of this correction exists but at the same scale as in \( \Sigma_{GW} \).

We finally would like to address a highly interesting question on the accuracy of the GW calculations in predicting the energy gaps in various semiconductors and insulators. We have performed such calculations with and without imposing the self–consistency for the Green function which in the latter case corresponds to the LDA Green function used in evaluating the interactions and the self–energies. We refer to these calculations as self–consistent (SC) and "first shot" (FS) ones. We include the core exchange effects, whose importance has been recently pointed out \[14]\]. The results of these studies are presented in Table III where we list the obtained energy gaps for a whole series of materials such as C, Si, MgO, and AlAs. The available previous calculations and experimental data are also listed in this table for comparison. Despite the possible inaccuracies introduced by the use of a limited basis set, which does not include very high–energy states, we see that our non–self–consistent calculations are in good agreement with the published data. The self–consistency is not only of conceptual importance, since it makes the solution of the problem independent on the starting point, but can also affect the quality of the results in some systems such as AlAs.

In conclusion we have developed a self-consistent cluster DMFT methodology which allows us to monitor the locality of the self–energy in the real space. As a first application of the method we evaluated first contribution in Hedin’s perturbation series for the self–energy in Si and found it to be completely local. Our calculated energy gap values for a number of semiconductors and insulators are found in good agreement with experiment. The fast convergence in real space demonstrated in this paper simplifies and accelerates the GW approximation which is useful in many solids. Our approach is also the ideal starting point for resuming the perturbation theory at the local level using non–perturbative solvers as was done in Ref. \[13\]. This step will allow us to study very strongly correlated systems completing the first principles C–DMFT program for solids.

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![Figure 2](image-url)  
**FIG. 2:** Direct and indirect energy gaps as well as valence bandwidth for Si in eV calculated by varying the size of the cluster used when evaluating correlational part of the self–energy within the GW method.

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**TABLE III:** Comparison between calculated energy gaps (eV) in semiconductors and insulators using non–self–consistent “first shot” (FS) and self–consistent (SC) GW methods obtained in the present work, results of other available GW calculations and experiment.

| Material | FS (this work) | SC (this work) | FS | SC | Exp. |
|----------|----------------|----------------|----|----|------|
| C        | 5.00           | 5.02           | 4.92\(^a\) | –  | 5.48\(^b\) |
| Si       | 0.86           | 1.10           | 0.85\(^b\) | 1.05\(^c\) | 1.17\(^b\) |
| MgO      | 8.00           | 5.90           | 8.3\(^d\) | –  | 7.8\(^d\) |
| AlAs     | 1.33           | 1.90           | 1.05\(^e\) | –  | 2.24\(^b\) |

\(^{a}\)Ref.14; \(^{b}\)Ref.20; \(^{c}\)Ref.16; \(^{d}\)Ref.21; \(^{e}\)Ref.22.
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