

Local Self-Energy Approach for Electronic Structure Calculations

N. E. Zein,^{1,2} S. Y. Savrasov,² and G. Kotliar^{3,4}

¹RRC “Kurchatov Institute”, Moscow 123182, Russia

²Department of Physics, University of California, Davis, California 95616, USA

³Center for Material Theory, Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA

⁴École Polytechnique, 91128 Palaiseau Cedex, France

(Received 29 November 2005; published 7 June 2006)

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.

DOI: 10.1103/PhysRevLett.96.226403

PACS numbers: 71.28.+d, 71.20.-b, 75.30.Mb

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. Dynamical mean field theory (DMFT) and its cluster extensions (C-DMFT) [1,2] can be considered as candidates for such a controlled approximation as they permit one to improve accuracy in a systematic way increasing the number of electronic states per site and the number of lattice sites in a cluster.

The central goal is the computation of the one-electron Green 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 $W(\mathbf{r}, \mathbf{r}', \omega)$. The solution of the full many-body problem can be formulated as the extremization of a functional $L[G, W] = \text{Tr} \ln G + \text{Tr} \ln W - \Sigma G - \Pi W + \Phi[G, W]$. It is defined as the Legendre transform of thermodynamic potential with respect to noninteracting Green function and bare Coulomb interaction [4]. It strongly resembles the Luttinger-Ward functional [5] but has extremum both in the self-energy Σ and polarizability Π , which plays the role of the self-energy for W .

The interaction functional $\Phi[G, W]$ 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 Φ over G and W give us Σ and Π . 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 Φ , Σ , and Π by setting its variables, i.e., the Green functions, equal to zero beyond a given range R [2]. 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 Letter we address the central prob-

lem 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_{max} , (b) the order of the perturbation theory kept n_{max} , and (c) the range of the graphs R_{max} which needs to be kept to obtain accurate approximation. R_{max} depends on L and n . We do not consider in this Letter the important issue of convergence as a function of L_{max} nor the dependence of the range on the type of the 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 .

Keeping R_{max} equal to one lattice spacing and $n_{\text{max}} = \infty$ results in the multiband single site DMFT approximation. Keeping $R_{\text{max}} = \infty$ and $n = 1$ corresponds to the famous GW approximation [3,6–9]. $R_{\text{max}} = 1$ and $n_{\text{max}} = 1$ are 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 $GW + \text{DMFT}$ approximation [10–13]. Until now, this approximation has been fully implemented only in the context of model Hamiltonians [13], and its more realistic implemen-

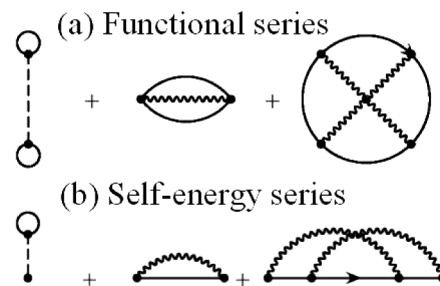


FIG. 1. Diagrammatic representation of the interaction energy functional Φ (a) and the self-energy Σ (b). The first term in both graphs corresponds to Hartree, the second term is GW [3], and the third term is a correction to GW .

tations [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 nonlocal 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 wave vectors increases the role of large momentum leading to the locality in real space. Here we show that in many real solids, the truncation of diagrams beyond one loop to the range of one lattice constant is already very accurate.

Our approach allows us to obtain fully self-consistent results, independent of the starting point where local density approximation (LDA) to density functional theory [15] serves in many cases [6–9]. We establish that even in the case of semiconductors where the Coulomb interactions have an infinite range due to lack of screening, a reasonably 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 the 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 past *GW* studies. Some aspects of this problem are still debated, such as the effect of higher lying energy states, core exchange, and pseudopotential vs all-electron approximations [16,17]. 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 [18], which has been already used in realizations of *GW* [6,19]. The LMTO basis functions separate the wave vector and radial dependences: $\chi_{\alpha}^{\mathbf{k}}(\mathbf{r}) = \Phi_{\alpha}^H(\mathbf{r}) + \sum_L \Phi_L^J(\mathbf{r}) S_{L\alpha}^{\mathbf{k}}$, where $S_{L\alpha}^{\mathbf{k}}$ are the LMTO structure constants while $\Phi_L^{H,J}$ are linear combinations of radial wave functions as well as their energy derivatives matched to Hankel (*H*) and Bessel (*J*) functions at the sphere boundary.

In order to find the matrix elements $\Sigma_{\alpha\beta}(\mathbf{k}, i\omega_n)$ of the self-energy operator $\Sigma(\mathbf{r}, \mathbf{r}', i\omega_n)$ in brackets of the LMTOs for a set of imaginary Matsubara frequencies $\omega_n = (2n + 1)\pi T$, we use atomic sphere approximation and represent real-space vectors $\mathbf{r} = \rho + \mathbf{R}$ and $\mathbf{r}' = \rho' + \mathbf{R}'$, where ρ, ρ' are restricted by the unit cell and $\mathbf{R}, \mathbf{R}'$ are the lattice translations. We redenote $\Sigma(\mathbf{r}, \mathbf{r}', i\omega_n) = \Sigma_{\mathbf{R}}(\rho, \rho', i\omega_n)$ (due to translational invariance we can always set $\mathbf{R}' = 0$). Then, as discussed in Ref. [20], $\Sigma_{\alpha\beta}(\mathbf{k}, i\omega_n)$ has the following structure:

$$\begin{aligned} \Sigma_{\alpha\beta}(\mathbf{k}, i\omega_n) = & \Sigma_{\alpha\beta}^{(HH)}(\mathbf{k}, i\omega_n) + \sum_L \Sigma_{\alpha L}^{(HJ)}(\mathbf{k}, i\omega_n) S_{L\beta}^{\mathbf{k}} \\ & + \sum_L S_{L\alpha}^{\mathbf{k}*} \Sigma_{L\beta}^{(JH)}(\mathbf{k}, i\omega_n) \\ & + \sum_L S_{L\alpha}^{\mathbf{k}*} \Sigma_{LL'}^{(JJ)}(\mathbf{k}, i\omega_n) S_{L\beta}^{\mathbf{k}}, \end{aligned} \quad (1)$$

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

$$\Sigma_{LL'}^{(\mu\nu)}(\mathbf{R}, i\omega_n) = \int \Phi_L^{(\mu)*}(\rho) \Sigma_{\mathbf{R}}(\rho, \rho', i\omega_n) \Phi_{L'}^{(\nu)}(\rho') d\rho d\rho'. \quad (2)$$

As we see, even if $\Sigma(\mathbf{r}, \mathbf{r}', i\omega_n)$ can be local (i.e., nonzero only when both $\mathbf{r}$ and $\mathbf{r}'$ are in the same cell), the matrix elements $\Sigma_{\alpha\beta}(\mathbf{k}, i\omega_n)$, Eq. (1), acquire some $\mathbf{k}$ dependence through the structure constants. It is due to the tails of the basis functions extended over all space, and it is quite analogous to the $\mathbf{k}$ dependence of local potential matrix elements in LDA. Such $\mathbf{k}$ dependence can be called “kinematical,” and in the following we will distinguish it from the dynamical $\mathbf{k}$ dependence connected to the existence of $\mathbf{R} \neq 0$ elements of $\Sigma_{\mathbf{R}}(\rho, \rho', i\omega_n)$, which is the main focus of the present work.

In our implementation, we solve the equation for the dynamically screened interaction $W = V - V\Pi W$ on the product of basis functions following Ref. [21]. After finding $W(\mathbf{r}, \mathbf{r}', i\omega_n)$ the self-energy is calculated either as $\Sigma(\mathbf{R}) = G(\mathbf{R})W(\mathbf{R})$ ($\mathbf{R}$ -space version) or as $\Sigma(\mathbf{k}) = \sum_{\mathbf{q}} G(\mathbf{k})W(\mathbf{k} + \mathbf{q})$ ($\mathbf{k}$ -space version). All calculations are performed on the imaginary energy axis. Because of the large frequency behavior of the Green function proportional to $1/i\omega_n$, special care should be taken for the direct exchange contribution to the self-energy ($\Sigma_x = -GV$), as the sum over large ω_n needs to be done analytically. The remaining portion, $\Sigma_c = G(V\Pi W)$, is due to correlations, and the sum over internal frequencies is rapidly convergent. Finally, in order to obtain the electronic spectrum for real frequencies we analytically continue the Green function using 40th to 60th order Padé’s approximation [22]. For the energies near E_f the accuracy of this procedure is checked by independent computations of quasiparticle Green functions.

We perform self-consistent *GW* calculations for Fe, Ni, Na, and Si using our newly developed cluster algorithm

and obtain the self-energies in real space. To discuss the results of these calculations, Table I lists the diagonal matrix elements of the correlational part of the self-energy $\Sigma_{c,ll}^{HH}(\mathbf{R}, i\omega_0)$, as a function of $\mathbf{R}$ for the value of $\omega_0 = \pi T = \pi 400K$. [In case of magnetic ground state $\Sigma_{c,ll}^{HH}(i\omega_0)$ is for majority spins.] From Table I it follows that $\Sigma_{c,dd}(\mathbf{R} = 0)$ dominates in transition metals and falls off very quickly in nearest neighbors, because of both small overlap between d orbitals and large screening at small energies. The $\Sigma_{c,ss}(\mathbf{R})$ in these metals falls off more gradually, but its value is negligible in comparison with d . It explains why the recently developed one-site approach [10] is successful in this case. In simple metals like Na and Al, only Σ_s and Σ_p are significant; they fall off gradually, but nevertheless on the third coordination sphere they become small as compared to $\Sigma(\mathbf{R} = 0)$, even if they are multiplied by a number of nearest neighbors at this sphere. In Si with its two atoms per unit cell (denoted by vectors τ), translation $\mathbf{R}$ should be replaced by nearest distance $\mathbf{R}_{ij} = \mathbf{R} + \tau_i - \tau_j$, and both $\Sigma_{c,ss}(\mathbf{R}_{ij})$ and $\Sigma_{c,pp}(\mathbf{R}_{ij})$ fall off pretty slowly but nevertheless become very small at $\mathbf{R}$'s comparable with the size of the unit cell in accord with the conclusions reached in the pioneering work [8].

Turning to a similar study for the polarizability Π function we should point out that for a semiconductor it is intrinsically nonlocal because one has to satisfy the f -sum rule $\Pi(\mathbf{k} \rightarrow 0, \omega \equiv 0) \rightarrow 0$, which requires cancellation between on-site and intersite terms. We examined how this sum rule is fulfilled for Si, where values of $\Pi(\mathbf{R}, \omega \equiv 0)$ are computed for several $\mathbf{R}$'s. We conclude that this has rather long range expansion and we need cluster sizes comparable with the Si lattice parameter to produce the desired accuracy.

We now investigate the convergency of the electronic structure of Si using the cluster GW method. Both the direct and indirect energy gaps as well as the valence band width are calculated by varying the size of the cluster used when evaluating the correlational part of the self-energy. The behavior of the electronic structure as a func-

TABLE I. Correlational contribution to the self-energy matrix element, $\Sigma_{c,ll}^{HH}(\mathbf{R}, i\omega_0)$, in eV as a function of $\mathbf{R}$ for Fe, Ni, Na, Al, and Si. $\mathbf{R}_1 = a/\sqrt{2}$, $\mathbf{R}_2 = a$, $\mathbf{R}_3 = a\sqrt{2}$ in fcc structure; $\mathbf{R}_1 = a\sqrt{3}/2$, $\mathbf{R}_2 = a$, $\mathbf{R}_3 = a\sqrt{2}$ in bcc structure; $\mathbf{R}_1 = a\sqrt{3}/4$, $\mathbf{R}_2 = a/\sqrt{2}$, $\mathbf{R}_3 = a$ 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

tion of the cluster size is schematically shown on Fig. 2. They indicate that the nonlocality of the self-energy 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: $\Delta\Sigma_s(0) = 0.22$ eV and $\Delta\Sigma_p(0) = -0.14$ eV. The self-energies at first and second coordination sphere are given by $\Delta\Sigma_s(\mathbf{R}_1) = 0.002$ eV, $\Delta\Sigma_p(\mathbf{R}_1) = -0.002$ eV, $\Delta\Sigma_s(\mathbf{R}_2) = 0.0003$ eV, and $\Delta\Sigma_p(\mathbf{R}_2) = -0.0005$ eV. We see that the correction to GW is completely local and permits us to calculate it in the real space which is 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 Σ_{GW} . To check whether the convergence of the self-energy in the real space is influenced by higher energy states we have performed LMTO calculations with doubling the basis set using the so-called multiple kappa technique. We did not find any significant changes compared to the data obtained with single kappa minimal LMTO basis. This is readily understood based on the quasiclassical argument which was noted earlier in Ref. [23].

We finally would like to address a question on predicting the energy gaps in semiconductors and insulators widely discussed in the current literature [16,17]. We have performed such calculations with and without imposing 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 the self-consistent and “first shot” ones. In both cases Π was calculated as a product of two corresponding Green functions without inclusion of vertex terms. We include the core exchange effects, whose importance has been recently pointed out [16]. The results of these studies are presented in Table II where we list the obtained energy gaps for a whole series of materials, such

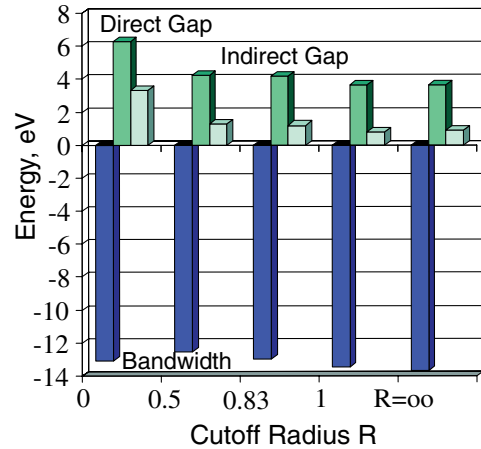


FIG. 2 (color online). Direct and indirect energy gaps as well as valence bandwidth for Si in eV calculated by varying the size of the cluster used when evaluating the correlational part of the self-energy within the GW method.

TABLE II. 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, and results of other available *GW* calculations and experiment.

	FS (this work)	SC (this work)	FS	SC	Experiment
C	5.00	5.02	5.33 ^a	...	5.48 ^b
Si	0.86	1.10	1.24 ^a , 0.85 ^c	1.05 ^c	1.17 ^b
MgO	8.00	5.90	8.2 ^d	...	7.8 ^e
AlAs	1.33	1.90	2.18 ^a , 1.65 ^f	...	2.24 ^b

^aReference [9].

^bReference [24].

^cReference [16].

^dReference [25].

^eReference [26].

^fReference [27].

as C, Si, MgO, and AlAs. The available previous calculations and experimental data are also listed in Table II for comparison. As we conclude, our present implementation shows that all our obtained *GW* values are well within the range of the published data by highly accurate pseudopotential and linear augmented plane wave based calculations, which gives us a foundation to believe that our evaluated corrections beyond *GW* are correct. However, due to the use of minimal LMTO basis sets, issues connected with the omission of full potential terms, as well as errors introduced by energy linearization procedure we are unable to provide further comments on the *GW* accuracy.

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, we evaluated first contribution in Hedin’s perturbation series for the self-energy in Si and found it to be completely local. Our approach is ideal for resuming the perturbation theory at the local level as was recently done in Ref. [13]. This step will allow us to study strongly correlated systems completing the first principles C-DMFT program for solids.

This work was supported by the Council for the Support of Leading Scientific Schools of Russia under Grant No. NS-1572.2003.2. Support from NSF-ITR Grants No. 0312478 and No. 0604531 and the DOE Computational Material Science network is gratefully acknowledged together with NSF DMR Grants No. 0096462 and No. 0608283, and DOE Grants No. DEFG02-99ER45761 and No. LDRD-DR 200030084. G.K. is supported by the Blaize Pascal Chair of the Foundation de l’Ecole Normale.

[1] For a review, see A. Georges, G. Kotliar, W. Krauth, and M. Rozenberg, *Rev. Mod. Phys.* **68**, 13 (1996).

- [2] For a review, see G. Kotliar, S. Savrasov, K. Haule, V. Oudovenko, O. Parcolett, and C. Marianetti, *Rev. Mod. Phys.* (to be published).
- [3] L. Hedin, *Phys. Rev.* **139**, A796 (1965).
- [4] C. O. Almbladh, U. von Barth, and R. van Leeuwen, *Int. J. Mod. Phys. B* **13**, 535 (1999); R. Chitra and G. Kotliar, *Phys. Rev. B* **63**, 115110 (2001).
- [5] J.M. Luttinger and J.C. Ward, *Phys. Rev.* **118**, 1417 (1960).
- [6] For a review, see F. Aryasetiawan and O. Gunnarson, *Rep. Prog. Phys.* **61**, 237 (1998).
- [7] G. Strinati, H.J. Mattausch, and W. Hanke, *Phys. Rev. Lett.* **45**, 290 (1980).
- [8] M. S. Hybertsen and S. G. Louie, *Phys. Rev. Lett.* **55**, 1418 (1985).
- [9] R. W. Godby, M. Schlüter, and L. J. Sham, *Phys. Rev. B* **37**, 10 159 (1988).
- [10] N. E. Zein and V. P. Antropov, *Phys. Rev. Lett.* **89**, 126402 (2002).
- [11] G. Kotliar and S. Y. Savrasov, in *New Theoretical Approaches to Strongly Correlated Systems*, edited by A. M. Tsvelik (Kluwer Academic Publishers, Dordrecht, 2001), p. 259.
- [12] S. Biermann, F. Aryasetiawan, and A. Georges, *Phys. Rev. Lett.* **90**, 086402 (2003).
- [13] P. Sun and G. Kotliar, *Phys. Rev. Lett.* **92**, 196402 (2004).
- [14] V. A. Khodel and E. E. Saperstein, *Phys. Lett.* **36B**, 429 (1971).
- [15] For a review, see, e.g., *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and S. H. March (Plenum, New York, 1983).
- [16] W. Ku and A. Eguiluz, *Phys. Rev. Lett.* **89**, 126401 (2002).
- [17] M. L. Tiago, S. Ismaili-Beigi, and S. G. Louie, *Phys. Rev. B* **69**, 125212 (2004); Kris Delaney, P. García-González, Angel Rubio, Patrick Rinke, and R. W. Godby, *Phys. Rev. Lett.* **93**, 249701 (2004); P. Rinke, A. Qteish, J. Neugebauer, C. Freysoldt, and M. Scheffler, *New J. Phys.* **7**, 126 (2005).
- [18] O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).
- [19] S. V. Faleev, M. van Schilfgaarde, and T. Kotani, *Phys. Rev. Lett.* **93**, 126406 (2004).
- [20] S. Y. Savrasov and G. Kotliar, *Phys. Rev. B* **69**, 245101 (2004).
- [21] F. Aryasetiawan and O. Gunnarson, *Phys. Rev. B* **49**, 16 214 (1994).
- [22] H. J. Vidberg and J. Serene, *J. Low Temp. Phys.* **29**, 179 (1977).
- [23] W. Kohn and L. Sham, *Phys. Rev.* **137**, A1697 (1965).
- [24] *Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, M. Schultz, and H. Weiss, Landolt-Bornstein, Group III, Vol. 17a (Springer, New York, 1982).
- [25] A. Yamasaki and T. Fujiwara, *Phys. Rev. B* **66**, 245108 (2002).
- [26] R. C. Whited, C. J. Flaten, and W. C. Walker, *Solid State Commun.* **13**, 1903 (1973).
- [27] S. Lebegue, B. Arnaud, M. Alouani, and P. Blochl, *Phys. Rev. B* **67**, 155208 (2003).