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First-principles calculations of the electronic structure and spectra of strongly correlated systems: dynamical mean-field theory

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Abstract. A recently developed dynamical mean-field theory, in the iterated perturbation theory approximation, was used as a basis for the construction of a 'first-principles' calculation scheme for investigating the electronic structure of strongly correlated electron systems. This scheme is based on the local density approximation (LDA) within the framework of the linearized muffin-tin orbitals (LMTO) method. The classical example of the doped Mott insulator $La_{1-x}Sr_xTiO_3$ was studied by the new method, and the results showed qualitative improvement when compared with experimental photoemission spectra.

1. Introduction

The accurate calculation of the electronic structure of materials starting from first principles is a challenging problem in condensed-matter science, since, unfortunately, except for small molecules, it is impossible to solve many-electron problems without imposing severe approximations.

For materials for which the kinetic energy of the electrons is more important than the Coulomb interactions, the most successful first-principles method is the density functional theory (DFT) within the local (spin-) density approximation (L(S)DA) [1], in which the many-body problem is mapped onto a non-interacting system with a one-electron exchange–correlation potential approximated by that of the homogeneous electron gas.

It is now generally accepted that the spin-density functional theory within the local density approximation is a reliable starting point for first-principles calculations of material properties of weakly correlated solids (for a review, see [2]). The situation is very different when we consider more strongly correlated materials (systems containing f and d electrons). In a very simplified view, the LDA can be regarded as a Hartree–Fock approximation with an orbital-independent (averaged) one-electron potential. This approximation is very crude for strongly correlated systems, where the on-site Coulomb interaction between d (or f) electrons of transition metal (or rare-earth metal) ions (Coulomb parameter U) is strong enough to overcome the kinetic energy, which is of the order of the band width W. As a result, the LDA gives a qualitatively wrong answer even for such simple systems as Mott insulators with integer numbers of electrons per site (the so-called 'undoped Mott insulators'). For example, the insulators CoO and La_2CuO_4 are predicted to be metallic by the LDA.

The search for a 'first-principles' computational scheme for the physical properties of strongly correlated electron systems that is as successful as the LDA is for weakly correlated systems is very important, in view of the considerable significance of this class of materials, and is an area of intensive current research. Notable examples of first-principles schemes that have been applied to strongly correlated electron systems are the $LDA + U$ method [3], which is akin to the orbital–spin-unrestricted Hartree–Fock method using a basis of LDA wave functions, *ab initio* unrestricted Hartree–Fock calculations [4], and the use of a constrained LDA to derive model parameters of model Hamiltonians which are then treated by means of the exact diagonalization of small clusters or other approximations [5].

Many interesting effects, such as orbital and charge ordering in transition metal compounds, were successfully described by the LDA+U method [6]. However, for strongly correlated metals, the Hartree–Fock approximation is too crude, and more sophisticated approaches are needed.

Recently, a dynamical mean-field theory was developed [7] that is based on the mapping of lattice models onto quantum impurity models subject to a self-consistency condition. The resulting impurity model can be solved by means of various approaches (e.g. quantum Monte Carlo, exact diagonalization), but the most promising for possible use in a 'realistic' calculation scheme is the iterated perturbation theory (IPT) approximation, which was proved to give results in a good agreement with more rigorous methods.

This paper is the first in a series, in which we plan to integrate recent developements of the dynamical mean-field approach with state-of-the-art band-structure calculation techniques, to generate an *'ab initio'* scheme for the calculation of the electronic structure of correlated solids. For a review of the historical development of the dynamical mean-field approach in its various implementations, see reference [7]. In this paper, we implement the dynamical mean-field theory in the iterated perturbation theory approximation, and carry out band-structure calculations using a LMTO basis. The calculational scheme is described in section 2. We present results obtained by applying this method to $La_{1-x}Sr_xTiO_3$, which is a classical example of a strongly correlated metal.

2. The calculation scheme

In order to be able to implement the achievements of the Hubbard model theory within the LDA, one needs a method that could be mapped onto the tight-binding model. The linearized muffin-tin orbitals (LMTO) method within the orthogonal approximation [8] can be naturally presented as tight-binding calculation scheme (in a real-space representation):

$$H_{LMTO} = \sum_{ilm, jl'm', \sigma} (\delta_{ilm, jl'm'} \epsilon_{il} \hat{n}_{ilm\sigma} + t_{ilm, jl'm'} \hat{c}^\dagger_{ilm\sigma} \hat{c}_{jl'm'\sigma}) \tag{1}$$

(i is the site index, and l and m are orbital indices).

As we have mentioned above, the LDA one-electron potential is orbital independent, and Coulomb interaction between d electrons is taken into account in this potential in an averaged way. In order to generalize this Hamiltonian by including Coulomb correlations, one must add an interaction term:

$$H_{int} = \frac{1}{2} \sum_{ilmm'\sigma\sigma' m\sigma \neq m'\sigma'} U_{il} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma'}. \tag{2}$$

We have temporarily neglected the exchange terms and the dependence of the Coulomb parameter U on the particular pair of orbitals mm'. Throughout the following, we will assume that only for one shell, l_d, of one type of atom, i_d (for example, d orbitals of

the transition metal ions), does the Coulomb interaction need to be taken into account ($U_{il} = U\delta_{il,i_d l_d}$), and in the following the indices il will be omitted. All other orbitals will be considered as resulting in itinerant bands, and to be well described by the LDA. Such separation of the electronic states into localized and itinerant is close in spirit to the Anderson model.

To avoid double counting, one must at the same time subtract the averaged Coulomb interaction energy term, which we assume is present in the LDA. Unfortunately, there is no direct connection between the Hubbard model and the LDA (because the LDA is based on the homogeneous electron gas theory and not on the localized atomic-type orbitals representation), and it is impossible to express the LDA energy rigorously through the d–d Coulomb interaction parameter U. However, it is known that the LDA total energy as a function of the total number of electrons is a good approximation, and the value of the Coulomb parameter U obtained in the LDA calculation agrees well with experimental data and the results from the more rigorous calculations [9]. This leads us to suggest that a good approximation for the LDA part of the Coulomb interaction energy is

$$E_{Coul} = \frac{1}{2}Un_d(n_d - 1) \tag{3}$$

($n_d = \sum_{m\sigma} n_{m\sigma}$ is the total number of d electrons).

In the LDA Hamiltonian, ϵ_d has the meaning of the LDA one-electron eigenvalue for d orbitals. It is known that in the LDA the eigenvalue is the derivative of the total energy over the occupancy of the orbital:

$$\epsilon_d = \frac{\mathrm{d}}{\mathrm{d}n_d}E_{LDA}. \tag{4}$$

If we want to introduce new ϵ_d^0 where d–d Coulomb interaction is excluded, we must define them as

$$\epsilon_d^0 = \frac{\mathrm{d}}{\mathrm{d}n_d}(E_{LDA} - E_{Coul}) = \epsilon_d - U\left(n_d - \frac{1}{2}\right). \tag{5}$$

Then the new Hamiltonian will have the form

$$H = H^0 + H_{int}$$
$$H^0 = \sum_{ilm,jl'm',\sigma}(\delta_{ilm,jl'm'}\epsilon_{il}^0\hat{n}_{ilm\sigma} + t_{ilm,jl'm'}\hat{c}_{ilm\sigma}^\dagger\hat{c}_{jl'm'\sigma}). \tag{6}$$

In reciprocal space, the matrix elements of the operator H^0 are

$$H_{qlm,q'l'm'}^0(\boldsymbol{k}) = H_{qlm,q'l'm'}^{LDA}(\boldsymbol{k}) - \delta_{qlm,q'l'm'}\delta_{ql,i_d l_d}U\left(n_d - \frac{1}{2}\right) \tag{7}$$

(q is an index of the atom in the elementary unit cell).

In the dynamical mean-field theory, the effect of Coulomb correlation is described by the self-energy operator in the local approximation. The Green function is

$$G_{qlm,q'l'm'}(\mathrm{i}\omega) = \frac{1}{V_B}\int \mathrm{d}\boldsymbol{k}\ [\mathrm{i}\omega + \mu - H_{qlm,q'l'm'}^0(\boldsymbol{k}) - \delta_{qlm,q'l'm'}\delta_{ql,i_d l_d}\Sigma(\mathrm{i}\omega)]^{-1} \tag{8}$$

($[\cdots]^{-1}$ means inversion of the matrix, integration is over the Brillouin zone, μ is the chemical potential, and V_B is the volume of the Brillouin zone).

In the following, we will consider the paramagnetic case and an orbitally and spin-degenerate system, so that the self-energy $\Sigma(\mathrm{i}\omega)$ does not depend on the orbital and spin indices. One can define the effective Anderson model Green function through

$$G(\mathrm{i}\omega) = G_{i_d l_d m, i_d l_d m}(\mathrm{i}\omega) = (\mathrm{i}\omega + \mu - \Delta(\mathrm{i}\omega) - \Sigma(\mathrm{i}\omega))^{-1} \tag{9}$$

where $\Delta(i\omega)$ is the effective-impurity hybridization function. The effective-medium 'bath' Green function G^0 is defined as

$$G^0(i\omega) = (i\omega + \tilde{\mu} - \Delta(i\omega))^{-1} = (G^{-1}(i\omega) + \Sigma(i\omega) + \tilde{\mu} - \mu)^{-1} \tag{10}$$

($\tilde{\mu}$ is the chemical potential of the effective medium).

The chemical potential of the effective medium $\tilde{\mu}$ is varied to satisfy the Luttinger theorem condition:

$$\frac{1}{\beta} \sum_{i\omega_n} e^{i\omega_n 0^+} G(i\omega_n) \frac{d}{d(i\omega_n)} \Sigma(i\omega_n) = 0. \tag{11}$$

In the iterated perturbation theory approximation, the *ansatz* for the self-energy is based on the second-order perturbation theory term calculated with the 'bath' Green function G^0:

$$\Sigma^0(i\omega_s) = -(N-1)U^2 \frac{1}{\beta^2} \sum_{i\omega_n} \sum_{ip_m} G^0(i\omega_m + ip_n) G^0(i\omega_m) G^0(i\omega_s - ip_n). \tag{12}$$

N is the degeneracy of the orbitals, including spin; $\beta = 1/kT$; the Matsubara frequencies $\omega_s = (2s+1)\pi/\beta$; $p_n = 2n\pi/\beta$; and s and n are integers.

The term Σ^0 is renormalized to ensure the correct atomic limit:

$$\Sigma(i\omega) = Un(N-1) + \frac{A\Sigma^0(i\omega)}{1 - B\Sigma^0(i\omega)} \tag{13}$$

(n is the orbital occupation number: $n = (1/\beta)\sum_{i\omega_n} e^{i\omega_n 0^+} G(i\omega_n)$) where

$$B = \frac{U[1-(N-1)n] - \mu + \tilde{\mu}}{U^2(N-1)n_0(1-n_0)} \tag{14}$$

$$A = \frac{n[1-(N-1)n] + (N-2)D[n]}{n_0(1-n_0)} \tag{15}$$

$$n_0 = \frac{1}{\beta} \sum_{i\omega_n} e^{i\omega_n 0^+} G^0(i\omega_n) \tag{16}$$

and the correlation function $D[n] \equiv \langle \hat{n}\hat{n} \rangle_{CPA}$ is calculated using the coherent potential approximation (CPA) for the Green function, with the parameter $\delta\mu$ chosen to preserve the orbital occupation number n:

$$G_{CPA}(i\omega) = \frac{[1 - n(N-1)]}{i\omega + \mu - \Delta(i\omega) + \delta\mu} + \frac{n(N-1)}{i\omega + \mu - \Delta(i\omega) - U + \delta\mu} \tag{17}$$

$$n = \frac{1}{\beta} \sum_{i\omega_n} e^{i\omega_n 0^+} G_{CPA}(i\omega_n) \tag{18}$$

$$D[n] = n \sum_{i\omega_n} e^{i\omega_n 0^+} \frac{1}{i\omega + \mu - \Delta(i\omega_n) - U + \delta\mu}. \tag{19}$$

The Matsubara frequency convolution in (12) was performed with the time variables representation using a fast-Fourier-transform algorithm for the transition from energy to time variables and back:

$$G^0(\tau) = \frac{1}{\beta} \sum_{i\omega_n} e^{-i\omega_n \tau} G^0(i\omega_n) \tag{20}$$

$$\Sigma(\tau) = -(N-1)U^2 G^0(\tau) G^0(\tau) G^0(-\tau) \tag{21}$$

$$\Sigma^0(i\omega_n) = \int_0^\beta d\tau \, e^{i\omega_n \tau} \Sigma(\tau). \tag{22}$$

The serious problem is that of how to perform the integration in k-space over the Brillouin zone. For this we used the generalized Lambin–Vigneron algorithm [10]. We define a new matrix $H(k, z)$ as

$$H(k, z) = H^0(k) + \Sigma(z) \tag{23}$$

where z is the complex energy, and the term $\Sigma(z)$ is added only to diagonal elements of the H-matrix corresponding to d orbitals. In this matrix notation, the Green function is

$$G(z) = \frac{1}{V_B} \int dk \ [z - H(k, z)]^{-1}. \tag{24}$$

After diagonalization, the matrix $H(k, z)$ can be expressed in terms of the diagonal matrix of its eigenvalues $D(k, z)$ and its eigenvector matrix $U(k, z)$:

$$H(k, z) = U(k, z)D(k, z)U^{-1}(k, z) \tag{25}$$

and Green function:

$$G(z) = \frac{1}{V_B} \int dk \ U(k, z)[z - D(k, z)]^{-1}U^{-1}(k, z). \tag{26}$$

A particular matrix element of the Green function is calculated as

$$G_{ij}(z) = \sum_n \frac{1}{V_B} \int dk \ \frac{U_{in}(k, z)U_{nj}^{-1}(k, z)}{z - D_n(k, z)}. \tag{27}$$

In the analytical tetrahedron method, the irreducible wedge of the Brillouin zone is divided into a set of tetrahedra, and the total integral is calculated as a sum over the tetrahedra. To perform the integration over a given tetrahedron with its four corners at the positions given by the vectors k_i ($i = 1, 2, 3, 4$), the denominator of the fraction in equation (27) is interpolated as a linear function in k-space. In the result, the integral over one tetrahedron is expressed in terms of the values of the numerator and denominator at the corners of the tetrahedron:

$$\sum_n \frac{1}{V_B} \int_v dk \ \frac{U_{in}(k, z)U_{nj}^{-1}(k, z)}{z - D_n(k, z)} = \sum_n \sum_{i=1}^{4} r_i^n U_{in}(k_i, z)U_{nj}^{-1}(k_i, z)\frac{v}{V_B} \tag{28}$$

where v is the tetrahedron volume, and

$$r_i^n = (z - D_n(k_i, z))^2 \Big/ \left(\prod_{k(\neq i)} (D_n(k_k, z) - D_n(k_i, z)) \right)$$

$$+ \sum_{j(\neq i)} \left[(z - D_n(k_j, z))^3 \Big/ \left(\prod_{k(\neq j)} (D_n(k_k, z) - D_n(k_j, z)) \right) \right]$$

$$\times \frac{\ln[(z - D_n(k_j, z))/(z - D_n(k_i, z))]}{(D_n(k_i, z) - D_n(k_j, z))}. \tag{29}$$

The self-energy $\Sigma(i\omega_n)$ and Green function $G(i\omega_n)$ are calculated at the imaginary Matsubara frequencies $i\omega_n = i\pi(2n + 1)/\beta$. It is sufficient to calculate expectation values, such as the orbital occupancies n, but in order to calculate spectral properties one needs to know the Green function on the real axis. The real-axis equivalent of equations (12) is much more complicated and hard to implement numerically than the Matsubara frequencies version. It is much more convenient to perform analytical continuation from imaginary energy values to the real ones. For such continuation, we have used a Padé approximant
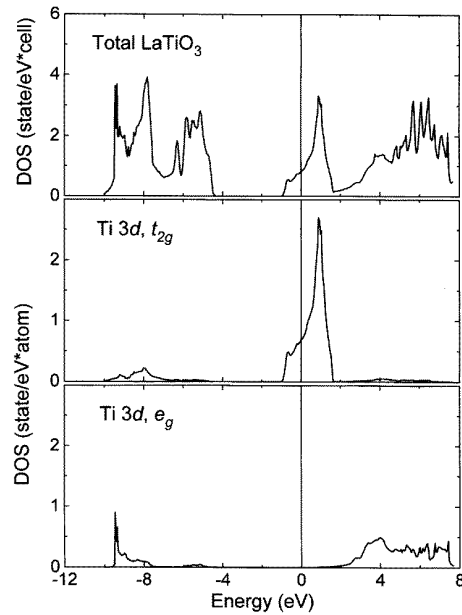
Figure 1. Non-interacting ($U = 0$) total and partial densities of states (DOS) for LaTiO$_3$.

algorithm [11]. If one has a set of complex energies z_i ($i = 1, \ldots, M$) and a set of values of the analytical function u_i, then the approximant is defined as a continued fraction:

$$C_M(z) = \cfrac{a_1}{1 + \cfrac{a_2(z - z_{2)}}{1 + \cdots \cfrac{a_M(z - z_{M-1})}{1}}} \tag{30}$$

where the coefficients a_i are to be determined in such a way that

$$C_M(z_i) = u_i \qquad i = 1, \ldots, M. \tag{31}$$

The coefficients a_i are then given by the recursion

$$a_i = g_i(z_i) \qquad g_1(z_i) = u_i \qquad i = 1, \ldots, M \tag{32}$$

$$g_p(z) = \frac{g_{p-1}(z_{p-1}) - g_{p-1}(z)}{(z - z_{p-1})g_{p-1}(z)} \qquad p \geqslant 2. \tag{33}$$

The recursion formula for the continued fraction finally yields
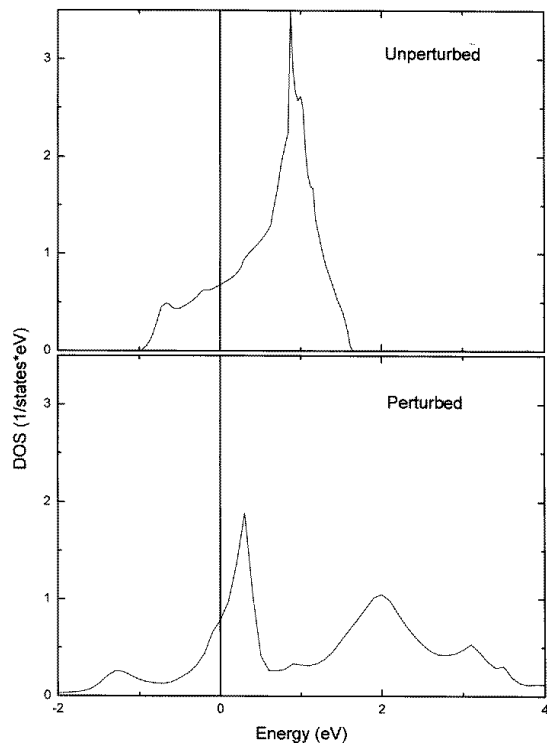
$$C_M(z) = A_M(z)/B_M(z) \tag{34}$$

where

$$A_{n+1}(z) = A_n(z) + (z - z_n)a_{n+1}A_{n-1}(z)$$
$$B_{n+1}(z) = B_n(z) + (z - z_n)a_{n+1}B_{n-1}(z) \tag{35}$$

and

$$A_0 = 0 \qquad A_1 = a_1 \qquad B_0 = B_1 = 1.$$

We have found that the most convenient method is to use analytical continuation not for the Green function G but only for the the self-energy Σ, and then to calculate G directly on the real axis through the Brillouin zone integration (28).

**Figure 2.** The partial (t_{2g}) DOS obtained from IPT calculations, in comparison with the non-interacting DOS.

3. Results

We have applied the above-described calculation scheme to the doped Mott insulator $La_{1-x}Sr_xTiO_3$. $LaTiO_3$ is a Pauli paramagnetic metal at room temperature, and below $T_N = 125$ K it is an antiferromagnetic insulator with a very small gap value (0.2 eV). Doping with a very small amount of Sr (a few per cent) leads to the transition to a paramagnetic metal with a large effective mass. As photoemission spectra of this system also show a strong deviation from the non-interacting-electrons picture, $La_{1-x}Sr_xTiO_3$ is regarded as an example of a strongly correlated metal.

The crystal structure of $LaTiO_3$ is that of a slightly distorted cubic perovskite. The Ti ions have octahedral coordination of the oxygen ions, and the t_{2g}–e_g crystal-field splitting of the d shell is strong enough to survive in the solid. In figure 1, the total and partial DOS of paramagnetic $LaTiO_3$ are presented, as obtained from LDA calculations (the LMTO method). At 3 eV above the O 2p band, there is a Ti 3d band split into t_{2g} and e_g subbands, which are well separated from each other. The Ti^{4+} ions have the d^1 configuration, and the t_{2g} band is one sixth filled.

As only the t_{2g} band is partially filled, and the e_g band is completely empty, it is reasonable to consider Coulomb correlations between t_{2g} electrons only, and the degeneracy factor N in equation (12) is equal to 6. The value of the Coulomb parameter U was calculated by the supercell procedure [9], regarding just the t_{2g} electrons as localized ones, and allowing the e_g electrons to participate in the screening. This calculation resulted in a
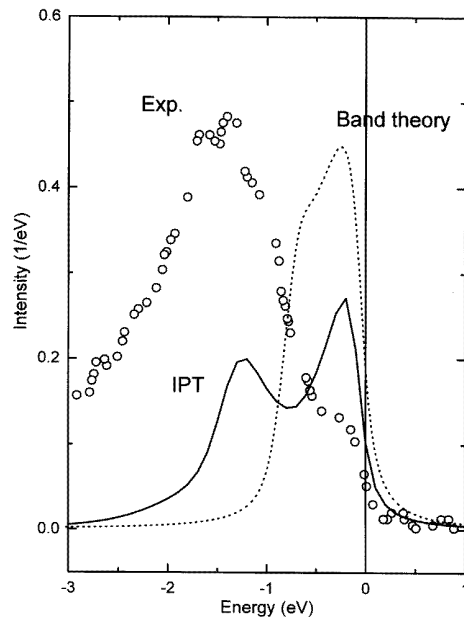
Figure 3. Experimental and theoretical photoemission spectra of $La_{1-x}Sr_xTiO_3$ ($x = 0.06$).

value of 3 eV. As the localization must lead to an energy gap between electrons with the same spin, the effective Coulomb interaction will be reduced by the value of the exchange parameter $J = 1$ eV. So we have used the effective Coulomb parameter $U_{eff} = 2$ eV. The results of the calculation for $x = 0.06$ (doping with Sr was imitated by decreasing the total number of electrons as in the rigid-band approximation for alloys) are presented in the form of the t_{2g} DOS in figure 2. Its general form is the same as for the model calculations: a strong quasiparticle peak at the Fermi energy, and incoherent subbands below and above it corresponding to the lower and upper Hubbard bands.

The appearance of the incoherent lower Hubbard band in our DOS leads to qualitatively better agreement with photoemission spectra. In figure 3, the experimental XPS for $La_{1-x}Sr_xTiO_3$ ($x = 0.06$) [12] is presented with the non-interacting (LDA) and interacting (IPT) occupied DOS broadened to imitate the experimental resolution. The main correlation effect, namely the simultaneous presence of coherent and incoherent bands in the XPS, is successfully reproduced in the IPT calculation. However, as one can see, the IPT overestimates the strength of the coherent subband.

In this article, we have presented results for the one-particle spectral function at a specific density. Before any serious comparison with experiment can be made, one has to perform a convolution with the instrumental resolution function, and take into account the possible effects of surface disorder which can be present in the sample. For model Hamiltonians, a dynamical mean-field study of models of this kind has recently been performed by Sarma *et al* [13].

4. Conclusions

In this article, we have described how one can interface methods for realistic band-structure calculations with the recently developed dynamical mean-field technique to obtain a fully

'*ab initio*' method for calculating the electronic spectra of solids.

In comparison with earlier calculations, this work introduces several methodological advances: the dynamical mean-field equations are incorporated into a realistic electronic structure calculation scheme, with parameters obtained from a first-principles calculation and with the realistic orbital degeneracy of the compound.

To check our method, we applied it to doped titanates, for which a large body of model calculation studies using dynamical mean-field theory are available. The results are very encouraging, considering the experimental uncertainties of the analysis of the photoemission spectra of these compounds.

We have used two relatively accurate (but still approximate) methods for the solution of the band-structure aspect and the correlation aspects of this problem: the LMTO in the ASA approximation, and the IPT approximation. In principle, one can use other techniques for handling these two aspects of the problem, and further applications to more complicated materials are necessary to determine the degree of quantitative accuracy of the method.

Acknowledgments

References

[1] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[2] Jones R O and Gunnarsson O 1989 *Rev. Mod. Phys.* **61** 689
[3] Anisimov V I, Zaanen J and Andersen O K 1991 *Phys. Rev.* B **44** 943
[4] Massida S, Posternak M and Baldareschi A 1992 *Phys. Rev.* B **46** 11 705
Towler M D, Allan N L, Harrison N M, Sunders V R, Mackrodt W C and Apra E 1994 *Phys. Rev.* B **50** 5041
[5] Hybertsen M S, Schlueter M and Christensen N 1989 *Phys. Rev.* B **39** 9028
[6] Anisimov V I, Aryasetiawan F and Lichtenstein A I 1997 *J. Phys.: Condens. Matter* **9** 767
[7] Georges A, Kotliar G, Krauth W and Rozenberg M J 1996 *Rev. Mod. Phys.* **68** 13
[8] Andersen O K 1975 *Phys. Rev.* B **12** 3060
Gunnarsson O, Jepsen O and Andersen O K 1983 *Phys. Rev.* B **27** 7144
[9] Anisimov V I and Gunnarsson O 1991 *Phys. Rev.* B **43** 7570
[10] Lambin P and Vigneron J P 1984 *Phys. Rev.* B **29** 3430
[11] Vidberg H J and Serene J W 1977 *J. Low Temp. Phys.* **29** 179
[12] Fujimori A, Hase I, Namatame H, Fujishima Y, Tokura Y, Eisaki H, Uchida S, Takegahara K and de Groot F M H 1992 *Phys. Rev. Lett.* **69** 1796
(Actually, in this article, the chemical formula of the sample was $LaTiO_{3.03}$, but the excess of oxygen produces 6% holes, which is equivalent to doping with 6% Sr.)
[13] Sarma D D, Barman S, Kajueter H and Kotliar G 1996 *Europhys. Lett.* **36** 307