Multiple LMTO method and down folding

Shoji Kobayashi and Takeo Fujiwara
Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan
(Received 4 September 1996)

The multiple linear muffin-tin-orbital method is reexamined from viewpoints of the Hermitian property of the Hamiltonian and down folding. It is stressed that, without down folding, the same angular-momentum components should be included in every energy channel. To reduce the number of basis orbitals, the down-folding procedure is essential. The energy band structure in paramagnetic nickel is exemplified in several choices of basis functions, using the down folding and the combined correction. [S0163-1829(97)04811-X]

I. INTRODUCTION

We are now in a new era of first-principle electronic structure calculations. One of recent vital development is the methodological one for strongly correlated electron systems, e.g., local density approximation plus Hubbard-type Coulomb interactions method,[1] and the GW approximation for the excitation spectra.[2]

In order to develop methods, a crucial point is the amount of computation. The linear muffin-tin orbital (LMTO) method is advantageous from this viewpoint, e.g., the storage and CPU time is very light, although the accuracy can be very high and controllable, and the muffin-tin orbital basis is very convenient for an analysis of calculated results and further calculation using the outcome of the LMTO calculation. The LMTO method even makes it possible to construct the model Hamiltonian of the low-energy excitation directly.[3]

Instead of a light amount of computation, the original LMTO method does not make it easy to calculate the electronic structure over a wide range of energy, because the original LMTO method uses one orbital per angular momentum $L\equiv(l,m)$. In order to investigate over a wider energy range, we should divide the energy range into several energy panels, and different LMTO calculations should be pursued separately in each energy panel.[4]

In order to improve this ''patched-together'' LMTO band structure in the original LMTO method, a multiple LMTO method was recently proposed by Aryasetiawan and Gunnarson,[5] who calculated the energy-loss spectrum.[6] This method, the multiple LMTO method, prepares several orbitals corresponding to different principal quantum numbers with the same angular momentum (l,m), and calculation can be performed at the same time. This extension is very promising to apply to the all-electron calculations with core or semicore orbitals, and to the GW approximation which requires the higher excited orbitals. On the other hand, this method has not yet matured, and many methodological attempts should be tested. For the further development of applications of the multiple LMTO method, we should develop the multiple LMTO method up to the same stage of the LMTO method with a single energy channel.

When we studied multiple LMTO computations, we noticed a very important point of the Hermitian property of the Hamiltonian and the effect of the down folding different from those observed by the original LMTO method. In Sec. II, we will give a short but comprehensive review, just for beginners, of the LMTO method and of our further developments. Section III is devoted to a discussion of the development of the multiple LMTO method, especially a discussion of the Hermitian property of the Hamiltonian, inclusion of the combined correction, and down folding. The down folding procedure is essential to reduce the number of basis orbitals. Examples of the calculation will be given for paramagnetic nickel in Sec. IV with special attention paid to the combined correction and down folding.

II. LMTO WITH MOST LOCALIZED BASIS

In this section, we will give a short review of the LMTO method, especially the most localized basis formalism,[7–9] that makes it convenient to develop the multiple LMTO method in later sections.

A. LMTO

The wave function $\psi_j(\mathbf{r})$ of the eigenstate j may be expanded, using the LMTO basis functions $\overline{\chi_{\mathbf{R}L,\infty}}$, as

$$\psi_j(\mathbf{r})=\sum_{\mathbf{R}L,\infty}\overline{\chi_{\mathbf{R}L,\infty}}(\mathbf{r})u_{\mathbf{R}L,j}, \tag{1}$$

with expansion coefficients $u_{\mathbf{R}L,j}$. The LMTO is defined as

$$\overline{\chi_{\mathbf{R}L,\infty}}=\phi_{\mathbf{R}L}+\sum_{\mathbf{R}'L'}\overline{\dot{\phi}_{\mathbf{R}'L'}}\overline{h_{\mathbf{R}'L':\mathbf{R}L}}+\overline{\chi^{t}_{\mathbf{R}L}} \tag{2}$$

or, in matrix form,

$$|\overline{\chi}\rangle_{\infty}=|\phi\rangle+|\overline{\dot{\phi}}\rangle\overline{h}+|\overline{\chi}\rangle^{t}, \tag{3}$$

with

$$\overline{\dot{\phi}_{\mathbf{R}L}}=\dot{\phi}_{\mathbf{R}L}+\phi_{\mathbf{R}L}\overline{o_{\mathbf{R}L}}. \tag{4}$$

The label $\mathbf{R}$ denotes the atomic position. Here $\phi_{\mathbf{R}L}$ and $\dot{\phi}_{\mathbf{R}L}$ are a wave function and its energy derivative function, respectively, at an arbitrary fixed energy $E_{\nu l}$, usually chosen in the energy region of interest. They satisfy equations

$$(-\nabla^2+V-E_\nu)|\phi\rangle=0,$$
$$(-\nabla^2+V-E_\nu)|\dot{\phi}\rangle=|\phi\rangle. \tag{5}$$

The subscript ∞ means that the function is defined over whole space. The function without the subscript ∞ is defined only within the specified augmentation sphere and is zero outside. The function $\overline{\chi^l_{\mathbf{R}L}}$, on the other hand, is zero inside augmentation spheres and equal to the original wave function in the interstitial region between the spheres. The matrix $\overline{o}$ is diagonal with respect to $\mathbf{R}$ and L, and defines the bar representation. The matrix $h_{\mathbf{R}'L':\mathbf{R}L}$ can be determined so that the LMTO is continuously connected over the whole space.

The envelope function for the LMTO may be chosen to be the singular solution of the equation

$$(-\nabla^2-\kappa^2)K^0_{\mathbf{R}L,\infty}=0, \tag{6}$$

where $\kappa^2=E-V_{\mathrm{MTZero}}$ and V_{MTZero} is the flat potential in the interstitial region. The envelope function $K^0_{\mathbf{R}L,\infty}$ can be expanded with the well-known one-center expansion formula as

$$K^0_{\mathbf{R}L,\infty}=K^0_{\mathbf{R}L}-\sum_{\mathbf{R}'L'} J^0_{\mathbf{R}'L'}S^0_{\mathbf{R}'L':\mathbf{R}L}+K^{0\,i}_{\mathbf{R}L} \tag{7}$$

or

$$|K^0\rangle_\infty=|K^0\rangle-|J^0\rangle S^0+|K^0\rangle^i, \tag{8}$$

and $J^0_{\mathbf{R}L}$ is the regular solution of the Eq. (6). The function $S^0_{\mathbf{R}'L':\mathbf{R}L}$ is called the bare structure constant, which depends upon the atomic structure and κ^2.

The envelope function $K^0_{\mathbf{R}L,\infty}$ may be inconvenient, because the bare structure constant S^0 is not short ranged. To modify the envelope function, we add the singular solution K^0 to the regular solution J^0 as

$$|J\rangle=|J^0\rangle-|K^0\rangle\alpha. \tag{9}$$

The matrix α is diagonal with respect to $\mathbf{R}$ and L, and defines the screened representation. According to Eq. (9), the envelope function, or the screened multipole field, is defined as

$$|K\rangle_\infty=|K^0\rangle-|J\rangle S+|K\rangle^i. \tag{10}$$

From Eqs. (8), (9), and (10), we obtain the screened structure constant

$$S=S^0(1-\alpha S^0)^{-1} \tag{11}$$

and the relations between $|K^0\rangle$ and the screened multipole field $|K\rangle$ as

$$|K\rangle_\infty=|K^0\rangle_\infty(1+\alpha S),$$
$$|K\rangle^i=|K^0\rangle^i(1+\alpha S). \tag{12}$$

B. Most localized basis

The normalization condition within a sphere can be written by matrix equations

$$\langle\phi|\phi\rangle=1,$$
$$\langle\dot{\phi}|\dot{\phi}\rangle\equiv p,$$
$$\langle\dot{\phi}|\phi\rangle=0, \tag{13}$$
$$\langle\dot{\overline{\phi}}|\phi\rangle=\overline{o},$$
$$\langle\dot{\overline{\phi}}|\dot{\phi}\rangle=\overline{o^2}+p.$$

Since the tail of the multipole field $|K\rangle_\infty$ should be continuously connected with the tail of the LMTO, i.e., $D\{J\}=D\{\dot{\overline{\phi}}\}$, $\overline{o}$ is related with α as

$$\overline{o}=-\frac{W\{J^0,\dot{\phi}\}-W\{K^0,\dot{\phi}\}\alpha}{W\{J^0,\phi\}-W\{K^0,\phi\}\alpha}, \tag{14}$$

and α is explicitly determined as

$$\alpha=\frac{W\{J^0,\dot{\overline{\phi}}\}}{W\{K^0,\dot{\overline{\phi}}\}}. \tag{15}$$

Here $D\{f\}$ is a logarithmic derivative of a radial function f at the sphere edge $r=s$,

$$D\{f\}=s\frac{f'(s)}{f(s)},$$

and $W\{a,b\}$ is a (diagonal) Wronskian matrix of radial functions $a(r)$ and $b(r)$ at the sphere edge $r=s$, i.e.,

$$W\{a,b\}=a(s)b(s)[D\{b\}-D\{a\}].$$

Once we fix the matrix α as in Eq. (18), the matrix $\overline{o}$ is determined by a choice of E_ν where ϕ and $\dot{\phi}$ are defined.

By the condition of continuous connection of K and J to ϕ and $\dot{\overline{\phi}}$ at the sphere edge, we obtain an explicit expression of the continuity,

$$|K\rangle_\infty\rightarrow-|\overline{\chi}\rangle_\infty W\{K^0,\dot{\overline{\phi}}\}=|\overline{\chi}\rangle_\infty\left(\frac{w}{2\Delta}\right)^{1/2}, \tag{16}$$

and an explicit expression of the matrix $\overline{h}$,

$$\overline{h}=-\frac{W\{K^0,\phi\}}{W\{K^0,\dot{\overline{\phi}}\}}+\left(\frac{2}{w}\right)^{1/2}W\{J,\phi\}SW\{J,\phi\}\left(\frac{2}{w}\right)^{1/2}$$
$$\equiv(C-E_\nu)+\Delta^{1/2}S\Delta^{1/2}, \tag{17}$$

where w is the scaling factor of the lattice structure, and C and Δ are diagonal matrices defined above. Independent parameters may be E_ν and α (or $\overline{o}$). Other parameters ϕ, $\dot{\phi}$, $\overline{o}$ (or α), C, and Δ can be all uniquely determined after choosing E_ν and α (or $\overline{o}$).

The elements of the matrix α for the most localized basis may be chosen as

$$\alpha_{s,p,d}=0.3485,\quad 0.053\,03,\quad 0.010\,714,$$
$$\alpha_l=0\quad \text{for } l\geqslant 3. \tag{18}$$

C. Overlap and Hamiltonian matrices

The overlap matrix can be easily written down, using Eqs. (3) and (13), as

$$\overline{O}={}_\infty\langle\overline{\chi}|\chi\rangle_\infty=(1+\overline{oh})^\dagger(1+\overline{oh})+\overline{h}^\dagger p\overline{h}+{}^i\langle\overline{\chi}|\chi\rangle^i. \tag{19}$$

Noting Eq. (5), the Hamiltonian matrix can be also easily calculated as

$$\overline{H}={}_\infty\langle\overline{\chi}|(-\nabla^2+V)|\overline{\chi}\rangle_\infty=(1+\overline{oh})^\dagger\overline{h}+(1+\overline{oh})^\dagger E_\nu(1+\overline{oh})+\overline{h}^\dagger E_\nu p\overline{h}+{}^i\langle\overline{\chi}|V|\overline{\chi}\rangle^i. \tag{20}$$

D. Atomic sphere approximation

In order to simplify the expression and treatment, we will introduce an approximation where the spheres fill the whole space while overlapping with each other and where the sum of sphere volume is equal to the volume of the whole space. This is called the atomic sphere approximation (ASA), where the augmentation sphere is the atomic sphere. Here, in the ASA, there is no interstitial region. Thus the $\overline{\chi^i_{\mathbf{R}L}}$ should be redefined so as to compensate for effects of overlapping spheres. (See Sec. II E.) Based on the ASA, κ^2 is essentially arbitrary because there is no interstitial region. The simplest choice $\kappa^2=0$ is often used, and we will also adopt this approximation here for simplicity. The ASA is not essential for a formulation of the muffin-tin orbital basis.

E. Combined correction

The ASA works well near the Fermi energy when the system is closely packed and the sphere-overlapping region is small. Once the overlapping region is not negligible or the interesting energy is rather high, we introduce the combined correction which compensates for the error introduced by the ASA. Then the overlap matrix ${}^i\langle\overline{\chi}|\chi\rangle^i$ and the corresponding matrix of the Hamiltonian ${}^i\langle\overline{\chi}|V|\chi\rangle^i$ are not simply quantity integrated over the interstitial region, but should be quantity-compensating-introduced errors. The correction term for the overlap matrix should, therefore, be a form of

$${}^i\langle\overline{\chi}|\chi\rangle^i=[{}_\infty\langle\overline{\chi}|\chi\rangle_\infty]^{\text{exact}}-[{}_\infty\langle\overline{\chi}|\chi\rangle_\infty]^{\text{sphere}}, \tag{21}$$

which is the difference between the exact overlap (first term) and the sum of the overlap within spheres (second term). This can be calculated, using Eqs. (12) and (16), as

$${}^i\langle\overline{\chi}|\chi\rangle^i=\left(\frac{2\Delta}{w}\right)^{1/2}(1+S\alpha)\{[{}_\infty\langle K^0|K^0\rangle_\infty]^{\text{exact}}-[{}_\infty\langle K^0|K^0\rangle_\infty]^{\text{sphere}}\}(1+\alpha S)\left(\frac{2\Delta}{w}\right)^{1/2}. \tag{22}$$

The matrix elements for the Hamiltonian may be approximated as

$${}^i\langle\overline{\chi_{\mathbf{R}L}}|V|\overline{\chi_{\mathbf{R}'L'}}\rangle^i={}^i\langle\overline{\chi_{\mathbf{R}L}}|\overline{\chi_{\mathbf{R}'L'}}\rangle^i[V(s_{\mathbf{R}})+V(s_{\mathbf{R}'})]/2. \tag{23}$$

F. Down folding

When a reduction of the number of orbitals is necessary, one should apply down folding. This procedure may be explained from the viewpoint of the basis transformation, using $\bar{\bar{o}}$ instead of $\overline{o}$, from the bar to the double-bar representation:

$$|\bar{\bar{\chi}}\rangle_\infty=|\overline{\chi}\rangle_\infty[1+(\bar{\bar{o}}-\overline{o})\bar{\bar{h}}],$$
$$\bar{\bar{h}}=\overline{h}[1+(\overline{o}-\bar{\bar{o}})\overline{h}]^{-1}. \tag{24}$$

In the double-bar representation, the eigenvalue equation may be written down in the Korringa-Kohn-Rostoker ASA equation or the tail-cancellation condition

$$\det[\bar{\bar{P}}(E)-\bar{\bar{S}}]=0, \tag{25}$$

where

$$\bar{\bar{P}}(E)=\frac{P^0(E)}{1-\beta P^0(E)},$$
$$P^0(E)=\frac{W\{K^0,\phi(E)\}}{W\{J^0,\phi(E)\}}, \tag{26}$$
$$\bar{\bar{S}}=S+S(\beta-\alpha)\bar{\bar{S}}.$$

The matrices $P^0(E)$ and $\bar{\bar{P}}(E)$ are the potential functions corresponding to the bare structure constant and in the double-bar representation, respectively. Both are diagonal with respect to $\mathbf{R}$ and L. The diagonal matrix β defines the structure constant matrix of β representation.

We reduce the number of basis orbitals in the double-bar representation. The space of the basis orbitals can be divided into lower and higher subsets, $|\bar{\bar{\chi}}_L\rangle_\infty$ and $|\bar{\bar{\chi}}_H\rangle_\infty$. If we can choose the potential function of the higher subset $\bar{\bar{P}}_H(E)$ to be infinity, the rectangular block matrix $[\bar{\bar{P}}(E)-\bar{\bar{S}}]_{HL}$ is negligible compared with the diagonal block. Then the size of the secular matrix can be reduced, and the eigenvalue equation becomes

$$\det[\bar{\bar{P}}_L(E)-\bar{\bar{S}}_{LL}]=0. \tag{27}$$

This is an achievement of the reduction of the orbital set. The choice $\bar{\bar{P}}_H(E)=\infty$ of the tail cancellation condition for the higher subset is equivalent to the equation

$$\beta_H=\{P^0_H(E)\}^{-1}. \tag{28}$$

Comparison of Eq. (28) with the continuity condition for β [see the condition for α, Eq. (15)], the higher tail function $\dot{\bar{\bar{\phi}}}_H$ should be equal to ϕ_H, $\dot{\bar{\bar{\phi}}}_H=\phi_H$.

The unfolded lower tail function $\dot{\overline{\phi_L}}$ should be unchanged and, therefore, chosen as

$$\dot{\bar{\bar{\phi}}}_L=\dot{\overline{\phi_L}}\ \text{ or }\ \bar{\bar{o}}_L=\overline{o_L}\ \text{ or }\ \beta_L=\alpha_L. \tag{29}$$

In the LMTO-ASA method, the tail cancellation condition for the higher subset becomes much simpler. The condition for $P_H^0(E)$ is chosen at a certain fixed energy $E={}_\nu E_H$, and we usually choose the value of ${}_\nu E_H$ to be the value averaged over all E_ν of unfolded orbitals. Once the expression of the bare potential function $P^0(E)$ is approximated in second order, the explicit expression of $\bar{\bar{o}}$ can be read as

$$\bar{\bar{o}}_H^{-1}={}_\nu E_H - E_{\nu H}. \tag{30}$$

Now the lower orbital subset can be written down explicitly using known quantities, and the resultant overlap and Hamiltonian matrices are evaluated as

$$\bar{\bar{O}}_{LL}={}_\infty\langle\bar{\bar{\chi}}_L|\bar{\bar{\chi}}_L\rangle_\infty=\overline{O_{LL}}+A_{LH}\overline{O_{HL}}+\overline{O_{LH}}A_{HL}+A_{LH}\overline{O_{HH}}A_{HL} \tag{31}$$

and

$$\bar{\bar{H}}_{LL}={}_\infty\langle\bar{\bar{\chi}}_L|-\nabla^2+V|\bar{\bar{\chi}}_L\rangle_\infty=\overline{H_{LL}}+A_{LH}\overline{H_{HL}}+\overline{H_{LH}}A_{HL}+A_{LH}\overline{H_{HH}}A_{HL} \tag{32}$$

with

$$A_{HL}\equiv(\bar{\bar{o}}_H-\overline{o_H})\bar{\bar{h}}_{HL},\quad A_{LH}\equiv A_{HL}^\dagger.$$

III. MULTIPLE LMTO

In the original LMTO method, as explained in Sec. II F, the basis functions are labeled by the atoms **R** and by the angular momentum $L=(l,m)$. This restriction may be sufficient if we discuss only a narrow energy range where only one orbital for $L=(l,m)$ contributes at one atomic site **R**. If this is not the case, e.g., for an investigation in a wider energy range, we cannot avoid the patched-together method if we use the original method. In order to avoid a cumbersome procedure for the patched-together band structure, the multiple LMTO method may be used.[5] The multiple LMTO method is developed for discussing general cases which requires multiple $L=(l,m)$ at one atomic site **R**.

The most important point for constructing the multiple LMTO may be to return Hermitian properties at every step. We will stress that, at the starting stage, the various angular momentum components included in every energy channel should be the same, or otherwise the formulation may destroy the Hermitian property of the Hamiltonian.

A. Multiple LMTO basis and structure constant

The multiple LMTO is, in general, defined as

$$\overline{\chi_{\mathbf{R}Ln,\infty}}=\phi_{\mathbf{R}Ln}+\sum_{\mathbf{R}'L'n'}\dot{\overline{\phi}}_{\mathbf{R}'L'n'}\overline{h}_{\mathbf{R}'L'n':\mathbf{R}Ln}+\overline{\chi^l_{\mathbf{R}Ln}}, \tag{33}$$

where

$$\overline{h}_{\mathbf{R}'L'n':\mathbf{R}Ln}\equiv(C_{\mathbf{R}Ln}-E_{\nu\mathbf{R}Ln})\delta_{\mathbf{R}',\mathbf{R}}\delta_{L',L}\delta_{n',n}+\Delta^{1/2}_{\mathbf{R}'L'n'}S_{\mathbf{R}'L'n':\mathbf{R}Ln}\Delta^{1/2}_{\mathbf{R}Ln}. \tag{34}$$

The index n denotes the multiple orbital or essentially the principal quantum number. Like Aryasetiawan and Gunnarson,[5] we assume the simplest form of the structure constant as

$$S_{\mathbf{R}'L'n':\mathbf{R}Ln}=S_{\mathbf{R}'L':\mathbf{R}L}\delta_{n,n'}. \tag{35}$$

Therefore, the $\overline{h}$ matrix from now on is written as

$$\overline{h}_{\mathbf{R}'L'n':\mathbf{R}Ln}=\overline{h^n_{\mathbf{R}'L':\mathbf{R}L}}\delta_{n,n'}. \tag{36}$$

This assumption implies that the tail of a LMTO $\phi_{\mathbf{R}Ln}$ within one sphere of an atom **R** is augmented by $\dot{\phi}_{\mathbf{R}'L'n}$ in a sphere of another atom $\mathbf{R}'$ in the same energy channel. We believe that the augmentation is arbitrary, and that it may not cause any error.

B. Overlap and Hamiltonian matrices

With the multiple LMTO, the overlap and Hamiltonian matrices are given as

$$\overline{O^{nn'}}=\langle\phi^n|\phi^{n'}\rangle+\overline{h^{n\dagger}}\langle\dot{\overline{\phi^n}}|\phi^{n'}\rangle+\langle\phi^n|\dot{\overline{\phi^{n'}}}\rangle\overline{h^{n'}}+\overline{h^{n\dagger}}\langle\dot{\overline{\phi^n}}|\dot{\overline{\phi^{n'}}}\rangle\overline{h^{n'}}+{}^i\langle\overline{\chi^n}|\overline{\chi^{n'}}\rangle^i \tag{37}$$

and

$$\overline{H^{nn'}}=\langle\phi^n|\phi^{n'}\rangle E_\nu^{n'}+[\langle\phi^n|\phi^{n'}\rangle+\langle\phi^n|\dot{\overline{\phi^{n'}}}\rangle E_\nu^{n'}]\overline{h^{n'}}+\overline{h^{n\dagger}}\langle\dot{\overline{\phi^n}}|\phi^{n'}\rangle E_\nu^{n'}+\overline{h^{n\dagger}}[\langle\dot{\overline{\phi^n}}|\phi^{n'}\rangle+\langle\dot{\overline{\phi^n}}|\dot{\overline{\phi^{n'}}}\rangle E_\nu^{n'}]\overline{h^{n'}}+{}^i\langle\overline{\chi^n}|V|\overline{\chi^{n'}}\rangle^i. \tag{38}$$

These equations are valid for both $n\neq n'$ and $n=n'$. It should be noted that the products $\langle\phi^n|\phi^{n'}\rangle$ for a pair of wave functions with different principal quantum numbers $(n\neq n')$ do not vanish, because the integral is only within the same atomic sphere.

C. Combined correction

The combined correction for the overlap and Hamiltonian matrices given in Eqs. (22) and (23) should be generalized as

$${}^i\langle\overline{\chi^n}|\overline{\chi^{n'}}\rangle^i=\left(\frac{2\Delta^n}{w}\right)^{1/2}(1+S\alpha)\{[{}_\infty\langle K^{0n}|K^{0n'}\rangle_\infty]^{\text{exact}}-[{}_\infty\langle K^{0n}|K^{0n'}\rangle_\infty]^{\text{sphere}}\}(1+\alpha S)\left(\frac{2\Delta^{n'}}{w}\right)^{1/2} \tag{39}$$

and

$${}^i\langle\overline{\chi^n_{\mathbf{R}L}}|V|\overline{\chi^{n'}_{\mathbf{R}'L'}}\rangle^i={}^i\langle\overline{\chi^n_{\mathbf{R}L}}|\overline{\chi^{n'}_{\mathbf{R}'L'}}\rangle^i[V(s_{\mathbf{R}})+V(s_{\mathbf{R}'})]/2. \tag{40}$$

Matrices such as ${}_\infty\langle K^{0n}|K^{0n'}\rangle_\infty$ should have nonvanishing elements both within the same energy channel $(n=n')$ and between different channels $(n\neq n')$, and these blocks should

be the same block matrices. This is consistent with the evaluation of the overlap and Hamiltonian matrices in Eqs. (37) and (38).

D. Hermitian property of overlap and Hamiltonian matrices

The overlap matrix Eq. (37) is clearly Hermitian. The Hamiltonian matrix Eq. (38) can be proved Hermitian, using the relations

$$\begin{aligned}
&\langle \phi^n | \phi^{n'} \rangle (E_\nu^{n'} - E_\nu^n) = -W\{\phi^n, \phi^{n'}\} \\
&\langle \phi^n | \dot{\overline{\phi^{n'}}} \rangle (E_\nu^{n'} - E_\nu^n) + \langle \phi^n | \phi^{n'} \rangle = -W\{\phi^n, \dot{\overline{\phi^{n'}}}\} \\
&\langle \dot{\overline{\phi^n}} | \dot{\overline{\phi^{n'}}} \rangle (E_\nu^{n'} - E_\nu^n) - \langle \phi^n | \dot{\overline{\phi^{n'}}} \rangle + \langle \dot{\overline{\phi^n}} | \phi^{n'} \rangle \\
&\quad = -W\{\dot{\overline{\phi^n}}, \dot{\overline{\phi^{n'}}}\} \quad (n \neq n')
\end{aligned} \tag{41}$$

and some subsidiary conditions. The most crucial point, not mentioned before,[5] is that the Hamiltonian can be Hermitian only if every energy channel n contains the same angular momentum components $s,p,d,f,\ldots$, and any orbital with the same $L=(l,m)$ in different energy channels is constructed under a condition that the decaying behavior is independent on n and identical with other orbitals,

$$D\{\dot{\overline{\phi^n}}\} = D\{J\}. \tag{42}$$

Using Eq. (41), we can derive a result

$$\begin{aligned}
\overline{H^{nn'}} - (\overline{H^\dagger})^{nn'} = &-W\{\phi^n, \phi^{n'}\} - W\{\phi^n, \dot{\overline{\phi^{n'}}}\}\overline{h^{n'}} \\
&- \overline{h^n} W\{\dot{\overline{\phi^n}}, \phi^{n'}\} - \overline{h^n} W\{\dot{\overline{\phi^n}}, \dot{\overline{\phi^{n'}}}\}\overline{h^{n'}},
\end{aligned} \tag{43}$$

where the last term vanishes or

$$W\{\dot{\overline{\phi^n}}, \dot{\overline{\phi^{n'}}}\} = 0,$$

under the condition Eq. (42). After a tedious calculation using the Wronskian properties, Eq. (43) can be reduced to

$$\begin{aligned}
[\overline{H^{nn'}} - (\overline{H^\dagger})^{nn'}]_{\mathbf{R}L:\mathbf{R}'L'} = &-\Delta^{n1/2}_{\mathbf{R}L} S^{nn}_{\mathbf{R}L:\mathbf{R}'L'} \Delta^{n'1/2}_{\mathbf{R}'L'} \\
&+ \Delta^{n1/2}_{\mathbf{R}L} S^{nn'}_{\mathbf{R}L:\mathbf{R}'L'} \Delta^{n'1/2}_{\mathbf{R}'L'}.
\end{aligned} \tag{44}$$

If $n=n'$, Eq. (44) vanishes. If $n\neq n'$, we should be very careful.

Let us assume two energy channels. We denote the first and second channels of the multiple LMTO as F and S, respectively. In order to reach a more concrete understanding, we specify the two channels as $n=F=(4s4p3d)$ and $n'=S=(4d)$. Then the structure constant matrices $S^{FF}_{\mathbf{R}L:\mathbf{R}'L'}$ and $S^{SS}_{\mathbf{R}L:\mathbf{R}'L'}$ contain s, p, d, and d blocks, respectively. Finally, we have

$$\overline{H}^{FS}_{\mathbf{R}4s:\mathbf{R}'4d} - (\overline{H^\dagger})^{FS}_{\mathbf{R}4s:\mathbf{R}'4d} = -\Delta^{F1/2}_{\mathbf{R}4s} S^{FF}_{\mathbf{R}s:\mathbf{R}'d} \Delta^{S1/2}_{\mathbf{R}'4d}, \tag{45}$$

where the structure constant comes from the first channel, and the second term of Eq. (44) vanishes because in the second channel the sd block $S^{SS}_{s:d}$ does not exist. This means that, in this case, the resultant multiple LMTO Hamiltonian is not Hermitian.

Therefore, we can conclude that it is not allowed to include orbitals in different ways in each energy channel such as $F=(4s4p3d4f)$ and $S=(4d)$, but to include equally $F=(4s4p3d4f)$ and $S=(5s5p4d5f)$. In order to have different sets such as $F=(4s4p3d4f)$ and $S=(4d)$, down folding of the remaining orbitals, i.e., $5s5p5f$, must be employed.

TABLE I. The values E_ν (in Rydberg units) used in the calculations except set 1c.

	$4s$	$4p$	$3d$	$4f$
E_ν	-0.5145	-0.3675	-0.1856	$+2.9412$
	$5s$	$5p$	$4d$	$5f$
E_ν	$+4.0$	$+8.0$	$+2.5$	$+10.0$

E. Down folding of multiple LMTO

Now we want to reduce the number of orbitals in each energy channel, because in an interesting energy region it is not necessary to include all kinds of $L=(l,m)$ per atomic site. Furthermore, it may be crucial to reduce the number of basis functions for future development. We can follow the standard down-folding procedure explained in Sec. II F with some caution of multiple LMTO's. Of course, the Hermitian property is not destroyed if we simply reduce the size of resultant multiple LMTO Hamiltonian after constructing it with the same sets of angular momentum. However, this may be inconsistent from a theoretical viewpoint.

The structure constant S consists of nonvanishing block matrices only within the same energy channel, and the matrices $\overline{h}$, $\overline{\overline{h}}$ and A_{HL} act in the same way. Then the effects of multiple orbitals come into the calculation through the matrix S_{HL}. This is the important point we should keep in mind; the remaining procedure is the same as in the standard down-folding procedure of the original LMTO method. For example, assuming two energy channels $F=(4s4p3d4f)$ and $S=(5s5p4d5f)$, we can fold down $5p5f$ with $L=(4s4p3d4f,5s4d)$ and $H=(5p5f)$.

IV. EXAMPLES: PARAMAGNETIC NICKEL

Here we show the energy bands of paramagnetic nickel in a wide energy range. Valence bands in nickel, just below the Fermi energy, are $4s3d$ states with a rather strong mixing of $4p$ states. Then at about 1 Ry above the Fermi energy, $4d$ and $4f$ states show appreciable contributions, because of the strong attractive d and f potentials. In order to treat all these bands and to investigate the wide-range conduction-band spectra, the multiple LMTO method may be very helpful. The possibility of the discussion over a wide energy range is essential to investigate the self-energy of the one-particle Green's function, or the GW approximation for the band gap of insulators and for the excitation spectra.

For a systematic study of the effects of the combined correction and the down folding, we prepare the following

TABLE II. The values E_ν (in Rydberg units) used in the calculation of set 1c.

	$4s$	$4p$	$3d$	$4f$
E_ν	+1.0294	+1.0294	+2.5	+2.5

set of orbitals: (i) set 1a, $4s4p3d4f$ (one channel) with combined correction; (ii) set 1b, $4s4p3d4f$ (one channel) without combined correction; (iii) set 1c, $4s4p4d4f$ (one channel) with combined correction; (iv) set 2, $F=(4s4p3d4f)$ and $S=(5s5p4d5f)$ (two channels) with combined correction; (v) set 3a, $F=(4s4p3d4f)$ and $S=(5s4d)$ (two channels) with combined correction and down folded $(5p5f)$; and (vi) set 3b, $F=(4s4p3d4f)$ and $S=(4d)$ (two channels) with combined correction and down folded $(5s5p5f)$. We use the observed lattice constant in these calculations $a=6.6622$ a.u., and the parameters E_ν are summarized in Tables I and II. The ${}_\nu E_H$ for $\bar{\bar{o}}_H$ are chosen as the value averaged over E_ν's of remaining (i.e., unfolded) orbitals. It should be mentioned that the values of E_ν for sets 2, 3a, and 3b are the same.

First the calculated results for a single channel are shown in Figs. 1(a) and 1(b), using (set 1a) and (set 1b) with and without the combined correction. Figure 1(c) shows a $4s4p4d4f$ band structure. The bands near the Fermi energy are also shown in Fig. 1(d). The $4d$ eigenstates do not appear

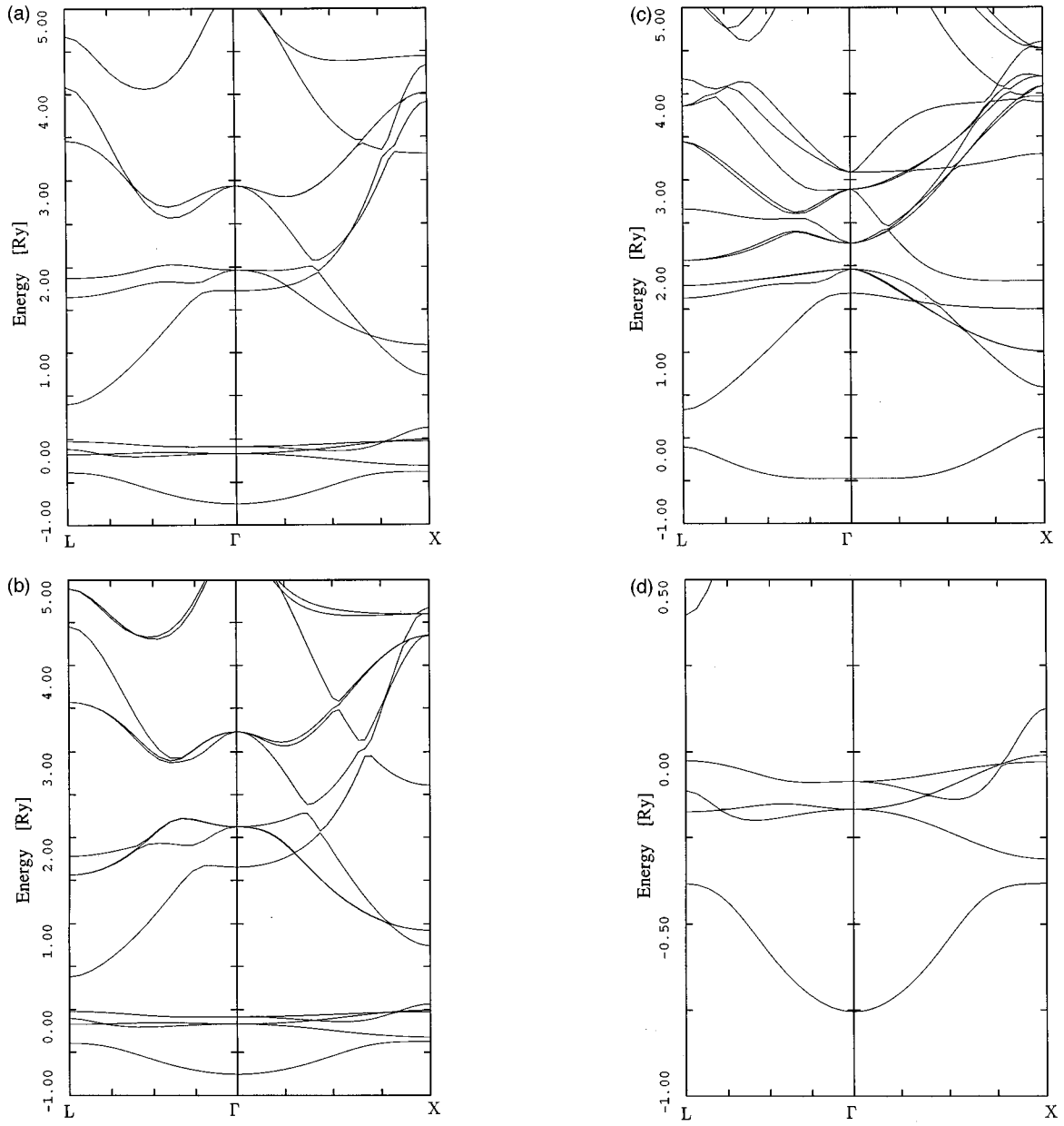

FIG. 1. Energy bands of paramagnetic nickel using the following: (a) set 1a, $4s4p3d4f$ (one channel) with combined correction; (b) set 1b, $4s4p3d4f$ (one channel) without combined correction; (c) set 1c, $4s4p4d4f$ (one channel) with combined correction; (d) enlarged energy bands in the region near and below the Fermi energy using $4s4p3d4f$ (one channel).

TABLE III. The energy eigenvalues (in Rydberg units) of three k points (Γ, L, and X points) in the calculation of sets 1a, 1c, 2, and 3a. The second column denotes the degeneracy of each eigenenergy.

		Set 1a	Set 1c	Set 2	Set 3a
L point	1	−0.3830		−0.3838	−0.3838
	2	−0.1743		−0.1743	−0.1743
	1	−0.1118	−0.1056	−0.1131	−0.1118
	2	−0.0253		−0.0254	−0.0254
	1	0.3967	0.3282	0.3874	0.3874
	1	1.6514	1.6278	1.6343	1.6514
	2	1.8785	1.7693	1.7646	1.8785
	2		2.0637	2.0646	2.0646
	1		2.6607	2.6727	2.6727
	2	3.4549	3.4473	3.3853	3.4549
	1	4.0851	4.1766	3.8995	4.0851
	2		3.8528	3.9142	3.9142
	2	4.6788	5.1424	4.6329	4.6788
Γ point	1	−0.7549	−0.4735	−0.7549	−0.7549
	3	−0.1667		−0.1667	−0.1667
	2	−0.0847		−0.0847	−0.0847
	1	1.7257	1.6792	1.7056	1.7257
	3	1.9676	1.9582	1.9525	1.9675
	3		2.2611	2.2615	2.2615
	3	2.9374	2.8882	2.8300	2.9373
	2		3.0869	3.0883	3.0884
X point	1	−0.3821		−0.3824	−0.3824
	1	−0.3113		−0.3124	−0.3124
	1	−0.0287		−0.0288	−0.0288
	2	−0.0095		−0.0096	−0.0096
	1	0.1251	0.1081	0.1150	0.1251
	1	0.7313	0.5875	0.6450	0.6450
	2	1.0840	1.0083	1.0368	1.0840
	1		1.4986	1.5027	1.5027
	1		1.8225	1.8134	1.8134
	1	3.3047	3.3007	3.2260	3.3047
	1	3.9102	3.9635	3.8333	3.9101
	2	4.0164	4.0851	3.8528	4.0164
	1		3.8952	3.9438	3.9438
	2	4.4434	4.5241	4.2237	4.4434
	2		4.1932	4.3049	4.3049
	1	4.3386	4.5997	4.3384	4.3386

in Figs. 1(a) and 1(b), comparing with Fig. 1(c), because we do not include $4d$ states as the basis orbitals. The $4d$ and $5s$ states mix strongly in Fig. 1(c). At the L point, $\mathbf{k}=(\pi/2)(1,1,1)$; the state at $E=2.0637$ Ry is a pure $4d$ state; and that at $E=2.6607$ Ry is the state mixed with $4d$ and $5s$. At the X point, $\mathbf{k}=\pi(1,0,0)$, and those at $E=1.4986$ and 1.8225 Ry are the states of pure $4d$ and of mixed $4d5s$, respectively. The behavior of the latter state in the down folding should be noticed later. The numerical values at Γ, L and X points for sets 1a, 1c, 2, and 3a are summarized in Table III.

We should notice that the combined correction is vital in the higher-energy region, in contrast to the negligible small effects in the lower-energy region near the Fermi energy. The states in the higher-energy region spill out in the overlapping region of spheres or outside spheres, and the combined correction gives an appreciable improvement to compensate for errors introduced by the ASA. The combined correction shifts down the higher-energy bands, and also changes the order of eigenenergies. Of course, this tendency of the combined correction is also true in the case of the multiple LMTO.

The results of the multiple LMTO method are shown in Fig. 2 with the combined correction. All bands included in the basis set appear and, especially, $4d$ bands do so in the energy region about 1 Ry above the Fermi energy. Bands $4s4p3d4d4f$ are reproduced nicely, compared with those shown in Figs. 1(a) and 1(c). We also calculated the case

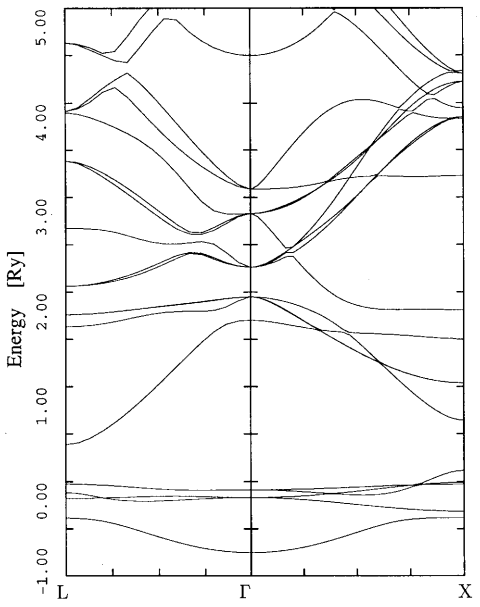

FIG. 2. Energy bands of paramagnetic nickel using set 2, $F=(4s4p3d4f)$ and $S=(5s5p4d5f)$, with combined correction.

including $5g$ and $6g$ states as basis orbitals. The $5g$ orbital slightly changes the structure in this energy region, and $4d$ bands become slightly narrower as already seen before.[5]

In Figs. 3(a) and 3(b), we show the calculated results of the multiple LMTO of set 3a: $F=(4s4p3d4f)$ and $S=(5s4d)$, with combined correction and down folded $(5p5f)$; and set 3b, $F=(4s4p3d4f)$ and $S=(4d)$, with combined correction and down folded $(5s5p5f)$. Because the energy region shown in the figure is $4s4p3d4d4f5s$, and mixes only slightly with $5p5f$, any change can hardly be seen by the down-folding procedure of $5p5f$. On the other hand, the down folding of $5s5p5f$ changes states at $E=2.6727$ Ry for the L point and at $E=1.8134$ Ry for the X point, because these levels originate from $5s4d$ mixing, and the down folding of one orbital among two may not be satisfied with fixing E_ν as above.

From examples above we have the following conclusions. (i) The combined correction may be comparably important in the higher-energy region. (ii) It is not allowed to include orbitals in different ways in each energy channel without down folding. (iii) One should apply the down folding to reduce the number of orbitals in the higher-energy panel in the multiple LMTO method.

V. SUMMARY

We have developed a multiple LMTO method, and discussed the effects of the combined correction and down folding. The combined correction may be comparably important in the higher-energy region both in the original and the multiple LMTO methods. The asymmetric sets of the angular momentum in each energy panel in the multiple LMTO method break the Hermitian property of the Hamiltonian matrix. The down folding is essential to reduce the number of orbitals in the higher-energy region. We show resultant bands of down folding of $(5p5f)$, and explicit basis orbitals

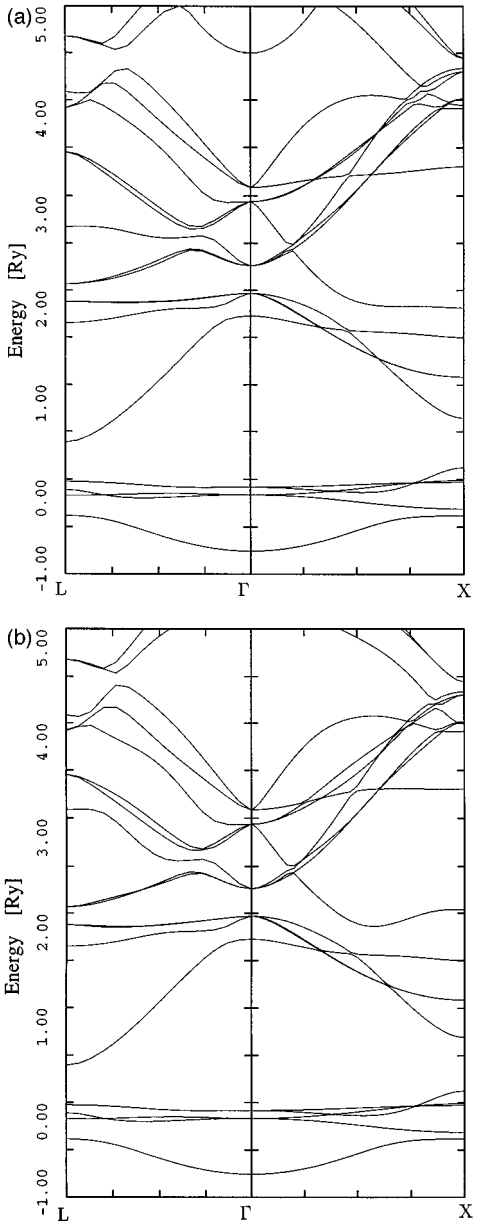

FIG. 3. Energy bands of paramagnetic nickel using the following: (a) set 3a, $F=(4s4p3d4f)$ and $S=(5s4d)$ with combined correction and down folded $(5p5f)$; (b) set 3b, $F=(4s4p3d4f)$ and $S=(4d)$ with combined correction and down folded $(5s5p5f)$.

$F=(4s4p3d4f)$, $S=(5s4d)$ with combined correction. For further possibilities of the multiple LMTO method, e.g., applications to the GW approximation, a reduction of basis orbitals by down folding may be very crucial.

ACKNOWLEDGMENTS

We thank M. Arai for useful discussion about the Hermitian property of the Hamiltonian for the multiple LMTO. This work is supported by a Grant-in-Aid from the Japan Ministry of Education, Science and Culture. Numerical calculation was carried out by the computer facilities at the Institute of Molecular Science at Okazaki and at the Institute for Solid State Physics, the University of Tokyo.

[1] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991); V. I. Anisimov, M. A. Korotin, J. Zaanen, and O. K. Andersen, Phys. Rev. Lett. **68**, 345 (1992).

[2] L. Hedin, Phys. Rev. **139**, A796 (1965); M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).

[3] O. K. Andersen, A. I. Liechtenstein, O. Jepsen, and F. Paulsen (unpublished); O. K. Andersen, A. I. Lichtenstein, and I. I. Mazin, Phys. Rev. B **49**, 4145 (1994).

[4] J. E. Müller, O. Jepsen, O. K. Andersen, and J. W. Wilkins, Phys. Rev. Lett. **40**, 720 (1978).

[5] F. Aryasetiawan and O. Gunnarson, Phys. Rev. B **49**, 7219 (1994).

[6] F. Aryasetiawan and O. Gunnarson, Phys. Rev. B **49**, 16 214 (1994).

[7] O. K. Andersen, O. Jepsen, and D. Grötzel, in *Highlight of Condensed Matter Theory*, edited by F. Bassani, F. Fumi, and M. Tosi (North-Holland, Amsterdam, 1985), p. 59.

[8] W. R. L. Lambrecht and O. K. Andersen, Phys. Rev. B **34**, 2439 (1986).

[9] O. K. Andersen, Z. Pawlowska, and O. Jepsen, Phys. Rev. B **34**, 5253 (1986).