Linear Muffin Tin Orbital method with multiple orbitals per L channel

F. Aryasetiawan and O. Gunnarsson
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1, 70569 Stuttgart
Federal Republic of Germany

A method for calculating both the valence and high lying conduction bandstructure of a solid is developed. The basis functions are Linear Muffin-Tin Orbitals with multiple orbitals per angular momentum channel corresponding to different energies. In contrast to the conventional panelling method, our method treats the valence and conduction bands on equal footing so that the wavefunctions are orthogonal, which avoids the non-orthogonality problem when calculating transition matrix elements between occupied and unoccupied states and the discontinuity in the bandstructure. An empty lattice test reproduces the free-electron band up to at least 50 eV. The method is applied to Nickel and a comparison with a different approach based on a modified Linear Augmented Plane Wave method is made.

I. Introduction

There are several practical methods currently used for calculating bandstructures of solids. Among the most popular are the pseudopotential method[1] which uses plane waves as basis functions, the Linear Muffin Tin Orbital (LMTO) method[2,3] which uses muffin tin orbitals as the basis, the Linear Combination of Atomic Orbitals (LCAO) method[4,5] which starts from atomic orbitals as basis functions and the Linear Augmented Plane Wave (LAPW)[2] which uses plane waves augmented by a linear combination of atomic orbitals.

The pseudopotential method is quite suitable to treat s-p (free electron) like systems but not appropriate to treat systems with very localized states such as the d-states in transition metals since at least a few thousands plane waves are needed to describe these localized states. The situation becomes worse when we want to include semicore states as part of the valence band since they require even more plane waves. To treat localized systems, the LAPW method is more suitable. While it is very accurate and can be applied to any system, it still requires a large number of basis functions, of the order of 50-100 per atom.

Of all band structure methods, the LMTO is the most efficient and versatile and also physically most transparent. This applies particularly to the LMTO method within the so called Atomic Sphere Approximation (ASA) in which the Wigner-Seitz (WS) cells are replaced by overlapping spheres. Other methods use a larger number of basis functions and they are usually difficult to interpret physically. The LMTO-ASA method is however less accurate than the LAPW method, but this is well compensated by the numerical simplicity and physical insight that one gains from this method.

The LMTO-ASA method, like other band structure methods, is designed, with the use of Density Functional Theory (DFT)[6], to describe the valence states from which groundstate properties such as total energy, charge density, magnetic moment etc. can be obtained. If we are interested in excited state properties such as optical absorption, energy loss spectra, or if we want to do many-body perturbation theory such as GW[7-9], we need both the valence and conduction bands, the latter may have to be calculated up to 50 eV or more.

In the conventional LMTO method, we use only one muffin tin orbital (MTO) per angular momentum $L \equiv lm$ channel. This is in contrast to the LCAO method which, for each L, normally includes several orbitals with different principal quantum number ν in the basis. The radial functions used to construct an LMTO are the solutions φ to the radial Schrödinger equation inside the muffin tin spheres at a certain fixed energy $\epsilon_{\nu l}$ and their energy derivatives $\dot{\varphi}$. The energy $\epsilon_{\nu l}$ is usually chosen at the center of the occupied band of interest. The calculated bands are accurate within an energy window centered around $\epsilon_{\nu l}$ with a width which is about twice the bandwidth, typically ± 15 eV for $s-p$ bands and ± 4 eV for d bands. However, higher-lying conduction bands cannot be properly described by the conventional LMTO with $\epsilon_{\nu l}$ in the occupied band. The bands arising from the next higher orbitals are of course entirely missing as will be shown later in Sec. III.

The traditional solution to the above problem, known as panelling, is to divide the energy range of interest in two or several panels. The energy $\epsilon_{\nu l}$ is chosen at the center of the panel considered and the secular equation is now solved with the LMTOs constructed at this $\epsilon_{\nu l}$. There is an advantage with this method, in particular with the LMTO method, because it suffices to describe each energy panel by a single ν basis so that the computational time will only increase linearly with the number of panels. There are, however, several problems associated with this procedure: in general, the wavefunctions from different panels are not exactly orthogonal because the Hamiltonian matrices corresponding to the different panels are not the same. This can lead to serious errors when calculating matrix elements of an operator between occupied and unoccupied states, encountered for example in optical absorptions. Moreover, ambiguities arise when defining the bandstructure around the boundaries between two neighbouring panels and the bands are discontinuous across the boundaries which in turn introduces discontinuities in quantities like the density of states.

Instead of panelling, we propose a different solution. We introduce additional LMTOs but calculated at higher energies $\epsilon_{\nu+1,l}$. These higher energy orbitals have more nodes than those of the conventional ones and correspond to conduction bands centered around $\epsilon_{\nu+1,l}$. When necessary, further higher orbitals with energies $\epsilon_{\nu+2,l}$ etc. may be included . The Hamiltonian can still be expressed in terms of the potential parameters (logarithmic derivatives at the Wigner-Seitz radii). The secular equation is now solved with the enlarged basis. The resulting valence and conduction band wavefunctions are orthogonal because they are obtained from the same Hamiltonian matrix and the band structure is well defined and has no discontinuities as in the case of panelling. The price is an increase in the number of basis functions, but only for the required angular momenta.

The higher energy orbitals should be matched on to the Hankel function with $\kappa_\nu^2 = \epsilon_{\nu l} - V_0$, corresponding to the kinetic energy in the interstitial region. In our actual applications, we have matched the higher energy orbitals to the same Hankel function as for the lower energy orbitals, ecorresponding to zero kinetic energy ($\kappa^2 = 0$).

Although it is not the subject of the present paper, the same method may be applied to systems with semicore states which should be treated as valence states because they are too shallow to be regarded as core states. If they are treated as core states they are not orthogonal to the valence and conduction states which can lead to serious errors when evaluating matrix elements of an operator between these states.

As applications of the method, we do an empty lattice test and calculate the bandstructure of nickel and compare it with result obtained with a different scheme based on a modified Linear Augmented Plane Wave (LAPW) method[10].

The plan of the paper is the following: in Sec. II we describe the theory, in Sec. III we present results of our calculations and in Sec. IV we make our conclusions.

II. Theory

For completeness, let us first define the following terms and discuss some basic concepts, which are described in more details in references[12,2,11,3].

A. *The Partial Waves and the Muffin Tin Orbital*

The band structure problem consists in finding single-particle eigenvalues and eigenfunctions of an electron moving in a periodic potential $V(\mathbf{r})$

$$V(\mathbf{r}) = \sum_{\mathbf{R}} v_{\mathbf{R}} + V_0 \tag{1}$$

where $v_{\mathbf{R}} \equiv v_{\mathbf{R}}(\mathbf{r}-\mathbf{R})$ is zero unless $\mathbf{r}$ is inside a sphere of radius $s_{\mathbf{R}}$ centered at $\mathbf{R}$. We further assume in this paper that $v_{\mathbf{R}}$ is spherically symmetric, although this assumption is not necessary. If we assume a muffin-tin potential then V_0 is a constant which is usually negative.

Before solving the band structure problem, we consider a much simpler problem of solving the Schrödinger equation for a single muffin tin well $v_{\mathbf{R}}(r) + V_0$. We may choose $\mathbf{R}$ to be the origin without loss of generality. The solutions are

$$\tilde{\phi}_{\mathbf{R}L}(\mathbf{r},\epsilon) = y_L(\hat{\mathbf{r}}) \begin{cases} N_l^0(\epsilon)\varphi_{\mathbf{R}l}(r,\epsilon) & r \le s_{\mathbf{R}} \\ n_l(\kappa r) - cot\delta_{\mathbf{R}l}(\kappa) j_l(\kappa r) & r \ge s_{\mathbf{R}} \end{cases} \tag{2}$$

These are called partial waves with kinetic energy $\kappa^2 = \epsilon - V_0$. N_l^0 is a normalization constant, y_L is a spherical harmonic, and $\varphi_{\mathbf{R}l}$ is normalized to unity inside the muffin tin sphere. j_l is the radial solution which is regular at the origin i.e. the spherical Bessel function, and n_l is a solution which is irregular at the origin. For $\kappa^2 < 0, n_l$ must be the decaying Hankel function and for $\kappa^2 \ge 0, n_l$ may be a spherical Neumann function. $\delta_l(\kappa)$ is the scattering phase shift which may be obtained by matching the logarithmic derivative at the muffin tin radius $r = s_{\mathbf{R}}$. The partial waves diverge at ∞ when $\kappa^2 < 0$.

The muffin tin orbital (MTO) was first constructed by Andersen[2] by adding $y_L(\hat{\mathbf{r}}) cot\delta_{\mathbf{R}l}(\kappa) j_l(\kappa r)$ to the partial wave yielding:

$$\tilde{\chi}_L(\mathbf{r},\epsilon) = y_L(\hat{\mathbf{r}}) \begin{cases} N_l^0(\epsilon)\varphi_{\mathbf{R}l}(r,\epsilon) + cot\delta_{\mathbf{R}l}(\kappa) j_l(\kappa r) & r \le s_{\mathbf{R}} \\ n_l(\kappa r); & r \ge s_{\mathbf{R}} \end{cases} \tag{3}$$

Unlike the partial waves, the MTO's are well behaved and their tails are independent of $\mathbf{R}$, $v_{\mathbf{R}}$ and $s_{\mathbf{R}}$.

B. *The Conventional and General Envelope Functions*

As can be seen in Eq. (3) the envelope function of the conventional MTO is the irregular solution to wave equation:

$$(-\nabla^2 - \kappa^2)|K^0>_\infty = 0 \tag{4}$$

It diverges at the origin but it does not matter since it will be augmented later by some regular function. It may be expanded as follows[2]:

$$K^0_{\mathbf{R}L,\infty} = K^0_{\mathbf{R}L} - \sum_{\mathbf{R}'L'} J^0_{\mathbf{R}'L'} S^0_{\mathbf{R}'L',\mathbf{R}L} + K^0_{\mathbf{R}L,I} \tag{5}$$

Or in vector-matrix notation with $\mathbf{R}L$ as an index

$$|K^0>_\infty = |K^0> - |J^0> S^0 + |K^0>_I \tag{6}$$

where the subscript ∞ means that the function is defined over all space and I means that the function is defined only in the interstitial region. No label means that the function is only defined inside a sphere of radius $s_{\mathbf{R}}$ centered at $\mathbf{R}$ e.g. $K^0_{\mathbf{R}L} \equiv K^0_{\mathbf{R}L}(\mathbf{r}-\mathbf{R})$ is zero unless $|\mathbf{r}-\mathbf{R}| < s_{\mathbf{R}}$. The first term on the right hand side of Eq. (6) is the irregular "head", the second and third terms are the "tail" in the other spheres and the interstitial region respectively. S^0 is the expansion coefficients of the tail in other spheres in terms of a complete set of regular functions $|J^0>$ and is known as the structure constant which has no on-site term i.e. $S^0_{\mathbf{R}L,\mathbf{R}L'} = 0$.

We should note at this point that J^0_l and K^0_l are proportional to j_l and n_l respectively. Explicitly, they are related as follows:

$$J^0_l(\kappa, r) = \frac{1}{2}\frac{(2l-1)!!}{(\kappa w)^l} j_l(\kappa r) \tag{7}$$

$$K^0_l(\kappa, r) = -\frac{(\kappa w)^(l+1)}{(2l-1)!!} n_l(\kappa r) \tag{8}$$

where w is the average Wigner-Seitz radius i.e. $(4\pi/3)w^3$ = (cell volume)/(number of atoms). These definitions remove the divergence of n_l and the zero of j_l for $\kappa = 0$. Thus for $\kappa = 0$ the above definitions yield

$$J^0_l(\kappa = 0, r) = [2(2l+1)]^{-1}(r/w)^l \tag{9}$$
$$K^0_l(\kappa = 0, r) = (r/w)^{-l-1} \tag{10}$$

The tail of the envelope function in Eq. 6 is long ranged, decaying as $\sim 1/r$ for the s-wave. To obtain a general e.g. short range (tight-binding) envelope function, we form a linear superposition of the conventional ones centered on different sites[13,11]. We may write the general envelope function in the same form as for the conventional one:

$$|K>_\infty = |K^0> - |J> S + |K>_I \tag{11}$$

Since it is a linear superposition of $|K^0>_\infty$ centered on different sites, at every sphere its tail $-|J> S$ contains some fraction of the irregular head $|K^0>$ in that sphere. Thus, $|J>$ must be of the form

$$|J> = |J^0> - |K^0> \alpha \tag{12}$$

From Eqns. (6), (11) and (12) we obtain the relations

$$|K>_\infty = |K^0>_\infty (1 + \alpha S) \tag{13}$$

and

$$S = (1 - S^0\alpha)^{-1} S^0 \tag{14}$$

as may be readily verified. Due to the linear superposition, the head may also have changed so that S can now have an on-site term to take into account for this change.

In practice a set of α can be found that yields a short range envelope function. α is known as a screening constant and is determined empirically. In principle, it may depend on the site index and angular momentum as well as energy κ^2, but in practice α is chosen to be site-independent and for $l \geq 3$, $\alpha = 0$. Recent progress in the determination and understanding of the screening constants α may be found in reference[12,14].

C. *The General Muffin Tin Orbital*

From the envelope function $|K>_\infty$ defined in Eq. (11), the MTO is obtained by augmenting the irregular radial function $|K^0>$ occuring in the head in the following way:

$$|K^0> \to |\phi> N + |J> P \tag{15}$$

$\phi_L \equiv \varphi_l \; y_L$ is still normalized to unity inside the sphere at any energy ϵ. For the conventional MTO, this is simply proportional to the first line of Eq. (3) and the constant of proportionality is given in Eqs. (7) and (8). P^0 is proportional to the cotangent of the scattering phase shift δ. ϵ, N and the potential function P are considered to be diagonal matrices in $\mathbf{R}L$. It is required that the augmentation is continuous up to the first derivative. This requirement determines N and P:

$$N = \frac{W[K^0, J]}{W[\phi, J]} \tag{16}$$

$$P = \frac{W[K^0, \phi]}{W[J, \phi]} \tag{17}$$

where the Wronskian W is defined as

$$W[a, b] \equiv r^2(ab' - a'b) \tag{18}$$

The one-center expansion of the general MTO is then given by

$$|\tilde{\chi}> = |\phi> N + |J> (P - S) + |K>_I \tag{19}$$

At this stage N, P, ϕ and S are *energy dependent*. In the so called atomic sphere approximation (ASA), the Wigner-Seitz cell is replaced by a sphere of equal volume and the interstitial region does not exist anymore so that the last term in Eq. (19) drops out.

From now on we work with the general formulation. The choice of the screening constants α determines the properties of the basis which can be orthogonal, but normally long range, or short range, but normally not orthogonal. Other choices of α may give different properties but all the different choices are equivalent since the basis functions are related to one another by linear transformations that do not alter the Hilbert space.

D. *Tail cancellation*

We first assume that an eigenfunction at some energy ϵ for the whole solid can be expressed as a linear combination of MTO's centered on different sites:

$$\Psi(\mathbf{r}) = \sum_{\mathbf{R}L} \tilde{\chi}_{\mathbf{R}L}(\mathbf{r}, \epsilon) c_{\mathbf{R}L}(\epsilon) \tag{20}$$

Any choice of $c_{\mathbf{R}L}(\epsilon)$ gives a solution to the Schrödinger equation in the interstitial region. Moreover, $\phi_{\mathbf{R}L}(\mathbf{r}, \epsilon)$ is also a solution inside a sphere centered at $\mathbf{R}$, by construction. This means that for each L component, the unphysical function $|J> P$ in the head must be cancelled by the tails $|J> S$ from all sites i.e.

$$P_{\mathbf{R}l}(\kappa) c_{\mathbf{R}L}(\epsilon) - \sum_{\mathbf{R}'L'} S_{\mathbf{R}L,\mathbf{R}'L'}(\kappa) c_{\mathbf{R}'L'}(\epsilon) = 0, \quad \textit{for all } \mathbf{R}, L \tag{21}$$

This is known as the KKR tail cancellation condition[15] and a solution is found when the determinant $|P - S| = 0$.

E. *Linearization of the MTO: augmentation of the tail*

In this section we discuss how we can form an optimal energy-independent basis from the MTO's by augmentation of the tails i.e. by replacing $|J>$ with some other functions[2]. When used in connection with the variational principle for the one-electron Hamiltonian, this basis set will lead to an algebraic eigenvalue problem rather than to a determinantal equation arising from the tail cancellation condition.

Suppose we are interested in solving for an eigenvalue ϵ close to some ϵ_ν. We make the following approximation: we fix $|K>_I$ at ϵ_ν and hence S, so that $\kappa^2 = \kappa_\nu^2$ and not necessarily equal to $\epsilon - V_0$. The kinetic energy of the trial function in the interstitial region is then in error by $(\epsilon - \epsilon_\nu)$. We also calculate $|\phi>$ at ϵ_ν so that P is also fixed. If we form a linear combination of $\tilde{\chi}$ like in Eq. (20) we will not be able to get a complete tail cancellation, unless

ϵ_ν happens to be an eigenvalue. What is the best thing we can do for $\tilde{\chi}$ to be an energy *independent* basis for a variational calculation ? We expand the eigenfunction as a superposition of the MTO's centered on different sites. To simplify the discussion, we use the ASA but the result is quite general.

$$\begin{aligned}\Psi &= \sum_{\mathbf{R}L} \tilde{\chi}_{\mathbf{R}L} c_{\mathbf{R}L} \\ &= \sum_{\mathbf{R}L} \left[\phi_{\mathbf{R}L} N_{\mathbf{R}L} + J_{\mathbf{R}L} P_{\mathbf{R}L} - \sum_{\mathbf{R}'L'} J_{\mathbf{R}'L'} S_{\mathbf{R}'L',\mathbf{R}L} \right] c_{\mathbf{R}L}\end{aligned} \tag{22}$$

The L component of the eigenfunction inside a sphere at $\mathbf{R}$ is given by

$$\Psi_{\mathbf{R}L} = (\phi_{\mathbf{R}L} N_{\mathbf{R}L} + J_{\mathbf{R}L} P_{\mathbf{R}L}) c_{\mathbf{R}L} - J_{\mathbf{R}L} \sum_{\mathbf{R}'L'} S_{\mathbf{R}L,\mathbf{R}'L'} c_{\mathbf{R}'L'} \tag{23}$$

The first two terms arise from the "head" of the L-orbital centered at the site $\mathbf{R}$ and the last term is the L-component of the tails from all spheres expanded inside the sphere at $\mathbf{R}$. It is clear that the second and last term together must be equated to $(\epsilon - \epsilon_\nu)\partial(\phi_{\mathbf{R}L} N_{\mathbf{R}L})/\partial\epsilon \mid_{\epsilon_\nu} c_{\mathbf{R}L}$ so that with the first term they form a solution to the Schrödinger equation, correct to $O[(\epsilon - \epsilon_\nu)]$. Adding and substracting $J_{\mathbf{R}L} P_{\mathbf{R}L}(\epsilon) c_{\mathbf{R}L}$ in the second and last term, we thus have

$$\begin{aligned}& J_{\mathbf{R}L}[P_{\mathbf{R}L}(\epsilon_\nu) - P_{\mathbf{R}L}(\epsilon)] c_{\mathbf{R}L} \\ &+ J_{\mathbf{R}L} \sum_{\mathbf{R}'L'} \left[P_{\mathbf{R}'L'}(\epsilon) \delta_{\mathbf{R}\mathbf{R}'} \delta_{LL'} - S_{\mathbf{R}L,\mathbf{R}'L'} \right] c_{\mathbf{R}'L'} \\ &= (\epsilon - \epsilon_\nu) \left. \frac{\partial}{\partial\epsilon} (\phi_{\mathbf{R}L} N_{\mathbf{R}L}) \right|_{\epsilon_\nu} c_{\mathbf{R}L} + O[(\epsilon - \epsilon_\nu)^2]\end{aligned} \tag{24}$$

By choosing

$$J_{\mathbf{R}L} = - \frac{\partial(\phi_{\mathbf{R}L} N_{\mathbf{R}L})}{\partial\epsilon} \left[\frac{\partial P_{\mathbf{R}L}}{\partial\epsilon} \right]^{-1}_{\epsilon_\nu} \tag{25}$$

we are left with the quantity

$$T_{\mathbf{R}L}(\epsilon) = \sum_{\mathbf{R}'L'} [P_{\mathbf{R}L}(\epsilon) \delta_{\mathbf{R}\mathbf{R}'} \delta_{LL'} - S_{\mathbf{R}L,\mathbf{R}'L'}] c_{\mathbf{R}'L'} \tag{26}$$

which is precisely the same as the tail cancellation condition in Eq. (21) except that the structure constant S and the potential functions P have been evaluated for a fixed κ. In the KKR method, $T_{\mathbf{R}L}(\epsilon)$ is exactly equal to zero when ϵ is an eigenvalue as follows from the tail cancelation condition (Eq. (21)). What we have to show is that the variational calculation using $\tilde{\chi}$ as a fixed basis, makes $T_{\mathbf{R}L}(\epsilon)$ equal to zero to $O(\epsilon - \epsilon_\nu)$. This will be shown shortly below.

The choice in Eq. (25) is equivalent to requiring

$$\left. \frac{\partial \tilde{\chi}_{\mathbf{R}L}}{\partial\epsilon} \right|_{\epsilon=\epsilon_\nu} = 0 \tag{27}$$

which is consistent with the requirement that the basis be as energy independent as possible. This choice has a further desirable property in that the tail becomes orthogonal to the core states at all sites.

The LMTO is thus defined as

$$\begin{aligned}|\chi> &= |\tilde{\chi}> N^{-1} \\ &= |\phi> + |\dot{\phi}^\alpha> h + |\kappa>_I\end{aligned} \tag{28}$$

where

$$|\dot{\phi}^\alpha> = |\dot{\phi}> + |\phi> o, \tag{29}$$

$$o = <\phi|\dot{\phi}^\alpha> = \dot{N} N^{-1} \tag{30}$$

$$|\kappa>_I = |K>_I N^{-1} \tag{31}$$

The quantity h is given by

$$h = \dot{P}^{-1/2}(P - S)\dot{P}^{-1/2} \tag{32}$$

which is often written in a physically more transparent form as

$$h = c - \epsilon_\nu + \sqrt{d}S\sqrt{d} \tag{33}$$

$$c - \epsilon_\nu = -P\dot{P}^{-1} \tag{34}$$

$$d = \dot{P}^{-1} \tag{35}$$

where c defines the center of the band, d is the width of the band. $|\tilde{\chi}>$ is given by Eq. (19) with $|J>$ given by Eq. (25). The dot denotes $\partial/\partial\epsilon$ The above equations are derived in Appendix A. In Eq. (28) the ϕ and $\dot{\phi}$ as well as N are calculated at some energy ϵ_ν so that the LMTO is *energy independent*.

We now show that the variational principle makes $T_{\mathbf{R}L}(\epsilon)$ equal to zero to $O(\epsilon - \epsilon_\nu)$. By evaluating the diagonal matrix element of the Hamiltonian H it is easy to show that the eigenvalue is given by

$$\epsilon = \epsilon_\nu + h \tag{36}$$

to first order in h. In fact in the orthogonal representation, it is correct to second order in h[12]. Inserting this into $T_{\mathbf{R}L}(\epsilon)$ and making a Taylor expansion and using the definition of h gives the desired result.

The physical interpretation of the tail augmentation by $\partial(|\phi > N)/\partial\epsilon$ is that the sum of the tails $-|J > S$ from neighboring sites (which may include the center site) and the unphysical head $|J > P$ provide a Taylor correction to $(|\phi > N)_{\epsilon_\nu}$, which add up to produce a solution to the Schrödinger equation inside the sphere. This is accomplished if Eq. (25) is satisfied. We also see that the error in the wavefunctions inside the spheres is of $O[(\epsilon - \epsilon_\nu)^2]$ and from perturbation theory the error in the eigenvalues is of $O[(\epsilon - \epsilon_\nu)^4]$.

In the Atomic Sphere Approximation (ASA), the Wigner-Seitz cell is replaced by a sphere of equal volume and the interstitial region does not exist anymore so that the last term in Eq. (28) drops out.

We would like to note again that since the tight-binding envelope function is a linear combination of the conventional ones, it follows that the tight-binding LMTO is simply a linear combination of the conventional LMTO's with the expansion coefficients chosen so that the long range part cancel one another, resulting in a short range or tight-binding LMTO. Physically one can think of this cancelation as a screening process. Take for example the $l = 0$ component. The tail $\sim 1/r$ may be thought of as a potential from a point charge which is screened by the neighbouring multipole charges.

F. *The Multiple LMTO*

In the conventional LMTO method, the basis functions are labelled by the atoms ($\mathbf{R}$) at which they are centered and by the angular momentum $L \equiv (l, m)$. These LMTO's are calculated at some ϵ_ν normally chosen to be the center of the valence band. As mentioned in the Introduction, there are cases, where not only low energy valence and conduction bands, but also high energy conduction bands are of interest. To handle these cases we construct for a given $\mathbf{R}L$ multiple LMTO's calculated at different energies ϵ_ν's, chosen at the centers of the bands of interest. These, for instance, can be high energy conduction bands or bands with the same angular momentum character in the valence region.

We define a multiple LMTO as follows

$$\chi_{\mathbf{R}Ln} = \phi_{\mathbf{R}Ln} + \sum_{\mathbf{R}'L'n'} \dot{\phi}^{\alpha}_{\mathbf{R}'L'n'} h_{\mathbf{R}'L'n',\mathbf{R}Ln} + \kappa^{I}_{\mathbf{R}Ln} \tag{37}$$

where

$$h_{\mathbf{R}'L'n',\mathbf{R}Ln} = (c_{\mathbf{R}Ln} - \epsilon_{\mathbf{R}Ln})\delta_{\mathbf{R}',\mathbf{R}}\delta_{n',n}\delta_{L',L} + \sqrt{d_{\mathbf{R}'L'n'}} S_{\mathbf{R}'L'n',\mathbf{R}Ln} \sqrt{d_{\mathbf{R}Ln}} \tag{38}$$

The index n labels the multiple orbital or denotes the energy of the multiple orbital for a given $\mathbf{R}L$, similar to the principal quantum number in atomic physics. We can divide the multiple LMTO's into lower and higher LMTO's, the lower ones correspond to the normal LMTO's. The multiple LMTO is essentially the same as the LMTO in terms of its construction. It is possible to use different tails with energies $\kappa^2_{\mathbf{R}Ln} = \epsilon_{\mathbf{R}Ln} - V_0$ for the multiple LMTO's leading to a different structure constant S which now depends also on the index n. However, a simplification can be made by having the same tail for *all* multiple LMTO's so that the structure constant does not depend on the index n i.e. the same as in the normal LMTO. We make this simplification in the actual application of the method leading to

$$\begin{aligned} h_{\mathbf{R}'L'n',\mathbf{R}Ln} &= (c_{\mathbf{R}Ln} - \epsilon_{\mathbf{R}Ln})\delta_{\mathbf{R}',\mathbf{R}}\delta_{n',n}\delta_{L',L} \\ &+ \sqrt{d_{\mathbf{R}'L'n'}} f_{\mathbf{R}'L'n',\mathbf{R}Ln} S_{\mathbf{R}'L',\mathbf{R}L} \sqrt{d_{\mathbf{R}Ln}} \end{aligned} \tag{39}$$

$f_{\mathbf{R}'L'n',\mathbf{R}Ln}$ is a matrix that gives us a freedom in choosing how much $\dot{\phi}^{\alpha}_{\mathbf{R}'L'n'}$ should be tacked on to the tail in the other neighboring spheres. For example, if we have two multiple orbitals for a given $\mathbf{R}L$, the tail can be augmented for angular momentum L by either $\dot{\phi}_{\mathbf{R}L1}$ or $\dot{\phi}_{\mathbf{R}L2}$ or a linear combination of the two and f determines the coefficients of this linear combination. In practice we found that $f_{\mathbf{R}'L'n',\mathbf{R}Ln} = \delta_{n,n'}$ gives the best results.

G. *The Hamiltonian and the Overlap Matrix*

With the multiple LMTO's as a basis, the overlap matrix is given by

$$\begin{aligned} O_{\mathbf{R}Ln,\mathbf{R}'L'n'} &= < \chi_{\mathbf{R}Ln} | \chi_{\mathbf{R}'L'n'} > \\ &= < \varphi_{\mathbf{R}ln} | \varphi_{\mathbf{R}ln'} > \delta_{\mathbf{R},\mathbf{R}'}\delta_{L,L'} \\ &+ \sum_{\mu} < \varphi_{\mathbf{R}ln} | \dot{\varphi}^{\alpha}_{\mathbf{R}l\mu} > h_{\mathbf{R}L\mu,\mathbf{R}'L'n'} \\ &+ \sum_{\mu} h^{\dagger}_{\mathbf{R}Ln,\mathbf{R}'L'\mu} < \dot{\varphi}^{\alpha}_{\mathbf{R}'l'\mu} | \varphi_{\mathbf{R}'l'n'} > \\ &+ \sum_{\mathbf{R}''L''\mu'',\mu} h^{\dagger}_{\mathbf{R}Ln,\mathbf{R}''L''\mu''} < \dot{\varphi}^{\alpha}_{\mathbf{R}''l''\mu''} | \dot{\varphi}^{\alpha}_{\mathbf{R}''l''\mu} > h_{\mathbf{R}''L''\mu,\mathbf{R}'L'n'} \end{aligned} \tag{40}$$

Keeping in mind that

$$H\phi_{\mathbf{R}Ln} = \epsilon_{\mathbf{R}Ln}\phi_{\mathbf{R}Ln} \tag{41}$$

$$H\dot{\phi}^{\alpha}_{\mathbf{R}Ln} = \epsilon_{\mathbf{R}Ln}\dot{\phi}^{\alpha}_{\mathbf{R}Ln} + \phi_{\mathbf{R}Ln} \tag{42}$$

where $H = -\nabla^2 + V(\mathbf{r})$, the Hamiltonian matrix is given by

$$\begin{aligned} H_{\mathbf{R}Ln,\mathbf{R}'L'n'} &= < \chi_{\mathbf{R}Ln} | H | \chi_{\mathbf{R}'L'n'} > \\ &= < \varphi_{\mathbf{R}ln} | \varphi_{\mathbf{R}ln'} > \epsilon_{\mathbf{R}ln'}\delta_{\mathbf{R},\mathbf{R}'}\delta_{L,L'} \\ &+ \sum_{\mu} < \varphi_{\mathbf{R}ln} | \dot{\varphi}^{\alpha}_{\mathbf{R}l\mu} > \epsilon_{\mathbf{R}l\mu} + < \varphi_{\mathbf{R}ln} | \varphi_{\mathbf{R}l\mu} > h_{\mathbf{R}L\mu,\mathbf{R}'L'n'} \\ &+ \sum_{\mu} h^{\dagger}_{\mathbf{R}Ln,\mathbf{R}'L'\mu} < \dot{\varphi}^{\alpha}_{\mathbf{R}'l'\mu} | \varphi_{\mathbf{R}'l'\mu} > \epsilon_{\mathbf{R}'l'n'} \\ &+ \sum_{\mathbf{R}''L''\mu''} \sum_{\mu} h^{\dagger}_{\mathbf{R}Ln,\mathbf{R}''L''\mu''} [< \dot{\varphi}^{\alpha}_{\mathbf{R}''l''\mu''} | \dot{\varphi}^{\alpha}_{\mathbf{R}''l''\mu} > \epsilon_{\mathbf{R}''l''\mu} \\ &+ < \dot{\varphi}^{\alpha}_{\mathbf{R}''l''\mu''} | \varphi_{\mathbf{R}''l''\mu} >] h_{\mathbf{R}''L''\mu,\mathbf{R}'L'n'} \end{aligned} \tag{43}$$

H. *Radial Overlap Integrals*

In the expressions for the overlap and Hamiltonian matrix we encounter radial integrals of the form $< \varphi_{\mathbf{R}ln} | \varphi_{\mathbf{R}ln'} >$, $< \varphi_{\mathbf{R}ln} | \dot{\varphi}^{\alpha}_{\mathbf{R}ln'} >$ and $< \dot{\varphi}^{\alpha}_{\mathbf{R}ln} | \dot{\varphi}^{\alpha}_{\mathbf{R}ln'} >$. These radial integrals can be evaluated from the Wronskians at the Wigner-Seitz radius. Let

$$u_n = r\varphi_n \tag{44}$$

φ_n is the radial part of $\varphi_{\mathbf{R}Ln}$ for a given $\mathbf{R}L$. u_n and $\dot{u}_n$ satisfy the radial equations (in Rydberg=13.6 eV)

$$[-\frac{d^2}{dr}+\frac{l(l+1)}{r^2}+V(r)]u_n=\epsilon_n u_n \tag{45}$$

$$[-\frac{d^2}{dr}+\frac{l(l+1)}{r^2}+V(r)]\dot{u}_n=\epsilon_n \dot{u}_n+u_n \tag{46}$$

We note first of all that

$$\frac{\partial}{\partial\epsilon}<u_n|u_n>=2<u_n|\dot{u}_n>=0 \tag{47}$$

A radial integral such as $<u_n|u_{n'}>$ can be evaluated by multiplying the equation for u_n by $u_{n'}$ and the equation for $u_{n'}$ by u_n, substracting one equation from the other and integrating from $r=0$ to $r=S_{\mathbf{R}}$. This yields for $n\neq n'$

$$<u_n|u_{n'}>=(\epsilon_n-\epsilon_{n'})^{-1}W[\varphi_n,\varphi_{n'}] \tag{48}$$

$$<u_n|\dot{u}_{n'}>=(\epsilon_n-\epsilon_{n'})^{-1}(W[\varphi_n,\dot{\varphi}_{n'}]+<u_n|u'_n>) \tag{49}$$

$$<\dot{u}_n|\dot{u}_{n'}>=(\epsilon_n-\epsilon_{n'})^{-1}(W[\dot{\varphi}_n,\dot{\varphi}_{n'}]-<u_n|\dot{u}_{n'}>+<\dot{u}_n|u_{n'}>) \tag{50}$$

II. Applications

In all applications, we have used $\kappa^2=0$ and the ASA plus the combined correction described in Refs.[2,11].

A. *Free Electron band structure*

As a first illustration for the relevance of having multiple LMTO's, we consider a free electron gas in an fcc lattice with a lattice constant $a=6.654\ a_0$ corresponding to nickel. An empty lattice is the hardest test for the LMTO-ASA method. In the language of LMTO we expand the solution in its angular momentum components:

$$e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}=\frac{1}{4\pi}\sum_L i^l(2l+1)j_l(|\mathbf{k}+\mathbf{G}|r)y_L(\widehat{\mathbf{k}+\mathbf{G}})y_L(\hat{\mathbf{r}}) \tag{51}$$

Let us suppose that we are interested in the energy range from 0 to $\sim$ 70 eV which encompasses $\mathbf{G}=(0\ 0\ 0)$, $(\pm 1\ \pm 1\ \pm 1)$ $(\pm 2\ 0\ 0)$. With such a large energy range, we will not be able to get an accurate band structure over the whole energy range with a linear method like the LMTO because the band structure is accurate within an energy window of $k_m axs\leq\pi$ which corrsponds in our case to about $\pm$ 15 eV around a chosen energy ϵ_ν. To get a good bandstructure over the whole range, the usual method is to divide the range into several panels and calculate the bandstructure within each panel separately, choosing ϵ_ν to be the center of the panel[16]. However, eigenfunctions belonging to different panels are not orthogonal and this leads to serious errors in calculating matrix elements and discontinuity in the bandstructure and other quantities such as density of states. This is precisely what we want to avoid.

We first calculate the bandstructure using the normal LMTO method with one orbital per L-channel and using merely one panel. By examining the Bessel function plot in Fig. 1 we can see that we have to include s,p,d,f and g orbitals since these orbitals have a significant weight inside $r=\sqrt{\epsilon}\ s=\sqrt(5\ Ry)\ 2.6\ a_0=5.8$. To get the best bandstructure over the whole energy range from 0 to 70 eV with one panel, we choose different ϵ_ν's for different angular momentum l. The best choice is $\epsilon_s=7\ eV$, $\epsilon_p=20\ eV$, $\epsilon_d=27\ eV$, $\epsilon_{f,g}=40\ eV$. While a change in ϵ_s and ϵ_p can give a qualitatively different result, a change in ϵ_d, ϵ_f and ϵ_g within at least $\pm$ 15 eV does not influence the result significantly. The resulting bandstructure is shown in Fig. 2a.

Very good agreement with the exact result is obtained for energy up to 25 eV but above this energy there are a number of discrepancies. A band along the ΓX starting at 36.4 eV and ending at 24.3 eV and two bands starting at 36.4 eV, 48.5 eV and ending at 33.4 eV are split whereas the exact bands are degenerate. Consider also the eigenvalues at the Γ-point. The eigenvalue corresponding to $\mathbf{G}=0$ comes from the $1s$ orbital. The next eigenvalues at 36.4 eV are 8-fold degenerate, corresponding to $\mathbf{G} = (\pm 1\ \pm 1\ \pm 1)$, but the calculated ones are 7-fold degenerate which implies that one band is missing.

To understand the above discrepancies[2], we examine the plot of the Bessel function for $l = 0$ in Fig. 1. We see that when $r = 3.1$ (19 eV), a node appears. This shows that to get a right free electron bandstructure for a range of energy from 0 to well above 19 eV with the LMTO method we must have more than one orbital per L-channel. We should include in the LMTO basis at least for $l = 0$ not only φ_s with no node but also φ_s with one node. If we insist on having only one s orbital, we can either describe the low or the high energy bands but not both. For example, if we choose to have one node, then the lowest band is poorly described. In fact it is qualitatively wrong. This will be true also for the higher angular momenta as we go to higher energy.

To see systematically what happens to the 8-fold degeneracy, we show in Table I the eigenvalues as we add new orbitals one at a time. As can be seen, the degeneracy is improved as we add higher angular momentum orbitals. Thus with ($1s$ $2p$ $3d$) orbitals we have six degenerate states, with ($1s$ $2p$ $3d$ $4f$) orbitals we have seven and with ($1s$ $2s$ $2p$ $3d$ $4f$) orbitals we have eight which is the right degeneracy. In particular we note that the 8-fold degeneracy cannot be obtained without having the $2s$ orbital and it does not originate from the g orbital. On the other hand, the 6-fold degeneracy at 48.5 eV corresponding to $\mathbf{G} = (\pm 2\ 0\ 0)$, is obtained when the g orbital is included.

We show in Fig. 2b the band structure with the additional $2s$ orbital. Significant improvements are obtained: the above mentioned split bands have now become almost degenerate and a new band coming from the $2s$ orbital appears which would otherwise be missing in the normal LMTO. The bandstructure at higher energy is also improved by the addition of the $2s$ orbital as may be seen in Fig. 2b. In Fig. 2c we compare the bandstructures with and without the additional $2s$ orbital. Addition of $3p$ orbitals does not improve the result since the energy is very high.

B. *Nickel band structure*

We choose Nickel as a test case because the unoccupied $4d$ orbital should have a relatively low energy due to the strong d-potential and it will therefore create an additional band which is not too far above the Fermi level. We also have in mind calculating the Electron Energy Loss Spectra which requires both occupied and unoccupied bands and which would be a good overall test for the multiple LMTO method.

To make a systematic study of the bandstructure, we have calculated the bandstructure with the following sets of orbitals:

$$\begin{aligned} &set\ 1:\ 4s\,4p\,3d\,4f \\ &set\ 2:\ 4s\,4p\,3d\,4d\,4f \\ &set\ 3:\ 4s\,4p\,3d\,4f\ 5g \\ &set\ 4:\ 4s\,4p\,3d\,4d\,4f\ 5g \end{aligned}$$

as basis functions. The $5s$ and $5p$ orbitals have much too high energies (66 and 88 eV respectively) and are therefore not included. The $4d$ orbital on the other hand creates a band which is centered at around $\sim$ 30 eV. The calculations have been done for the paramagnetic case since the spin splitting is much smaller than the energy scale of the conduction states. In what follows, we discuss the resulting bandstructures obtained from the differents sets of orbitals.

In Fig. 3 we show the valence bandstructures obtained with set 1 and 2. As expected, the additional $4d$ orbitals have virtually no effects on the valence bands. On the other hand, the addition of the $4d$ orbitals has a large effect on the conduction bands as can be seen in Fig. 4a. There are a number of new features associated with the addition of the $4d$ orbitals. The most important feature is the appearance of new bands at around $25 - 30$ eV. Due to the strong d potential, the separation between the $3d$ and $4d$ bands is relatively small compared to the separation between the $4s$ and $5s$ or $4p$ and $5p$ bands (70 and 90 eV respectively). Apart from giving new bands, the $4d$ orbitals have a drastic effect on the bandstructure above 30 eV, resulting in a very different bandstructure. The bands along the ΓX between 30 and 40 eV are split, due to the hybridization with the new bands. Between 40 and 60 eV further new bands appear.

To check that we have a right bandstructure, we also calculate the bandstructure with the panelling method. We choose the following energies for the orbitals: $\epsilon_s = 14\ eV$, $\epsilon_p = 14\ eV$, $\epsilon_d = \epsilon_f = 34\ eV$. Ideally, one would like to have all orbitals calculated at the center of the panel so that the bandstructure is most accurate inside an energy window of ± 15 eV around the center. In our case, however, this procedure gives spurious bands. If the $4s$ orbital is calculated at 34 eV, we get a so called ghost band. A similar problem arises when the d orbitals are calculated at 14 eV. This problem comes about when the chosen energy lies in the middle between two neighbouring bands of the same angular momentum character. The orbital at this energy just starts forming a node or has just formed a node. At one k point the energy derivative $\dot{\phi}$ takes ϕ to a solution with n nodes and at a neighbouring k point it gives a solution with $(n \pm 1)$ nodes. As a result, the band jumps from one main quantum number to another with a jump given approximately by the energy difference between the bottom of the higher band and the top of the lower band. We can also get a spurious band that does not jump from one band to another but lies in a wrong energy range simply because we force it to be there by choosing a wrong ϵ_ν that corresponds to a positive logarithmic derivative at the sphere boundary. The problem is particularly severe for narrow bands such as the d bands. To solve the problem, we choose different energies for different orbitals, making sure that each energy does not lie outside the width of the corresponding band.

In Fig. 4b we compare the bandstructure obtained with the multiple LMTO method and the one obtained with the panelling method. The agreement is strikingly close. To see how much the $4d$ orbitals have mixed into the states, we project them onto the $4d$ orbital: $| < \psi_{\mathbf{k}n} | \phi_{4d} > |^2$. A surprisingly large mixing is found in those states which are already well described without the $4d$ orbitals. For example, the lowest conduction state at the L point has 30 % $4d$ character and the second lowest state at the X point has 40 % $4d$ character. The valence states, however, have at most 5 % $4d$ character.

We have also calculated the bandstructure with the g orbitals, with and without the $4d$ orbitals (set 3 and 4). In Fig. 5a we see a similar drastic effect on the high lying bands upon introduction of the $4d$ orbitals. In Fig. 5b we compare the bandstructure with the one obtained from the panelling method. As in the previous case, the agreement is very good. To see the importance of higher angular momentum orbitals, we compare the bandstructure with and without the g orbitals (Fig. 6) The $4d$ orbitals are included in both bandstructures. The influence of the g orbitals on the bandstructure below 30 eV is small which is not surprising since the center of the g band is at 90 eV. Above 30 eV a few changes have occured. The $4d$ bands have been narrowed and a new band appears at around 50 eV resulting in a significant change of the bands in that region.

C. *Comparison of LMTO and a modified LAPW bandstructure*

We compare the bandstructure of Nickel obtained with our multiple LMTO method with the bandstructure obtained with a modified LAPW method[10]. In the LAPW method, the space is divided into muffin tin spheres and interstitial region. A set of plane waves define the basis functions which are augmented inside the spheres by a linear combination of orbitals ϕ, which are radial solutions to the Schrödinger equation, and their energy derivatives $\dot{\phi}$ at some energy ϵ_ν normally chosen at the band center. In the modified version of the LAPW method, the augmentation inside the spheres does not include $\dot{\phi}$ but the energies of the orbitals ϵ_ν are not fixed. Instead, they are allowed to follow the plane wave energies through matching the logarithmic derivatives at the sphere boundary. Thus higher energy plane waves are matched on to higher energy orbitals so that the basis can have several orbitals of the same angular momentum but with different numbers of nodes. In this fashion, the basis covers a large range of energy approximately equal to the highest plane wave energy and by construction, the method reproduces the free-electron case exactly.

In Figs. 7a,b we show the modified LAPW bandstructure obtained with 30-40 basis functions and the multiple LMTO bandstructure obtained with basis set 4. Reasonable agreement is found for energies below 30 eV. Above it, however, the two bandstructures are somewhat different. To trace the origin of this difference, we make the same comparison but now without the $4d$ orbitals in the multiple LMTO method (Fig. 7b). The agreement for energies > 30 eV becomes closer, which suggests that the $4d$ orbitals are responsible for the difference. We should point out, however, that we have only used a small number of basis functions in the modified LAPW bandstructure so that the $4d$ bands along the ΓL are missing, which should appear if we had used more basis functions. The two methods are expected to give a similar result as the number of basis functions in the modified LAPW method is increased. The $4d$ bands should be present because the d potential is very strong as indicated by the narrow $3d$ band and the relatively small separation between the $3d$ and $4d$ bands. Panelling calculation reproduces the $4d$ band almost exactly and addition of g orbitals does not change the $4d$ bands qualitatively. In the free-electron case the multiple LMTO method gives a satisfactory description of the bandstructure up to at least 50 eV. We expect the method to work even better for real systems.

The difference between the LMTO and LAPW methods rests on the starting basis functions. The LMTO method starts with an orbital whereas the LAPW method starts with a plane wave. The LMTO method is very efficient when a band still retains much of its orbital character. This is generally true for low lying bands. Thus, to describe the valence bands accurately, many more basis functions are needed in the LAPW method than in the LMTO method (typically 50-100 *vs* 9-16 per atom). The LAPW method on the other hand is more efficient when the band has lost its orbital character and become plane wave like which is generally true for high lying bands. Thus, for example, in the free-electron limit, the modified LAPW method reproduces the free-electron band exactly. There is a transition region in between these two extremes in which the two methods are equally competitive. Where this transition region lies depends on the system but one expects that the stronger the potential, the higher the transition region.

D. *Comparison Ni and the free-electron bandstructure*

It is interesting to compare the nickel bandstructure with the corresponding free-electron bandstructure calculated in the same lattice (this is the reason for choosing the nickel lattice in the free-electron test). In photoemission experiments, it is usually assumed that the emitted electrons reside in plane wave states. This is presumably valid when the kinetic energy of the electrons is of the order of $\sim$ keV like in XPS. In the UPS, however, the kinetic energy may vary from a few to a hundred eV. The question is then, at what energy the bandstructure starts to resemble the free-electron bandstructure.

In Fig. 8 we compare the nickel and free-electron bandstructures. The zero energy of the free-electrons has been adjusted so that the energy corresponding to $\mathbf{G} = (2\ 0\ 0)$ coincides with the state of nickel at 43 eV at the Γ point. Although the details of the bandstructures are certainly not the same, we can see a lot of resemblance in the main features. The opening of a "gap" at the zone boundaries is characteristic of a periodic perturbation on free-electrons. The degenaries of the nickel states can also be traced back to the free-electron case. For example, the four-fold free-electron states at 18 eV (X point) split into two states and a doubly degenerate state. Similarly the eight and six-fold degenerate free-electron states at the Γ point may be identified with the corresponding nickel states centered around them, although one state is still missing at 43 eV, most likely due to the neglect of the h orbitals. For energy $>$ 40 eV it seems reasonable to assume a free-electron bandstructure. In this respect, the common picture of a transition metal as consisting of a narrow d band embedded in a free-electron gas is very appropriate.

E. *Empty spheres*

There are three main approximations used in the present calculations: the ASA but with combined correction, zero kinetic energy of the tail ($\kappa^2 = 0$), and a finite number of angular momentum in the LMTO's. All three approximations can be improved by adding empty spheres. The empty spheres clearly reduce the sphere overlap in the ASA and improve the approximation of $\kappa^2 = 0$ by providing a tail with the right kinetic energy in the interstitial region. At the same time the dependence on higher angular momenta, which become more and more important as we go towards the WS sphere boundary, is also reduced because the spheres become smaller. The combined correction[2,11], eliminates most of the geometry violation in the ASA.

The tail of the LMTO with $\kappa = 0$ is a solution to the Schrödinger equation in the interstitial region corresponding to zero kinetic energy. This is a good approximation for the valence states or low lying conduction states but the approximation presumably becomes worse for high lying states. It is, however, clear from Fig. 2b that the error is not large which is surprising considering that the kinetic energy of these states is large. This implies that the variational principle has made the choice of the tail to be of secondary importance.

One would expect that if κ^2 correponds to the kinetic energy in the interstitial region, the tail cancellation in Eq. (26) is achieved with fewer angular momenta than in the case of $\kappa^2 = 0$ and the resulting eigenvalue is presumably closer to the true one. However, provided we have all angular momentum components, the tail cancellation in Eq. (26) is always satisfied, independent of κ, at some energies ϵ's and the wavefunctions in Eq. (23) are solutions to the Schrödinger equation at these energies to order $\epsilon - \epsilon_\nu$. On the other hand, if we do not use the ASA, the wavefunctions in the interstitial region with $\kappa = 0$ will never satisfy the Schrödinger equation unless the kinetic energy happens to be zero. In this sense, the use of overlapping spheres (ASA) is better than the use of non-overlapping muffin-tin spheres because in the ASA the wavefunctions in between the Wigner-Seitz and muffin-tin spheres have a kinetic energy closer to the true value. In practice, however, numerical experience shows that the error arising from the violation of geometry in the ASA appears to be larger than the gain in the kinetic energy i.e. the combined correction[2,11] improves the high lying bands.

To see the effects of the emtpy spheres we compare in Figs. 9a,b and c the bandstructures obtained from panelling calculations, with and without an empty sphere, with the exact free-electron band. It is not clear however, which of the three approximations discussed above is the main source of error because adding an empty sphere reduces simultaneously the dependence on higher angular momenta, κ and ASA. Addition of g orbitals, for example, improves the bandstructure but not as much as the improvement obtained by adding an empty sphere.

F. *Problems with linear dependency*

It may happen that as new orbitals with higher energies are added into the basis we run into linear dependency. This linear dependency arises from orbitals with the same angular momentum l since orthogonality of the spherical harmonics implies that LMTO orbitals of different angular momentum are almost orthogonal. This may be seen explicitly in Eq. (40) where the first term, which is the largest, is zero when $L \neq L'$. The rest of the terms is usually much smaller than the first term. On the other hand, when $L = L'$ but $n \neq n'$, the radial overlap integral $< \varphi_{\mathbf{R}ln} | \varphi_{\mathbf{R}ln'} >$ may not be small, depending on the values of φ's and their derivatives at the Wigner-Seitz radius.

To illustrate the problem with linear dependency, we calculate in Table 2 the radial overlap integrals $< j_0(k_1 r) | j_0(k_2 r) >$ for a given $k_1^2 = 7\ eV$ and a varying k_2^2. We see that the radial overlap integral given in Eq. (48) decreases as the energy of $j_0(k_2)$ increases. This is indeed a way of avoiding linear dependency when using multiple LMTOs i.e. by decreasing the energy of the lower orbital and increasing the energy of the higher orbital.

IV. Summary and Conclusions

We have developed a method for calculating both valence and high lying conduction bands using multiple LMTO orbitals as basis functions. The main advantage of the method over the panelling method is that the valence and conduction bands are treated on equal footing so that the bandstructure is obtained in one diagonalization which avoids discontinuity, in contrast to the panelling method. Since the valence and conduction bands are obtained from the same Hamiltonian, they form an orthogonal set, whereas in the panelling method, states belonging to different panels are not exactly orthogonal. The orthogonality is not only a question of convenience but it is also important in cases where matrix elements of some operator between the states are needed (e.g. optical absorptions, energy loss spectra). Non-orthogonality between the wavefunctions can lead to serious error in the matrix elements.

The method may also be used for dealing with systems with semicore states. It is important in many cases to treat the semicore states as valence states because they can affect the accuracy of the upper valence states significantly. Moreover, treating the semicore as core states results in non-orthogonality between these and the valence/conduction states which leads to the above mentioned problem associated with matrix elements.

We have done an empty lattice test to gauge the capability of our method. Apart from minor deviations, the free-electron band is well reproduced up to at least 50 eV. This is somewhat surprising considering that there are three approximations used in the calculations: $\kappa^2 = 0$, orbital angular momentum cut-off and the ASA. The ASA itself has been improved with the use of combined correction which implies that the variational principle has made the choice of the tail to be of secondary importance. A significant improvement is obtained when the bandstructure is calculated with an additional empty sphere which suggests that a larger fraction of the error originates from the use of $\kappa^2 = 0$ than from the cut-off in the orbital angular momenta. Since the empty lattice test is the hardest test for the LMTO-ASA method, we expect the method to work even better in real systems.

We have applied our method to calculate the bandstructure of nickel up to 60 eV. We found additional bands arising from the $4d$ orbitals at around 30 eV which would be missing in the normal LMTO method with one orbital per angular momentum channel and with ϵ_ν in the valence region. While the valence and low lying conduction bands are hardly affected by the $4d$ orbitals, the bandstructure above 30 eV changes drastically due to a strong hybridization with the $4d$ orbitals. The $4d$ orbitals are indispensible for a proper description of the conduction bands in nickel. This is presumably also true in other transition elements. In other systems where the higher orbitals have a relatively low energy, they are expected to have a similar efect. In a subsequent paper, we will show that these $4d$ orbitals are important for an accurate description of the energy loss spectra.

To check the validity of our bandstructure, we have also performed a panelling calculation. A very close agreement is found between the panelling and multiple LMTO bandstructures. We often run into a problem with spurious (ghost) bands when using the panelling method. To avoid this problem, the corresponding orbital should be downfolded[17] (not included in the Hamiltonian) or its ϵ_ν should be placed close to the center of the band. These procedures, however, slightly reduce the accuracy of the bandstructure in the region of interest. In our method, on the other hand, we never run into this problem because each orbital falls naturally into its own branch and the accuracy is maintained by having two orbitals to describe energy region between the two branches of a given l.

We have also made a comparison between the nickel bandstructure and the free-electron band. Although the details are different, the main features show a close resemblance. Many of the nickel conduction bands can be traced back to the free-electron band. The result suggests that the assumption made in photoemission experiments that the emitted electrons reside in plane waves is very reasonable.

Acknowledgements

We would like to thank O.K. Andersen for many stimulating discussions and a critical reading of the manuscript. We also thank O. Jepsen for valuable help during program development.

Appendix A

Derivation of the LMTO in terms of the structure constant and the potential parameters

From Eq. (25) we have

$$|J> = -[|\dot{\phi}> N + |\phi> \dot{N})]\dot{P}^{-1} \tag{52}$$

From Eq. (3) we have

$$\begin{aligned} |\chi> &= |\tilde{\chi}> N^{-1} \\ &= |\phi> + |J> (P-S)N^{-1} + |K>_I N^{-1} \\ &= |\phi> - (|(\dot{\phi}> N + |\phi> \dot{N})\dot{P}^{-1}(P-S)N^{-1} + |K>_I N^{-1} \end{aligned} \tag{53}$$

By taking the energy derivative of P in Eq. (17) it is easy to show that

$$N = W[K^0, J]\dot{P}^{1/2} \tag{54}$$

With the approximation $\kappa^2 = 0$ in Eq. (4), we have for the regular solution J^0 and irregular solution K^0

$$J_l^0 = [2(2l+1)]^{-1}(r/w)^l \tag{55}$$

$$K_l^0 = (r/w)^{-l-1} \tag{56}$$

where w is the average Wigner-Seitz radius i.e. $(4\pi/3)w^3$ = cell volume/number of atoms. In this case $W[K^0, J] = w/2$, independent of l. Eq. (53) then becomes

$$\begin{aligned} |\chi> &= |\phi> + (|\dot{\phi}> + |\phi> \dot{N}N^{-1})\dot{P}^{-1/2} > (P-S)\dot{P}^{-1/2} + |K>_I N^{-1} \\ &= |\phi> + |\dot{\phi}^{\alpha}> \dot{P}^{-1/2}(P-S)\dot{P}^{-1/2} + |K>_I N^{-1} \\ &= |\phi> + |\dot{\phi}^{\alpha}> h + |\kappa>_I \end{aligned} \tag{57}$$

with $|\dot{\phi}^{\alpha}>$, $|\kappa>_I>$ and h defined in Eqns. (31) and (38).

TABLE 1. Free-electron eigenvalues in eV at the Γ-point calculated with $(1s\ 2p\ 3d)$, $(1s\ 2p\ 3d\ 4f)$, $(1s\ 2s\ 2p\ 3d\ 4f)$, $(1s\ 2p\ 3d\ 4f\ 5g)$ and $(1s\ 2s\ 2p\ 3d\ 4f\ 5g)$ orbitals. The eigenvalues in the brackets have been obtained by having an empty sphere and using $(1s\ 2s\ 2p\ 3d\ 4f\ 5g)$ orbitals. The lattice is fcc with a lattice constant $a = 6.654\ a_0$.

Exact	*spd*	*spdf*	2*spdf*	*spdfg*	2*spdfg*	Degeneracy
0.0	0.0	0.0	0.0	0.0	0.0 (0.0)	1
36.4		37.4	37.5	37.2	37.2 (37.0)	1
36.4	35.5	37.9	37.9	37.6	37.3 (35.7)	3
36.4	41.5	38.1	38.2	37.6	37.4 (36.3)	3
36.4			40.6		38.8 (38.0)	1

TABLE 2. The radial overlap integral $< j_1(k_1)|j_1(k_2) >$ for a given $k_1^2 = 7\ eV$ and a varying k_2^2 (in eV)

k_2^2	overlap
13.6	0.96
20.4	0.86
27.2	0.49
34.0	0.39
40.8	0.16

[1] J.C. Phillips, L. Kleinman, Phys. Rev. **116**, 287 (1959); Phys. Rev. **116**, 880 (1959); see also *Solid State Physics* **24** (Academic, New York 1969)

[2] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975)

[3] H.L. Skriver, *The LMTO Method* Springer Series in Solid-State Sciences volume 41 (Springer-Verlag Berlin Heidelberg 1984)

[4] F. Bloch, Z. Phys. **52**, 555 (1928); N.F. Mott and H. Jones, *The Theory of Metals and Alloys* (Oxford University Press, London 1936)

[5] V. Heine, *Electronic Structure from the Point of View of the Local Atomic Environment* p.1 and D.W. Bullet, *The Renaissance and Quantitative Development of the Tight Binding Method*, in *Solid State Physics* **35** (Academic New York 1980)

[6] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964) ;
W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965) ;

[7] L. Hedin, Phys. Rev. **139**, A796 (1965) ;

[8] L. Hedin and S. Lundqvist, in *Solid State Physics* **23** (Academic New York 1969)

[9] F. Aryasetiawan, Phys. Rev. B **46**, 13051 (1992)

[10] F. Aryasetiawan, U. von Barth, P. Blaha and K. Schwarz, (preprint)

[11] O.K. Andersen, O. Jepsen and M. Sob, in *Electronic Band Structure and its Applications*, ed. M. Yussouff (Springer Lecture Notes, 1987)

[12] O.K. Andersen, A.V. Postnikov and S. Yu. Savarsov (preprint)

[13] O.K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984) and
O.K. Andersen, Z. Pawlowska, and O. Jepsen, Phys. Rev. B **34**, 5253 (1986)

[14] G. Krier, O. K. Andersen and O. Jepsen, (to be published)

[15] J. Korringa, Physica **13**, 392 (1947);
W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954)

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

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

Figure 1

$r \times$ radial Bessel functions $j(r)$ for different angular momenta.

Figure 2a

Comparison between the exact (solid line) and the LMTO (dotted line) free electron bands. The LMTO band is calculated with $1s\ 2p\ 3d\ 4f\ 5g$ orbitals with energies $\epsilon_{1s} = 7\ eV$, $\epsilon_{2p} = 14\ eV$, $\epsilon_{3d} = 27\ eV$, $\epsilon_{4f,5g} = 40\ eV$.

Figure 2b

Comparison between the exact (solid line) and the multiple LMTO (solid circles) free electron bands. The multiple LMTO band is calculated with $1s\ 2s\ 2p\ 3d\ 4f\ 5g$ orbitals with energies $\epsilon_{1s} = 7\ eV$, $\epsilon_{2s} = 55\ eV$, $\epsilon_{2p} = 14\ eV$, $\epsilon_{3d} = 27\ eV$, $\epsilon_{4f,5g} = 40\ eV$.

Figure 2c

Comparison between free electron bands obtained with the normal (solid line) and multiple (solid circles) LMTO methods with the sets of orbitals and energies as specified in the captions of Figs. 2a and 2b.

Figure 3

The valence bands of paramagnetic Ni obtained with the normal (solid line) and multiple (squares) LMTO methods. The energies are measured with respect to the Fermi level.

Figure 4a

The conduction bands of paramagnetic Ni obtained with the normal (solid line) and multiple (squares) LMTO methods. $4s, 4p, 3d$ and $4f$ orbitals have been used with the additional of $4d$ orbitals in the latter method. The orbital energies are $\epsilon_{4s} = -7.0\ eV$, $\epsilon_{4p} = -5.0\ eV$, $\epsilon_{3d} = -3.5\ eV$, $\epsilon_{4d} = 27.0\ eV$, $\epsilon_{4f} = 40.0\ eV$.

Figure 4b

Comparison between conduction bands of paramagnetic Ni obtained with the panelling (solid line) and multiple (squares) LMTO methods. $4s, 4p, 4d$ and $4f$ orbitals have been used in the panelling method with energies $\epsilon_{4s,4p} = 14\ eV$, $\epsilon_{4d,4f} = 34\ eV$.

Figure 5a

The conduction bands of paramagnetic Ni obtained with the normal (solid line) and multiple (squares) LMTO methods. $4s, 4p, 3d, 4f$ and $5g$ orbitals have been used with the additional of $4d$ orbitals the latter method. The orbital energies are $\epsilon_{4s} = -7.0\ eV$, $\epsilon_{4p} = -5.0\ eV$, $\epsilon_{3d} = -3.5\ eV$, $\epsilon_{4d} = 27.0\ eV$, $\epsilon_{4f} = 40.0\ eV$, $\epsilon_{5g} = 55.0\ eV$.

Figure 5b

Comparison between conduction bands of paramagnetic Ni obtained with the panelling (solid line) and multiple (squares) LMTO methods. $4s, 4p, 4d, 4f$ and $5g$ orbitals have been used in the panelling method with energies $\epsilon_{4s,4p} = 14\ eV$, $\epsilon_{4d,4f,5g} = 34\ eV$.

Figure 6

The effect of adding the g orbitals on the paramagnetic Ni conduction bandstructure. The solid and dotted lines correspond to the bandstructure with and without the g orbitals respectively.

Figure 7a

Comparison between conduction bands of paramagnetic Ni obtained with the multiple LMTO (solid line) and modified LAPW (squares) methods. The orbitals and energies used in the multiple LMTO method are the same as in Fig. 5a.

Figure 7b

Comparison between conduction bands of paramagnetic Ni obtained with the normal LMTO (solid line) and modified LAPW (squares) methods.

Figure 8

Comparison between conduction band of paramagnetic Ni (dotted line) and the free electron band (solid line). The Ni bandstructre has been obtained with the multiple LMTO method as in Fig. 5a or 7a.

Figure 9a

The effect of adding g orbitals on the free electron band. The solid and dotted lines show tha bandstructure with and without the g orbital, respectively. The energies are as in the caption of Fig. 2b.

Figure 9b

The effect of adding an empty sphere on the free electron band. The dotted and solid lines are the free electron band with and without an empty sphere respectively. The empty sphere is located at $(.5\ .5\ .5)a$ and occupies 15% of the cell volume. The choice of orbitals and energies is the same as in the caption of Fig. 2a.

Figure 9c

Comparison between the exact free electron band (solid) and the LMTO band including empty spheres (dotted) as in Fig. 9b.