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Reference:

Nikolaev A.V., Lamoen Dirk, Partoens Bart.- Extension of the basis set of linearized augmented plane wave (LAPW) method by using supplemented tight binding basis functions

The journal of chemical physics - ISSN 0021-9606 - 145(2016), p. 1-11

Full text (Publishers DOI): <http://dx.doi.org/doi:10.1063/1.4954962>

Extension of the basis set of linearized augmented plane wave method (LAPW) by using supplemented tight binding basis functions

A.V. Nikolaev*

*Skobeltsyn Institute of Nuclear Physics Lomonosov Moscow State University, Leninskie gory, Moscow 119991, Russia and
Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Russia*

D. Lamoen

*EMAT, Department of Physics, Universiteit Antwerpen,
Groenenborgerlaan 171, 2020 Antwerpen, Belgium*

B. Partoens

*CMT group, Department of Physics, Universiteit Antwerpen,
Groenenborgerlaan 171, 2020 Antwerpen, Belgium*

In order to increase the accuracy of the linearized augmented plane wave method (LAPW) we present a new approach where the plane wave basis function is augmented by two different atomic radial components constructed at two different linearization energies corresponding to two different electron bands (or energy windows). We demonstrate that this case can be reduced to the standard treatment within the LAPW paradigm where the usual basis set is enriched by the basis functions of the tight binding type, which go to zero with zero derivative at the sphere boundary. We show that the task is closely related with the problem of extended core states which is currently solved by applying the LAPW method with local orbitals (LAPW+LO). In comparison with LAPW+LO, the number of supplemented basis functions in our approach is doubled, which opens up a new channel for the extension of the LAPW and LAPW+LO basis sets. The appearance of new supplemented basis functions absent in the LAPW+LO treatment is closely related with the existence of the u_l -component in the canonical LAPW method. We discuss properties of additional tight binding basis functions and apply the extended basis set for computation of electron energy bands of lanthanum (face and body centered structures) and hexagonal close packed lattice of cadmium. We demonstrate that the new treatment gives lower total energies in comparison with both canonical LAPW and LAPW+LO, with the energy difference more pronounced for intermediate and poor LAPW basis sets.

I. INTRODUCTION

The choice of a basis set which may first appear as “the black art” [1] is being constantly debated within the quantum chemistry community. It is well known that in molecular calculations there are two main groups of molecular basis sets introduced by Pople and collaborators (see [1] and references therein) and more recently by Dunning [2]. Both groups supply us with the whole hierarchy of basis sets, where at each step we can enrich the main set by polarization functions of high orbital type or by diffuse functions. For example, one has to add polarization functions if polarization effects are expected to be important, or diffuse functions if we want to refine the description of extended molecular states. Not surprisingly, the actual choice of a basis set depends on the task to be solved and is considered as a difficult problem. For heavy and laborious calculations the choice of a basis set is crucial since on one hand we want to obtain a reliable result and on the other hand minimize the computer time to achieve the goal.

In contrast to this complicated hierarchy of molecular

basis sets, the choice of bases in electronic band structure calculations and here we imply mainly the linear augmented plane wave (LAPW) method [3–5], seems rather simple. The number of augmented plane waves is commonly determined by the parameter $R_{MT}K_{max}$, where R_{MT} is the smallest muffin-tin (MT) radius, and K_{max} is the maximal value of the plane wave vector. The K_{max} value implies that the kinetic energy cut off is $K_{max}^2/2$ (in atomic units, a.u.). However, in practice some band structure calculations can not be carried out without so called local orbitals (LO) [6]. Such situations occur in systems with semicore electron states which cannot be fully confined within the MT-spheres. The problem of extended core states and its relation to our approach is discussed in detail in the next section. What concerns us here is that the introduction of local orbitals represents an extension of the canonical LAPW basis set albeit the form of new basis states (local orbitals) is very different from the standard augmented plane wave basis function. The LAPW+LO scheme proposed by Singh [7], [6] is practical, but the form of the local orbital functions is not derived from a general approach, and arguments for adding LO basis states are purely variational.

In the present paper we show that the appearance of supplemented basis functions can be understood as a result of refinement of the LAPW band scheme when in

*Electronic address: alex_benik@yahoo.com

an effort to increase its accuracy we use two linearization energies (corresponding to two electron bands). We will demonstrate that the new basis states are of two types. The first group gives the local orbitals in the form suggested by Sing [7]. However, the basis functions of the second type have different form which is not used in the LAPW+LO method. Therefore, the canonical LAPW basis set and also the LAPW+LO basis set can be extended to a more complete basis set. New basis functions and consequences of their introduction are closely examined in the present work.

The paper is organized as follows. We start with revisiting the problem of extended core states which gives rise to the LAPW+LO scheme and formulate our initial statement for the refinement of the LAPW method, Sec. II. In Sec. III we present our method which results in adding tight binding basis functions to the canonical LAPW basis set. In Sec. IV we apply the method to electron band structure calculations of the face centered and body centered lattice of lanthanum and the hexagonal close packed lattice of cadmium. Our conclusions are summarized in Sec. V.

II. THE PROBLEM OF EXTENDED CORE STATES

The LAPW method [3–5] is probably the most precise method for electronic band structure calculations and is widely used for the calculation of material properties [6].

In the LAPW method [3–6] space is partitioned in the region inside the nonoverlapping MT -spheres and the interstitial region I . The basis functions $\phi_n(\vec{k}, \vec{R})$ where $n = 1, 2, \dots, N$ are given by

$$\phi_n(\vec{k}, \vec{R}) = \begin{cases} V^{-1/2} \exp(i(\vec{k} + \vec{K}_n)\vec{R}), & \vec{R} \in I \\ \sum_{l,m} \mathcal{R}_{l,m}^{n,\alpha}(r, E_l) Y_{l,m}(\hat{r}), & \vec{R} \in MT(\alpha) \end{cases} \quad (1)$$

with radial parts

$$\mathcal{R}_{l,m}^{n,\alpha}(r, E_l) = A_{l,m}^{n,\alpha} u_l(r, E_l) + B_{l,m}^{n,\alpha} \dot{u}_l(r, E_l). \quad (2)$$

Here the index α refers to the type of atom (or MT -sphere) in the unit cell, the radius r is counted from the center \vec{R}_α of the sphere α (i.e. $\vec{r} = \vec{R} - \vec{R}_\alpha$), V is the volume of the unit cell. Radial functions $u_{l,m}(r, E_l)$ are solutions of the Schrödinger equation in the spherically averaged crystal potential computed at the linearization energy E_l , and $\dot{u}_l(r, E_l)$ is the derivative of $u_{l,m}$ with respect to E at E_l . The coefficients $A_{l,m}^{n,\alpha}$ and $B_{l,m}^{n,\alpha}$ are found from the condition that the basis function ϕ_n is continuous with continuous derivative at the sphere boundary, $r = R_{MT}^\alpha$ (R_{MT}^α is the radius of the MT -sphere α). In the following for compactness we omit the index α and restore it when needed. Linearization energies E_l are chosen close to average values of corresponding band energies or to the Fermi level. A comprehensive study of the errors due to the linearization procedure, influence of

E_l and LOs on band properties is given in Ref. 8. The extended electron basis states defined by Eq. (1) are orthogonal to the core states. This is a consequence of the relation

$$\int_0^{R_{MT}} \mathcal{U}_v(r) \mathcal{U}_c(r) r^2 dr = \frac{R_{MT}^2}{2(E_c - E_v)} \times \left(\mathcal{U}_c(R_{MT}) \frac{\partial \mathcal{U}_v(R_{MT})}{\partial r} - \mathcal{U}_v(R_{MT}) \frac{\partial \mathcal{U}_c(R_{MT})}{\partial r} \right), \quad (3)$$

applied to a core state with orbital quantum numbers l, m and the radial wave function $\mathcal{U}_c(r)$, and a partial radial function of valence state, $\mathcal{U}_v(r) = \mathcal{R}_{l,m}^{n,\alpha}(r, E_l)$, Eq. (2), with the same angular dependence. Notice that Eq. (3) ensures the orthogonality between the extended and core states if two conditions at the sphere boundary are satisfied for each of the core states,

$$\mathcal{U}_c(R_{MT}) = 0, \quad (4a)$$

$$\frac{\partial \mathcal{U}_c(R_{MT})}{\partial r} = 0. \quad (4b)$$

Although these conditions are met for a great number of cases, they are violated for so called semicore states that are not fully contained in the MT -sphere [7, 9, 10].

Semicore states leaking out of the MT -regions should be treated as extended states. This in turn requires that the linearization energy E_l is chosen near the energy of the semicore level, $E_l \approx E_c$, because the LAPW basis describes only states near E_l well. However, as E_c is quite far from the Fermi energy E_F and the valence band energy, the choice $E_l \approx E_c$ inevitably gives poor description for partial $l = l_c$ valence states. On the other hand, the option $E_l = E_v$ is not satisfactory for the semicore states situated substantially deeper in energy. As discussed in Refs. [7, 10, 12–15] there is no simple solution to this dilemma. Even worse, in many cases the attempt to use a single value of E_l for both valence and semicore states leads to the appearance of so called “ghost bands” [7, 10] giving false band energy positions. As a remedy one can divide the energy spectrum in two windows (energy panels) and use two different sets of E_l for calculations of semicore and valence states, respectively [5]. This technique however is also not fully satisfactory because now there is no single Hamiltonian matrix for the problem and strict orthogonality between electron states belonging to different energy windows is not guaranteed. Ideally, in the MT -region there should be two different types of radial components with the same angular dependence $l = l_c$. That is, in Eq. (1)

$$\mathcal{R}_{l,m}^n(r) = \mathcal{R}_{l,m}^{(1),n}(r) + \mathcal{R}_{l,m}^{(2),n}(r), \quad (5a)$$

where

$$\mathcal{R}_{l,m}^{(1),n}(r, E_l^{(1)}) = A_{l,m}^{(1),n} u_l^{(1)}(r, E_l^{(1)}) + B_{l,m}^{(1),n} \dot{u}_l^{(1)}(r, E_l^{(1)}) \quad (5b)$$

refers to the semicore states with $E_l^{(1)} = E_c$, and

$$\mathcal{R}_{l,m}^{(2),n}(r, E_l^{(2)}) = A_{l,m}^{(2),n} u_l^{(2)}(r, E_l^{(2)}) + B_{l,m}^{(2),n} \dot{u}_l^{(2)}(r, E_l^{(2)}) \quad (5c)$$

refers to the valence states with $E_l^{(2)} = E_v \approx E_F$. Both states, Eqs. (5b) and (5c), should merge to a single l_c wave component of the plane wave

$$\phi_n(\vec{k}, \vec{R}) = V^{-1/2} \exp(i(\vec{k} + \vec{K}_n)\vec{R}) \quad (5d)$$

at the surface of MT sphere. Now, however the boundary problem becomes ill-defined, because for the $l = l_c$ component there are four coefficients, $A_{l,m}^{(1,n)}$, $B_{l,m}^{(1,n)}$, $A_{l,m}^{(2,n)}$ and $B_{l,m}^{(2,n)}$ for only two boundary conditions.

In Ref. [7] Singh has proposed to increase the number of boundary conditions to four by matching the value of the basis function and its first three radial derivatives at the sphere surface. This gives rise to super-linearized APW method denoted as SLAPW-4 [7] because four functions, four coefficients and four boundary conditions are involved. In a simpler super-linearized modification called SLAPW-3 [7] the first radial part $\mathcal{R}_{l,m}^{(1,n)}$, Eq. (5b), is supplemented by only one function $u_l^{(2)}$ (instead of $\mathcal{R}_{l,m}^{(2,n)}$, Eq. (5c)). The three coefficients ($A_{l,m}^{(1,n)}$, $B_{l,m}^{(1,n)}$, $A_{l,m}^{(2,n)}$) are determined by requiring continuity of the basis function and its two derivatives.

In comparison with standard LAPW method in both SLAPW modifications there are additional requirements for the plane wave convergence. Indeed, the plane wave expansion of the interstitial region must converge either to the correct second and third derivative (SLAPW-4) or to the second derivative (SLAPW-3). Because of that more plane waves are needed to satisfy these additional requirements, the plane wave energy cutoff parameter should be increased and calculations become much more costly [7],[5].

To circumvent the problem and improve the LAPW efficiency Singh put forward a third approach based on local orbitals (LAPW+LO) [7]. In the LAPW+LO approach the same three radial functions as in SLAPW-3 are used (i.e. $u_l^{(1)}$, $\dot{u}_l^{(1)}$ and $u_l^{(2)}$), but the coefficient of $u_l^{(2)}$ is fixed (say, $A_{l,m}^{(2,n)} = 1$) and the two remaining coefficients ($A_{l,m}^{(1,n)}$, $B_{l,m}^{(1,n)}$) are found from the conditions that the local orbital goes to zero with zero derivative at the sphere boundary. Nowadays, LAPW+LO is widely used for band structure calculations of solids with semicore states [5, 6]. However, conceptually the LAPW+LO method is understood as a procedure giving additional variational freedom through an increase of the number of basis functions.

Inspired by the LAPW+LO method [7] in the present study we formulate a more general approach to the problem. Unlike the LAPW+LO approach we will derive supplemented basis states from the initial requirement that two different radial functions (i.e. $\mathcal{R}_{l,m}^{(1,n)}$ and $\mathcal{R}_{l,m}^{(2,n)}$, Eqs. (5b), (5c)), having the same angular part merge in a single plane wave function ϕ_n , Eq. (5d), in the interstitial region. Unlike SLAPW-4 or SLAPW-3 we retain only two joining conditions across the MT -sphere boundary. As a result, we will obtain two types of supplementary

tight-binding basis functions (see Eqs. (15b) and (15c) below), satisfying Bloch's theorem.

III. DESCRIPTION OF THE METHOD

As discussed in Sec. II, in the case of semicore states we have two types of radial solutions in the MT-region with the same angular dependence $Y_{l,m}(\hat{r})$ but different linearization energies $E_l^{(1)}$ and $E_l^{(2)}$: $\mathcal{R}_{l,m}^{(1,n)}(r, E_l^{(1)})$, Eq. (5b), and $\mathcal{R}_{l,m}^{(2,n)}(r, E_l^{(2)})$, Eq. (5c). One of the radial functions can refer to extended states, i.e. $R_e(r) = \mathcal{R}_{l,m}^{(1,n)}(r, E_l^{(1)})$, while the other can refer to supplementary angular states $R_s(r) = \mathcal{R}_{l,m}^{(2,n)}(r, E_l^{(2)})$. As we will see later in Sec. IV in practice we describe the semicore states as extended states with $E_l = E_{core}$ and valence states with the same l as supplementary states for which $E_l = E_v$. (For metals one can take $E_l = E_v \approx E_F$.) Since in the interstitial I -region both types of solutions are represented by the plane wave function $\phi_n(\vec{k}, \vec{R})$, Eq. (5d), they become indistinguishable there. In the LAPW method there are two matching conditions (for the function and its derivative) on the sphere boundary. Therefore, in our case we have

$$A_e u_e + B_e \dot{u}_e + A_s u_s + B_s \dot{u}_s = \frac{4\pi}{\sqrt{V}} i^l j_l(k_n R_{MT}) Y_{l,m}^*(\hat{k}_n) e^{i\vec{k}_n \vec{R}_\alpha}, \quad (6a)$$

$$A_e u'_e + B_e \dot{u}'_e + A_s u'_s + B_s \dot{u}'_s = \frac{4\pi}{\sqrt{V}} i^l j'_l(k_n R_{MT}) Y_{l,m}^*(\hat{k}_n) e^{i\vec{k}_n \vec{R}_\alpha}. \quad (6b)$$

Here we adopt short notations $A_e = A_{l,m}^{(1,n)}$, $A_s = A_{l,m}^{(2,n)}$, $u_e = u_l^{(1)}(R_{MT}, E_l^{(1)})$, $u_s = u_l^{(2)}(R_{MT}, E_l^{(2)})$, $u'_e = \partial u_l^{(1)}(R_{MT}, E_l^{(1)})/\partial r$, $u'_s = \partial u_l^{(2)}(R_{MT}, E_l^{(2)})/\partial r$, and have used the Rayleigh expansion of the plane wave ϕ_n on the sphere surface. Since there are four coefficients (A_e , B_e , A_s and B_s) and only two equations, it is clear that the general solution to Eqs. (6a), (6b), forms a two dimensional linear space with two linear independent basis vectors.

Further, introducing standard LAPW quantities $a_e = a_l^{(1,n)}$, $b_e = b_l^{(1,n)}$, where

$$A_e = \frac{4\pi}{\sqrt{V}} i^l R_{MT}^2 Y_{l,m}^*(\hat{k}_n) e^{i\vec{k}_n \vec{R}_\alpha} a_e, \quad (7a)$$

$$B_e = \frac{4\pi}{\sqrt{V}} i^l R_{MT}^2 Y_{l,m}^*(\hat{k}_n) e^{i\vec{k}_n \vec{R}_\alpha} b_e. \quad (7b)$$

and analogous relations for a_s , b_s , we rewrite Eqs. (6a), (6b) as

$$a_e u_e + b_e \dot{u}_e + a_s u_s + b_s \dot{u}_s = j_l(k_n R_{MT}) \frac{1}{R_{MT}^2}, \quad (8a)$$

$$a_e u'_e + b_e \dot{u}'_e + a_s u'_s + b_s \dot{u}'_s = j'_l(k_n R_{MT}) \frac{1}{R_{MT}^2}. \quad (8b)$$

Notice that the standard LAPW solution for $a_e = a_e^0$ and $b_e = b_e^0$ without supplementary states, i.e. when $a_s = b_s = 0$, can be found from the following system

$$a_e^0 u_e + b_e^0 \dot{u}_e = j_l(k_n R_{MT}) \frac{1}{R_{MT}^2}, \quad (9a)$$

$$a_e^0 u'_e + b_e^0 \dot{u}'_e = j'_l(k_n R_{MT}) \frac{1}{R_{MT}^2}. \quad (9b)$$

Defining auxiliary quantities t_a and t_b

$$t_a = a_e - a_e^0, \quad (10a)$$

$$t_b = b_e - b_e^0. \quad (10b)$$

and subtracting Eq. (9a) from Eq. (8a), and Eq. (9b) from Eq. (8b) we arrive at

$$t_a u_e + t_b \dot{u}_e + a_s u_s + b_s \dot{u}_s = 0, \quad (11a)$$

$$t_a u'_e + t_b \dot{u}'_e + a_s u'_s + b_s \dot{u}'_s = 0. \quad (11b)$$

The solution to Eqs. (11a), (11b) can be found from the following two systems,

$$\begin{cases} a_{s,1} u_s + b_{s,1} \dot{u}_s = -u_e \\ a_{s,1} u'_s + b_{s,1} \dot{u}'_s = -u'_e \end{cases}, \quad (12a)$$

$$\begin{cases} a_{s,2} u_s + b_{s,2} \dot{u}_s = -\dot{u}_e \\ a_{s,2} u'_s + b_{s,2} \dot{u}'_s = -\dot{u}'_e \end{cases}. \quad (12b)$$

Solutions to the systems (12a) and (12b) are quoted explicitly in Appendix A, Eqs. (A1a)-(A2b). Having found $a_{s,i}$ and $b_{s,i}$ ($i = 1, 2$), we write the general solution to Eqs. (8a), (8b) as

$$a_e = a_e^0 + t_a, \quad (13a)$$

$$b_e = b_e^0 + t_b, \quad (13b)$$

$$a_s = t_a a_{s,1} + t_b a_{s,2}, \quad (13c)$$

$$b_s = t_a b_{s,1} + t_b b_{s,2}, \quad (13d)$$

where t_a and t_b are arbitrary numbers. The full radial component $\mathcal{R}_{l,m}^n(r)$ of the basis function inside the MT -sphere α , Eq. (5a), is written as

$$\mathcal{R}_{l,m}^n(r) \sim a_e^0 u_e + b_e^0 \dot{u}_e + t_a (u_e + a_{s,1} u_s + b_{s,1} \dot{u}_s) + t_b (\dot{u}_e + a_{s,2} u_s + b_{s,2} \dot{u}_s). \quad (14)$$

(Here notations $u_e = u_e(r)$, $u_s = u_s(r)$ etc. refer to radial functions.)

Notice that since the coefficients t_a and t_b are arbitrary, they should be found from the standard variational procedure by requiring the minimization of the LAPW ground state energy. Furthermore, the form (14) suggests considering three linear independent radial parts (i.e. $R_{l,m}^e(r)$, $R_{l,m}^{s,1}(r)$, $R_{l,m}^{s,2}(r)$) instead of the single function $\mathcal{R}_{l,m}^n(r) = R_{l,m}^e(r) + t_a R_{l,m}^{s,1}(r) + t_b R_{l,m}^{s,2}(r)$. Explicitly,

$$R_{l,m}^e(r) = C_n e^{i\vec{k}_n \cdot \vec{R}_\alpha} (a_e^0 u_e + b_e^0 \dot{u}_e), \quad (15a)$$

$$R_{l,m}^{s,1}(r) = C_n e^{i\vec{k}_n \cdot \vec{R}_\alpha} (u_e + a_{s,1} u_s + b_{s,1} \dot{u}_s), \quad (15b)$$

$$R_{l,m}^{s,2}(r) = C_n e^{i\vec{k}_n \cdot \vec{R}_\alpha} (\dot{u}_e + a_{s,2} u_s + b_{s,2} \dot{u}_s). \quad (15c)$$

Here $u_e = u_e(r)$, $u_s = u_s(r)$ etc. are corresponding radial functions and

$$C_n = \frac{4\pi}{\sqrt{V}} i^l R_{MT}^2 Y_{l,m}^*(\hat{k}_n). \quad (16)$$

The first function, Eq. (15a), is in fact the standard radial part of the l -type, $R_{l,m}^e = \mathcal{R}_{l,m}^{n,\alpha}$, Eq. (2), entering the usual LAPW basis function $\phi_n(\vec{k}, \vec{R})$, Eq. (1). Its coefficients a_e^0 and b_e^0 are given by the LAPW boundary relations, Eqs. (9a), (9b). Two other functions however are very different from $\phi_n(\vec{k}, \vec{R})$ and should be included to the LAPW basis set as extra basis states,

$$\phi_{s,i}(\vec{k}, \vec{R}) = Y_{l,m}^m(\hat{r}) R_{l,m}^{s,i}(r), \quad (17)$$

where $i = 1, 2$. The important thing is that their coefficients $a_{s,1}$, $b_{s,1}$ are found from Eq. (12a), while coefficients $a_{s,2}$, $b_{s,2}$ from Eq. (12b). With respect to the two new functions $R_{l,m}^{s,i}$, Eqs. (12a), (12b) impose the following boundary conditions

$$R_{l,m}^{s,i}(r) = 0, \quad (18a)$$

$$\frac{\partial R_{l,m}^{s,i}(r)}{\partial r} = 0. \quad (18b)$$

These relations have a simple interpretation: new supplementary basis functions $\phi_{s,i}(\vec{k}, \vec{R})$ are required to be orthogonal to the standard LAPW radial functions. We want to stress here, that the conditions (18a) and (18b) are not assumed or imposed by us. They are derived from the initial equations (6a), (6b) [or equivalently from Eqs. (8a), (8b)] and are used to obtain the general solution, Eqs. (13a)-(13d).

From Eq. (15b), (15c) and (16) it follows that the supplementary basis states in principle depend on the index n , i.e. $\phi_{s,i}(\vec{k}, \vec{R}) = \phi_{s,i}(\vec{k}_n, \vec{R})$. (We recall that $\vec{k}_n = \vec{k} + \vec{K}_n$, where \vec{K}_n is a vector of the reciprocal lattice.) However, since all functions $\phi_{s,i}(\vec{k}_n, \vec{R})$ with different index n have the same radial part, $\mathcal{U}^{s,1}(r) = u_e + a_{s,1} u_s + b_{s,1} \dot{u}_s$ for $i = 1$, or $\mathcal{U}^{s,2}(r) = \dot{u}_e + a_{s,2} u_s + b_{s,2} \dot{u}_s$ for $i = 2$, they are simply proportional to each other, $\phi_{s,i}(\vec{k}_n, \vec{R}) \sim \phi_{s,i}(\vec{k}_{n'}, \vec{R})$. Therefore, to avoid the linear dependence we should choose only one set of functions $\phi_{s,i}(\vec{k}_n, \vec{R})$ corresponding to a single index n . The obvious choice is to use the function $\phi_{s,i}(\vec{k}, \vec{R})$ with $n = 0$, $\vec{k}_0 = \vec{k}$ and the reciprocal lattice vector $\vec{K}_0 = 0$. In that case the coefficient $C_0 = \pi/V i^l R_{MT}^2 Y_{l,m}^*(\hat{k})$ [compare with Eq. (16)] can be further rationalized by omitting the multiplier $Y_{l,m}^*(\hat{k})$ [or equivalently, including it in factors t_a and t_b , Eq. (10a), (10b)]. Thus, we substitute C_0 with

$$C_0 = \frac{4\pi}{\sqrt{V}} i^l R_{MT}^2. \quad (19)$$

(In principle, since the local function is not orthonormal, we can simply put $C_0 = 1$, but the form (19) being similar

to the constant coefficient for the standard LAPW basis function simplifies some expressions for programming.) To study the transformational properties of supplementary basis functions $\phi_{s,i}(\vec{k}, \vec{R})$, Eq. (17), we first rewrite them in the following form,

$$\phi_{s,i}(\vec{k}, \vec{R}) = e^{i\vec{k}\vec{R}_\alpha} \psi_i^{l,m}(\vec{R} - \vec{R}_\alpha), \quad (20)$$

where for each site α we have introduced two local functions ($i = 1, 2$) of the l, m -type,

$$\psi_i^{l,m}(\vec{R} - \vec{R}_\alpha) = C_0 U^{s,i}(r) Y_l^m(\hat{r}). \quad (21)$$

Notice that each local function $\psi_i^{l,m}(\vec{R} - \vec{R}_\alpha)$ is strictly confined inside the MT -sphere α , because both $U^{s,i}(r)$ and $Y_l^m(\hat{r})$ satisfy the boundary conditions (18a), (18b). We can then extend the function $\phi_{s,i}(\vec{k}, \vec{R})$ to the interstitial region ($\vec{R} \in I$) by requiring $\phi_{s,i}(\vec{k}, \vec{R}) = 0$. For the whole crystal we thus have

$$\begin{aligned} \phi_{s,i}(\vec{k}, \vec{R}) &= \sum_\alpha e^{i\vec{k}\vec{R}_\alpha} \psi_i^{l,m}(\vec{R} - \vec{R}_\alpha), \quad \vec{R} \in MT, \\ \phi_{s,i}(\vec{k}, \vec{R}) &= 0, \quad \vec{R} \in I. \end{aligned} \quad (22)$$

This is a clear manifestation of the tight binding wave function. The multiplier $e^{i\vec{k}\vec{R}_\alpha}$ in Eqs. (22) and (20) ensures that the supplementary wave functions $\phi_{s,i}(\vec{k}, \vec{R})$ obey the Bloch theorem. It is worth noting that usually the tight-binding description is spoiled by the presence of overlap between tails of wave function centered at neighboring sites. In the present method the tight-binding functions, Eqs. (22) and (20), are free from this disadvantage because the local functions (and their first derivatives) go to zero at the sphere boundary and the overlap is absent. Thus, supplementary tight-binding functions can be considered as additional basis states orthogonal to the standard LAPW basis set.

All matrix elements between the supplementary basis functions $\phi_{s,i}$ in the spherically symmetric potential are quoted explicitly in Appendix B, and all matrix elements between $\phi_{s,i}$ and standard LAPW basis functions ϕ_n are listed in Appendix C. For brevity we do not quote here the partial charges and electron density associated with supplementary basis states. They are tightly connected with the overlap matrix elements given by Eqs. (B2a), (B4a) and (B5a) of Appendix B, and Eqs. (C2a), (C3a) of Appendix C. Concerning the full potential expressions for the extended basis set it is worth noting that after some algebraic transformations the equations can be obtained by selecting in standard FLAPW equations the contributions with the orbital indices l, m referring to the components of supplemented states and combining them together according to Eqs. (15b), (15c), (17).

The tight binding basis functions have a very important and practical property: they work even in the case when their expansion energy E_s lies not far from the LAPW linear expansion energy E_e . (We recall that the whole procedure is designed to treat the complicated case of semicore states when E_s is supposed to be separated

from E_e by at least 10 eV.) The limiting case $E_s \approx E_e$ is considered in detail in Appendix D, and also discussed in calculations of Cd in Sec. IV C.

IV. PRACTICAL IMPLEMENTATION

A. Face centered cubic structure of La

We have applied the method developed in Sec. III to full potential electron band structure calculations of face centered cubic (fcc) structure of lanthanum. A thorough account of band structure calculations of bcc, fcc, hcp, and double hcp structures of lanthanum for pressures up to 35 GPa is given in Ref. 16.

Atomic lanthanum has completely filled $5p$ semicore electron shell lying at -22.12 eV which can slightly mix with valence states ($5d, 6s, 4f$) at energies from -3 to -2 eV. For lanthanum here and below we use the Perdew-Burke-Ernzerhof (PBE) [17] variant of the generalized gradient approximation (GGA) which gives rather accurate lattice constants for our systems.

We have employed our original version of LAPW code with the potential of general form [18]. Integration in the irreducible part of the Brillouin zone has been performed over 240 special points. Angular expansions for the electron density and wave function inside MT -sphere have been done up to $L_{max} = 8$. The number of standard basis functions has been limited by conditions $R_{MT}K_{max} = 7, 7.5, 8, 9$ and 10 , resulting in 27, 51, 59, 65 and 113 basis states, respectively. In addition to the standard LAPW basis functions we have considered 6 supplementary tight binding basis functions with the p -angular dependence, which are located strictly inside the MT -sphere, Sec. III.

The $5p$ semicore states have been treated as band states with the LAPW linear expansion energy E_e lying 0.5 eV above the p -band bottom energy. The linear expansion energy for supplementary tight binding p -states has been fixed at 1 eV below the Fermi energy. For $a = 5.315 \text{ \AA}$, $R_{MT}K_{max} = 9$ two supplementary radial functions shown in Fig. 1 are given by

$$R_1(r) = u_e(r) + a_{s,1}u_s(r) + b_{s,1}\dot{u}_s(r), \quad (23a)$$

where $a_{s,1} = 0.1940$, $b_{s,1} = 0.4041$, and

$$R_2(r) = \dot{u}_e(r) + a_{s,2}u_s(r) + b_{s,2}\dot{u}_s(r), \quad (23b)$$

where $a_{s,2} = -1.9609$, $b_{s,2} = 1.0705$. Notice that the number of nodes for both radial functions is three (excluding points with $r = 0$ and $r = R_{MT}$) which allows us to consider these functions as ‘‘compressed’’ $5p$ basis states (i.e. with the principal quantum number $n = 5$) strictly confined within MT -sphere.

To compare our treatment with the standard (LAPW+LO) method which uses only the first local function $R_1(r)$, Eq. (23a), we have performed a series of calculations, the results of which are given in Tables I – IV. In the following in all Tables for brevity we

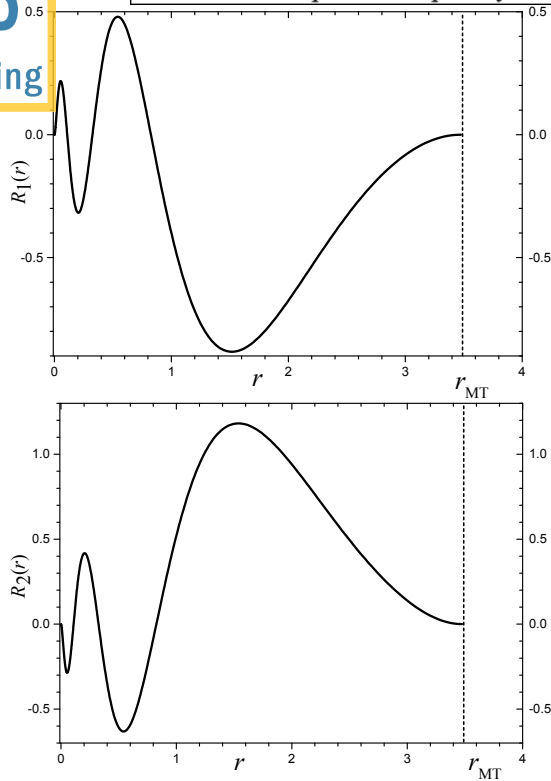


FIG. 1: Two supplemented tight binding radial functions of p -type for fcc structure of lanthanum. Radius is given in atomic units, $r_{MT} = 3.474$ a.u. stands for the MT radius.

TABLE I: Total energy of fcc-La (E_{tot} , in eV) for various basis sets relative to the FLAPW++ value for $R_{MT}K_{max} = 10$. $\Delta E = E_{tot}(\text{FLAPW++}) - E_{tot}(\text{FLAPW+LO})$, $a = 5.315$ Å.

$R_{MT} \cdot K_{max}$	FLAPW++	FLAPW+LO	ΔE
7.0	0.8996	1.0442	-0.1446
7.5	0.3592	0.4144	-0.0552
8.0	0.0512	0.0573	-0.0061
9.0	0.0239	0.0275	-0.0036
10.0	0	0.0013	-0.0013

TABLE II: Energy band parameters of fcc-La (in eV) for various basis sets with respect to E_F (E_{bot} is the energy bottom, E_{top} is the energy top, $a = 5.315$ Å.)

$R_{MT}K_{max}$	semicore 5 p -band		valence (spd)-band	
	E_{bot}	E_{top}	E_{bot}	
FLAPW++	7.0	-17.3952	-16.1301	-3.4343
	7.5	-17.2053	-15.8976	-3.3055
	8.0	-17.1110	-15.7456	-3.2730
	9.0	-17.0981	-15.7306	-3.2699
	10.0	-17.0885	-15.7165	-3.2669
FLAPW+LO	7.0	-17.3367	-16.0786	-3.4659
	7.5	-17.1712	-15.8675	-3.3216
	8.0	-17.1042	-15.7368	-3.2783
	9.0	-17.0935	-15.7245	-3.2737
	10.0	-17.0870	-15.7143	-3.2687

TABLE III: Energy band spectrum (in eV) of fcc-La at the Γ -point of the Brillouin zone with respect to E_F . ($R_{MT} \cdot K_{max} = 9$, $a = 5.315$ Å, deg. stands for the energy degeneracy).

band	deg.	FLAPW++	FLAPW+LO
1	(3)	-15.7306	-15.7245
2		-3.2699	-3.2737
3		1.4435	1.4563
4	(3)	1.5119	1.5108

will use the notation FLAPW++ for the present scheme (FLAPW + 2STBFs) with two radial functions.

Since in FLAPW++ there are more basis states than in FLAPW+LO, for a given lattice constant the present method gives lower values of the total energy in all cases, Table I. However, the total energy difference which amounts to 0.145 eV for the poor basis set ($R_{MT}K_{max} = 7$), becomes smaller for the intermediate basis sets and decreases to a very small value ($1.3 \cdot 10^{-3}$ eV) for the best basis set ($R_{MT}K_{max} = 10$). Energy band characteristics shown in Table II also demonstrate that the difference between FLAPW++ and FLAPW+LO methods decreases with basis set quality. Although the band energy mismatch is almost negligible ($\sim 10^{-3}$ eV) for the $R_{MT}K_{max} = 10$ basis set, it remains noticeable for other sets. In particular, the $R_{MT}K_{max} = 9$ basis leads to band energy differences of the order of $5 \cdot 10^{-3}$ eV, Tables II, III. Notice also that the FLAPW++ method gives lower band energies for all semicore p -states. We will discuss this issue in more detail for bcc-La in the next section (see Fig. 2).

Our main results are summarized in Table IV. Bulk moduli were obtained from the best fit to a Murnaghan equation [22]. The density of states was calculated by the tetrahedron method [23], using the MT radius and the set of k -points used for total energy calculations. Notice that equilibrium lattice constants, bulk modulus and $N(E_F)$ become identical for FLAPW++ and FLAPW+LO with $R_{MT}K_{max} = 10$ basis set. For other basis sets the FLAPW++ method gives better estimations with respect to the $R_{MT}K_{max} = 10$ reference data. The equilibrium lattice constant for the best basis set, 5.325 Å, lies between values calculated by Nixon et al. [16] and Gao et al. [20], and only slightly (0.28 %) overestimates the experimental value. It is worth noting that our FLAPW+LO calculation with the $R_{MT}K_{max} = 9$ basis set gives the lattice constant and $N(E_F)$, which are very close to PW GGA data of Nixon et al. [16], Table IV.

The CPU time spent by our code for various FLAPW++ and FLAPW+LO runs is quoted in Table V. The time difference between the two schemes is very small.

TABLE V: Calculated and experimental lattice constants, bulk moduli (B) and density of states at the Fermi energy ($N(E_F)$, in states/eV) of fcc lanthanum. (LMTO denotes linearized muffin-tin-orbital method, PW denotes the Perdew-Wang version of GGA, and PP denotes the pseudopotential plane-wave calculations with the ultrasoft Vanderbilt pseudopotential.)

	$R_{MT} \cdot K_{max}$	a (Å)	B (GPa)	$N(E_F)$
FLAPW++	8.0	5.287	28.1	2.19
	9.0	5.315	27.5	2.25
	10.0	5.325	26.5	2.27
FLAPW+LO	8.0	5.283	29.9	2.17
	9.0	5.309	25.7	2.23
	10.0	5.325	26.5	2.27
LMTO PW ^a		5.186	27.5	
PP PBE ^b		5.344	26.6	
FLAPW PW ^c	9.0	5.308	24.8	2.23
Expt. ^d		5.310±0.008	24.8±0.7	

^aReference [19], basis set: semicore 5p + valence 6s, 6p, 5d, 4f

^bReference [20], kinetic energy cut-off of 50 Ryd

^cReference [16], 5p states in valence

^dReference [21]

TABLE V: CPU time per self-consistent-field iteration (in sec) for various calculations of La and Cd with the Intel(R) Pentium(R) CPU G2030 3.00GHz processor (without core adjustments).

	$R_{MT} \cdot K_{max}$	FLAPW+LO	FLAPW++
fcc-La	7.5	23.794	24.088
	8.0	31.464	31.788
	9.0	38.111	38.442
	10.0	113.583	114.346
bcc-La	7.0	20.615	20.832
	8.0	32.432	32.732
	9.0	65.996	66.520
	10.0	193.721	195.025
hcp-Cd	7.0	94.065	94.882
	8.0	294.585	295.589
	9.0	435.415	437.304

B. Body centered cubic structure of La

In literature there are several theoretical studies of the body centered cubic (bcc) electronic structure of lanthanum (see Ref. 16 and references therein) performed within the local density approximation (LDA) but to the best of our knowledge there is only one [16] using GGA for exchange and correlation.

In our calculations of the bcc phase of lanthanum we have used a plane wave cut off parameter $R_{MT}K_{max} = 7, 8, 9, 10$, selecting 43, 55, 79, 135 basis states, respectively, plus 6 additional tight binding p -states, $L_{max} = 8$ for the expansion of the electron density and wave functions inside MT-spheres ($R_{MT} = 3.355$ a.u.) and 285 special points in the irreducible part of the Brillouin zone during the self-consistent procedure.

TABLE VI: Total energy of bcc-La (E_{tot} , in eV) for various basis sets relative to the FLAPW++ value for $R_{MT}K_{max} = 10$. $\Delta E = E_{tot}(\text{FLAPW++}) - E_{tot}(\text{FLAPW+LO})$, $a = 4.243$ Å.

$R_{MT} \cdot K_{max}$	FLAPW++	FLAPW+LO	ΔE
7.0	0.6557	0.7350	-0.0793
8.0	0.1156	0.1295	-0.0139
9.0	0.0149	0.0178	-0.0029
10.0	0	0.0009	-0.0009

TABLE VII: Energy band parameters of bcc-La (in eV) for various basis sets with respect to E_F (E_{bot} is the energy bottom, E_{top} is the energy top, $a = 4.243$ Å).

$R_{MT}K_{max}$	semicore 5p-band		valence (spd)-band	
	E_{bot}	E_{top}	E_{bot}	
FLAPW++	7	-17.3306	-16.1153	-3.4144
	8	-17.1372	-15.8569	-3.3107
	9	-17.1100	-15.8161	-3.2980
	10	-17.1038	-15.8075	-3.2969
FLAPW+LO	7	-17.2854	-16.0716	-3.4301
	8	-17.1232	-15.8405	-3.3170
	9	-17.1055	-15.8104	-3.3002
	10	-17.1024	-15.8055	-3.2980

As for fcc-La the LAPW linear expansion energy for the extended p -states of bcc-La has been chosen at 0.5 eV above the p -band bottom energy. The linear expansion energy for the supplemented tight binding p -states has been fixed at 1.0 eV below the Fermi energy. Two supplemented radial functions, quoted in Eqs. (23a) and (23b), are defined by the coefficients $a_{s,1} = 0.1502$, $b_{s,1} = 0.4844$ for $R_1(r)$, and $a_{s,2} = -1.8251$, $b_{s,2} = 0.7718$ for $R_2(r)$ (for $a = 4.243$ Å).

The results of the present and LAPW+LO approaches are compared in Tables VI – IX.

As for fcc-La, the present treatment having more basis functions gives lower values of total energy of bcc-La for all basis sets. The total energy difference increases steeply with worsening of the basis quality, Table VI. For the best basis set ($R_{MT} \cdot K_{max} = 10$) the energy band mismatch is rather small, $\sim 10^{-3}$ eV. From Tables VII, VIII it follows that the FLAPW++ method gives lower energies for the semicore p -states, which appar-

TABLE VIII: Energy band spectrum (in eV) of bcc-La at the Γ -point of the Brillouin zone with respect to E_F . ($R_{MT} \cdot K_{max} = 9$, $a = 4.243$ Å).

band	deg.	FLAPW++	FLAPW+LO
1	(3)	-15.8161	-15.8104
2		-3.2980	-3.3002
3	(3)	1.4884	1.4881
4	(3)	1.6492	1.6620

TABLE IX: Calculated and experimental lattice constants, bulk moduli (B) and density of states at the Fermi energy ($N(E_F)$, in states/eV) of bcc lanthanum. (PW denotes the Perdew-Wang version of GGA.)

	$R_{MT}K_{max}$	a (Å)	B (GPa)	$N(E_F)$
FLAPW++	8.0	4.190	33.5	4.22
	9.0	4.243	25.8	4.30
	10.0	4.245	27.8	4.30
FLAPW+LO	8.0	4.183	34.4	4.19
	9.0	4.241	25.5	4.29
	10.0	4.245	27.9	4.30
FLAPW PW ^a	9.0	4.239	27.02	
Expt. ^b		4.25	29.7	

^aReference [16], 5p states in valence

^bReference [24]

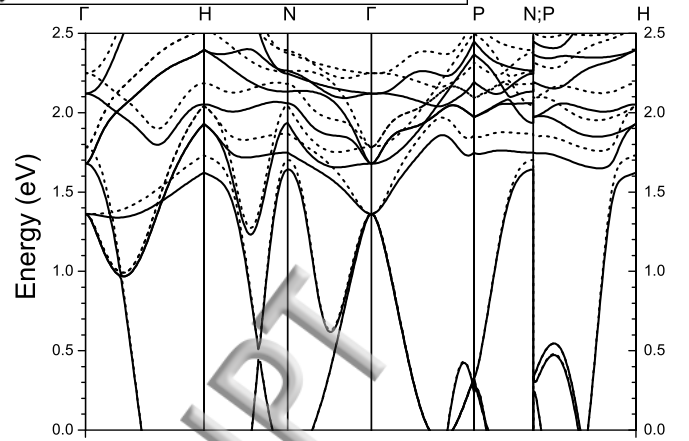
TABLE X: Calculated total energy difference between bcc and fcc La structures, $\Delta E(\text{bcc-fcc}) = E_{tot}(\text{bcc}) - E_{tot}(\text{fcc})$, in eV, for various basis sets ($R_{MT} = 3.355$ a.u. for both structures).

$R_{MT}K_{max}$	FLAPW++	FLAPW+LO
8	0.1564	0.1616
9	0.1042	0.1031
10	0.1210	0.1208

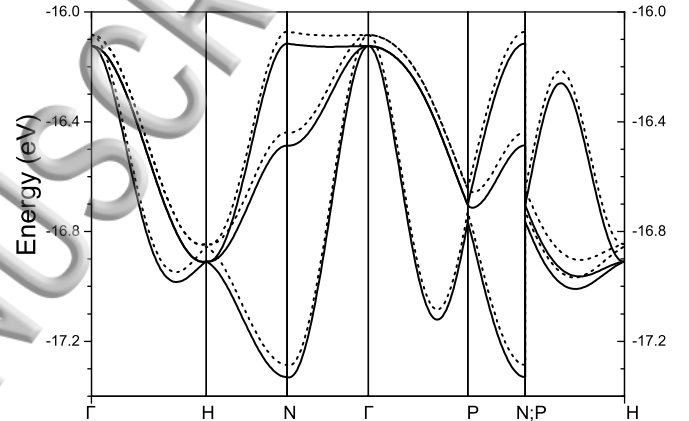
ently leads to lowering of the total energy. This conclusion is further illustrated by Fig. 2 where band energies of FLAPW++ and FLAPW+LO are shown in two energy panels, for the three occupied semicore p -states and unoccupied states above the Fermi level, where the energy difference is visible. Fig. 2 is obtained with the $R_{MT} \cdot K_{max} = 7$ basis set, when the energy shifts are maximal. Clearly, the bands having an appreciable admixture of p -states are affected the most due to a hybridization with additional p -type basis functions. The occupied bands which are not shown in Fig. 2 remain almost the same for the FLAPW+LO and FLAPW++ basis sets.

The main results are summarized in Table IX. Notice that the FLAPW++ and FLAPW+LO data practically coincide for the $R_{MT} \cdot K_{max} = 10$ basis set. For fewer basis functions FLAPW++ gives equilibrium lattice constants which lie closer to the converged value of 4.245 Å. The lattice constant of the best basis set is in very good agreement with experiment [24], and the PW GGA calculation of Nixon et al. [16]. Our best bulk modulus is about 6.4 % below the experimental value of 29.7 GPa, estimated from the elastic constants at 1163 K [24].

It is worth noticing that the total energy of bcc-La is higher the total energy of fcc-La. The energy difference for various basis sets and the same MT radius is quoted in Table X. From Table X we see that $\Delta E(\text{bcc-fcc})$ changes nonmonotonically reaching 0.12 eV for the best sets. This result is in agreement with the calculation of Nixon et al. [16] (~ 0.13 eV from Fig. 2). Experimentally, $\Delta E(\text{bcc-}$



(a)



(b)

FIG. 2: Energy shifts of electron bands of bcc γ -La along high symmetry lines of the Brillouin zone (solid lines stand for FLAPW++, dashed lines for FLAPW+LO). (a) above the Fermi level ($E_F = 0$), (b) semicore (5p) band.

fcc) is estimated to be 1138 K ≈ 0.1 eV, because at normal pressure γ -La exists only at high temperatures (>1138 K) in a narrow temperature range (53 K) [24].

C. Hexagonal close packed structure of Cd

Hexagonal close packed (hcp) cadmium is a special case because its $4d$ -states are not separated from the valence $5s$ -states by an energy gap, Fig. 3. In principle, the band structure of cadmium can be performed without local d -orbitals, but in that case the accuracy is poor [8]. The linear expansion energy of d -states was chosen at 0.5 eV above the band bottom energy for extended states, and at 1.0 eV below the Fermi energy for the supplemented d -states. In that case the energy difference $E_s(d) - E_e(d) \sim 8.5$ eV is a relatively small value, and we test the scenario described in Appendix D. (Two supplementary radial functions, Eqs. (23a) and (23b), are specified by the coefficients $a_{s,1} = -0.3448$, $b_{s,1} = 0.4643$

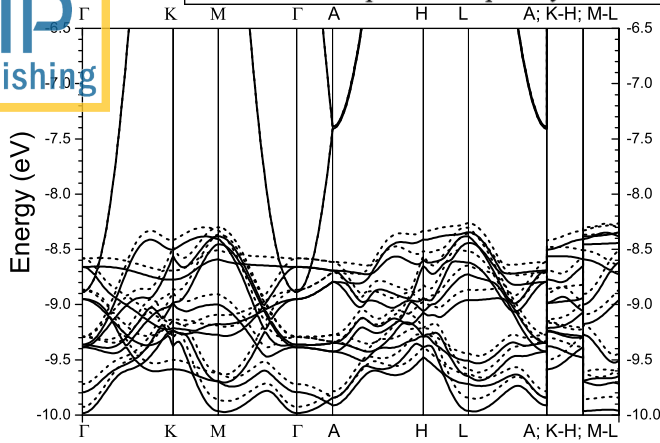


FIG. 3: (a) Energy shifts of $4d$ -electron bands of hexagonal close packed Cd along high symmetry lines of the Brillouin zone (solid lines stands for FLAPW++, dashed lines for FLAPW+LO, $E_F = 0$).

for $R_1(r)$ and $a_{s,2} = -1.9343$, $b_{s,2} = -0.2952$ for $R_2(r)$.)

The technical parameters of FLAPW calculations were the following: the best basis set was defined by the cut off parameter $R_{MT}K_{max} = 10$ (247 basis states and supplemented tight binding d -states), $L_{max} = 6$ for the expansion of electron density and $L_{max} = 10$ for wave functions inside the MT-spheres with the radius $R_{MT} = 2.74$ a.u., 125 (or 75) special points in the irreducible part of the Brillouin zone during the self-consistent procedure, and the PBE [17] form of the exchange correlation potential.

From the equation of states obtained with the best basis set ($R_{MT}K_{max} = 10$) we have found the equilibrium volume $V_{eq} = 23.008 \text{ \AA}^3$ and the bulk modulus $B = 41.53$ GPa. These numbers compares well with the benchmark calculations of various codes [25], giving $V_{eq} = 22.584 - 22.980 \text{ \AA}^3$ and $B = 42.213 - 44.082$ GPa. (A small difference is probably accounted for by a relatively coarse grid of k -points used in our calculations.) However, at this level of basis sets the difference between FLAPW++ and FLAPW+LO is negligible. Therefore, we have also performed the equation of state calculations with the $R_{MT}K_{max} = 9$ basis set and obtained 22.270 \AA^3 ($a = 3.051$, $c = 5.525 \text{ \AA}$) for FLAPW++ and 22.232 \AA^3 ($a = 3.045$, $c = 5.537 \text{ \AA}$) for FLAPW+LO. Thus, with respect to the benchmark volumes and our calculation with the $R_{MT}K_{max} = 10$ basis set, this FLAPW++ calculation perform slightly better (0.17 %) than FLAPW+LO.

Comparison between the present approach and the LAPW+LO treatment at experimental lattice constants ($a_{exp} = 2.9794 \text{ \AA}$ and $c_{exp} = 5.6186 \text{ \AA}$ [26]) is presented in Tables XI, XII and XIII. For all basis sets the present approach gives lower total energy values, Table XI. Notice, that the main effect of additional basis functions of FLAPW++ is lowering of low lying bands of d -type. This results in downward shifts of E_{bot} in Table XII and of low lying d -bands at the Γ -point of the Brillouin zone, Table XIII. At the Γ -point the shift of d -bands (num-

TABLE XI: Total energy of hcp-Cd (E_{tot} , in eV) for various basis sets relative to the FLAPW++ value for $R_{MT}K_{max} = 9$ at a_{exp} , c_{exp} . $\Delta E = E_{tot}(\text{FLAPW++}) - E_{tot}(\text{FLAPW+LO})$.

$R_{MT}K_{max}$	FLAPW++	FLAPW+LO	ΔE
7	2.9676	3.2418	-0.2742
7.5	1.0553	1.1169	-0.0616
8	0.2455	0.2752	-0.0297
8.6	0.1479	0.1678	-0.0199
9	0.0840	0.0935	-0.0095
10	0	0.0023	-0.0023

TABLE XII: Energy bottom of hcp-Cd (in eV) for various basis sets with respect to E_F .

$R_{MT}K_{max}$	FLAPW++	FLAPW+LO
7	-9.9798	-9.9246
7.5	-9.9898	-9.9634
8	-9.8981	-9.8791
8.6	-9.8833	-9.8681
9	-9.8701	-9.8605
10	-9.8595	-9.8557

bered as 1, 2, 3, 4, 6 and 7 in Table XIII) amounts to $\sim 0.008 - 0.012$ eV while the energy shift of s -bands is an order of magnitude smaller, $\sim 0.0004 - 0.002$ eV. The shifts are visualized in Fig. 3, where the d -bands of Cd are shown for FLAPW++ and FLAPW+LO with the $R_{MT}K_{max} = 7$ basis set. It is worth noting that for fcc-La, Sec. IV A, and bcc-La, Sec. IV B, we have also observed shifts of low lying states, which in that case were semicore p -states of lanthanum.

Our results are in agreement with previous calculations on Cd [27].

TABLE XIII: Energy band spectrum (in eV) of hcp structure of Cd at the Γ -point of the Brillouin zone with respect to E_F at a_{exp} , c_{exp} ; $R_{MT}K_{max} = 9$. (deg. is the energy degeneracy).

	deg.	FLAPW++	FLAPW+LO
1		-9.7489	-9.7408
2		-9.4792	-9.4710
3	(2)	-9.0806	-9.0695
4	(2)	-9.0288	-9.0174
5		-8.8436	-8.8432
6	(2)	-8.5560	-8.5445
7	(2)	-8.2998	-8.2882
8		-3.1023	-3.1036
9		-2.9070	-2.9051
10		10.3359	10.3368

V. CONCLUSIONS

APPENDIX A

We have presented a new method for the improvement of the LAPW description of the electronic band structure by using two linearization energies for the same (l, m) partial component. Starting with two LAPW radial functions, Eqs. (5b) and (5c), having the same angular dependence $Y_{l_c, m}(\hat{r})$ but different linearization energies ($E_l^{(1)}$ and $E_l^{(2)}$) inside MT-spheres, we have demonstrated that their augmentation to the basis plane wave can be performed by constructing additional basis functions $\phi_{s,i}$ ($i = 1, 2$) in the form of Eq. (17) [two functions, Eqs. (15b) and (15c), for each l, m -component]. The supplementary basis functions have zero values and slopes on the sphere surface, Eqs. (18a), (18b), and are linear independent of the usual LAPW basis states. The constructed basis functions are of the tight-binding type, Eq. (22), and obey Bloch's law.

In contrast to the LAPW+LO method with only one supplemented function, Eq. (15b), in our treatment for each l, m -component there are two supplemented functions [Eq. (15b) and (15c)]. The second basis function (absent in LAPW+LO) closely examined in this work, owes its appearance to the \dot{u}_l function in the canonical LAPW method. Thus, the basis sets of LAPW and LAPW+LO methods can be extended further by adding supplemented functions of the tight-binding type, Eq. (15c). The associated CPU time increase in our calculations was small, Table V.

In Sec. IV, the present method with extended basis set has been applied to the study of the face centered and body centered phases of lanthanum (β -La and γ -La) with the $5p$ -semicore shell separated by a gap of forbidden states from the valence states and to the hexagonal close packed structure of cadmium, where the semicore $4d$ -states overlap with the valence $5s$ -states. In all cases we have observed a systematic improvement in the values of total energy in comparison with the standard LAPW+LO treatment. The difference with LAPW+LO method practically disappears for large basis sets ($R_{MT} \cdot K_{max} = 10$) but significantly increases in going to intermediate ($R_{MT} \cdot K_{max} = 8.5$ or 8) and poor ($R_{MT} \cdot K_{max} = 7.5$ or 7) basis sets.

Acknowledgments

A.V.N. acknowledges useful discussions with B. Verberck, E.V. Tkalya, A.V. Bibikov.

Solution to the system of linear equations, Eq. (12a), is given by

$$a_{s,1} = \frac{1}{\Delta} (u_e \dot{u}'_s - u'_e \dot{u}_s), \quad (A1a)$$

$$b_{s,1} = \frac{1}{\Delta} (u'_e u_s - u_e u'_s), \quad (A1b)$$

and the solution to the system (12b) is

$$a_{s,2} = \frac{1}{\Delta} (\dot{u}_e \dot{u}'_s - \dot{u}'_e \dot{u}_s), \quad (A2a)$$

$$b_{s,2} = \frac{1}{\Delta} (\dot{u}'_e u_s - \dot{u}_e u'_s). \quad (A2b)$$

Here

$$\Delta = \dot{u}_s u'_s - u_s \dot{u}'_s \approx \frac{1}{R_{MT}^2}. \quad (A3)$$

APPENDIX B

The matrix elements for the overlap and Hamiltonian operator between supplementary states,

$$\langle \phi_{s,i} | O | \phi_{s,j} \rangle = O_{s,s}^{ij}, \quad (B1a)$$

$$\langle \phi_{s,i} | H | \phi_{s,j} \rangle = H_{s,s}^{ij}, \quad (B1b)$$

are partitioned in three different blocks, when $i = j = 1$ (block *I*), $i = j = 2$ (block *II*), and $i = 1, j = 2$ or $i = 2, j = 1$ (block *III*).

For the first block (*I*) we have

$$O_{s,s}^{11}(\vec{k}) = \mathcal{O}_{s,s} (1 + C_{s,s}^{11} + C_{e,s}^1), \quad (B2a)$$

where N_α is the number of equivalent spheres α , while

$$\mathcal{O}_{s,s} = \frac{(4\pi)^2}{V} (R_{MT}^\alpha)^4 N_\alpha, \quad (B2b)$$

$$C_{s,s}^{11} = a_{s,1} a_{s,1} + b_{s,1} b_{s,1} \mathcal{N}(\dot{u}_s, \dot{u}_s), \quad (B2c)$$

$$C_{e,s}^1 = a_{s,1} \mathcal{N}(u_e, u_s) + b_{s,1} \mathcal{N}(u_e, \dot{u}_s), \quad (B2d)$$

and \mathcal{N} stands for the integral over the product of two functions,

$$\mathcal{N}(u_1, u_2) = \int_0^{R_{MT}} u_1(r) u_2(r) r^2 dr. \quad (B3)$$

Notice that $\mathcal{N}(u_e, u_e) = \mathcal{N}(u_s, u_s) = 1$ and $\mathcal{N}(u_e, \dot{u}_e) = \mathcal{N}(u_s, \dot{u}_s) = 0$. It is also assumed here that the constant coefficient of the supplementary function is taken in the form of Eq. (19). If another form is used, the factor $\mathcal{O}_{s,s}$, Eq. (B2b), [and $\mathcal{O}_{e,s}(\vec{k}_n)$, Eq. (C2c)] should be changed accordingly.

For the block *II* we obtain

$$O_{s,s}^{22} = \mathcal{O}_{s,s} (\mathcal{N}(\dot{u}_e, \dot{u}_e) + C_{s,s}^{22} + C_{e,s}^2), \quad (B4a)$$

$$C_{s_s}^{22} = a_{s,2}a_{s,2} + b_{s,2}b_{s,2} \mathcal{N}(\dot{u}_s, \dot{u}_s), \quad (\text{B4b})$$

$$C_{e_s}^2 = a_{s,2} \mathcal{N}(\dot{u}_e, u_s) + b_{s,2} \mathcal{N}(\dot{u}_e, \dot{u}_s). \quad (\text{B4c})$$

Finally, for the block *III* we get

$$O_{s_s}^{12} = \mathcal{O}_{s,s} (C_{s_s}^{12} + C_{e_s}^1 + C_{e_s}^2), \quad (\text{B5a})$$

where

$$C_{s_s}^{12} = a_{s,1}a_{s,2} + b_{s,1}b_{s,2} \mathcal{N}(\dot{u}_s, \dot{u}_s), \quad (\text{B5b})$$

and $C_{e_s}^1$ is given by Eq. (B2d), while $C_{e_s}^2$ by Eq. (B4c).

For the matrix elements of the Hamiltonian $H_{s_s}^{ij}(\vec{k})$, Eq. (B1b), we also obtain three blocks. For the first block (*I*) we have

$$H_{s_s}^{11} = \mathcal{O}_{s,s} (E_e + E_s C_{s_s}^{11} + a_{s,1}b_{s,1} + (E_e + E_s) C_{e_s}^1 + b_{s,1} \mathcal{N}(u_e, u_s)). \quad (\text{B6})$$

Here E_e and E_s are energies at which the radial wave functions $u_e(r)$ and $u_s(r)$ are evaluated in the *MT*-sphere α .

For the second block (*II*) we get

$$H_{s_s}^{22} = \mathcal{O}_{s,s} (E_e \mathcal{N}(\dot{u}_e, \dot{u}_e) + E_s C_{s_s}^{22} + a_{s,2}b_{s,2} + (E_e + E_s) C_{e_s}^2 + \gamma_{e_s}^2), \quad (\text{B7a})$$

where

$$\gamma_{e_s}^2 = a_{s,2} \mathcal{N}(u_e, u_s) + b_{s,2} (\mathcal{N}(u_e, \dot{u}_s) + \mathcal{N}(\dot{u}_e, u_s)). \quad (\text{B7b})$$

For the third block (*III*) we have

$$H_{s_s}^{12} = \mathcal{O}_{s,s} (E_s (C_{s_s}^{12} + C_{e_s}^1) + a_{s,2}b_{s,1} + E_e C_{e_s}^2 + b_{s,1} \mathcal{N}(\dot{u}_e, u_s)). \quad (\text{B8})$$

APPENDIX C

In this section we quote the expressions for matrix elements for the overlap and Hamiltonian operator between supplementary and extended states,

$$\langle \phi_{s,i} | O | \phi_n \rangle = O_{s,e}^{i,n}(\vec{k}), \quad (\text{C1a})$$

$$\langle \phi_{s,i} | H | \phi_n \rangle = H_{s,e}^{i,n}(\vec{k}). \quad (\text{C1b})$$

The extended states here are the usual LAPW basis functions, Eq. (1), which are characterized by the wave vector $\vec{k}_n = \vec{k} + \vec{K}_n$. The supplementary functions have two components $i = 1, 2$, for each l, m -angular dependence, Eq. (15b), (15c), (17).

For the matrix of overlap we get

$$O_{s_e}^{1n}(\vec{k}) = \mathcal{O}_{e,s}(\vec{k}_n) S_{s_e}^{1n}, \quad (\text{C2a})$$

where

$$S_{s_e}^{1n} = a_e + a_{s,1}a_e \mathcal{N}(u_e, u_s) + a_{s,1}b_e \mathcal{N}(\dot{u}_e, u_s) + b_{s,1}a_e \mathcal{N}(u_e, \dot{u}_s) + b_e b_{s,1} \mathcal{N}(\dot{u}_e, \dot{u}_s), \quad (\text{C2b})$$

and the structure factor is

$$\mathcal{O}_{e,s}(\vec{k}_n) = \frac{(4\pi)^2}{V} (R_{MT}^\alpha)^4 Y_{lm}^*(\hat{k}_n) \times \sum_{\nu} \exp[i(\vec{k}_n - \vec{k}) \cdot \vec{r}_{\nu,\alpha}]. \quad (\text{C2c})$$

Here, $\vec{r}_{\nu,\alpha}$ stands for the coordinates of all ν centers of *MT*-spheres of the type α in the primitive unit cell. The factors $\mathcal{N}(u_1, u_2)$ in (C2b) are integrals between two functions given by Eq. (B3).

The quantities a_e and b_e in Eq. (C2b) and below are standard LAPW expansion coefficients for the component with l, m , defined by Eq. (9a) and (9b), i.e. $a_e = a_e^0$ and $b_e = b_e^0$. Since they depend on \vec{k}_n, l , and α , we can write $a_e = a_e^\alpha(\vec{k})$, $b_e = b_e^\alpha(\vec{k})$. Explicit expressions for them can be found in Ref. [4, 5].

The matrix element for the second case ($i = 2$) reads as

$$O_{s_e}^{2n}(\vec{k}) = \mathcal{O}_{e,s}(\vec{k}_n) S_{s_e}^{2n}, \quad (\text{C3a})$$

where

$$S_{s_e}^{2n} = b_e \mathcal{N}(\dot{u}_e, \dot{u}_e) + a_{s,2}a_e \mathcal{N}(u_e, u_s) + a_{s,2}b_e \mathcal{N}(\dot{u}_e, u_s) + b_{s,2}a_e \mathcal{N}(u_e, \dot{u}_s) + b_e b_{s,2} \mathcal{N}(\dot{u}_e, \dot{u}_s). \quad (\text{C3b})$$

Below we quote the matrix elements for the Hamiltonian,

$$H_{s_e}^{1n}(\vec{k}) = \mathcal{O}_{e,s}(\vec{k}_n) (E_e S_{s_e}^{1n} + b_e + a_{s,1}b_e \mathcal{N}(u_e, u_s) + b_{s,1}b_e \mathcal{N}(u_e, \dot{u}_s)), \quad (\text{C4})$$

$$H_{s_e}^{2n}(\vec{k}) = \mathcal{O}_{e,s}(\vec{k}_n) (E_e S_{s_e}^{2n} + a_{s,2}b_e \mathcal{N}(u_e, u_s) + b_{s,2}b_e \mathcal{N}(u_e, \dot{u}_s)). \quad (\text{C5})$$

Here $\mathcal{O}_{e,s}$ is given by Eq. (C2c), while $S_{s_e}^{in}$ by Eq. (C2b) for $i = 1$, and by Eq. (C3b) for $i = 2$.

APPENDIX D

Here we demonstrate that the two supplementary basis functions $\phi_{s,i}$ ($i = 1, 2$), Eq. (17), work even in the case when the expansion energies E_s and E_e lie not far from each other.

Consider $E_e = E_s + \varepsilon$, where $\varepsilon/E_s \ll 1$. Making use of the following expansions

$$u_e(r) = u_s(r) + \dot{u}_s(r) \varepsilon + \frac{1}{2} \ddot{u}_s(r) \varepsilon^2 + \frac{1}{6} \dddot{u}_s(r) \varepsilon^3 + O(\varepsilon^4), \quad (\text{D1a})$$

$$\dot{u}_e(r) = \dot{u}_s(r) + \ddot{u}_s(r) \varepsilon + \frac{1}{2} \dddot{u}_s(r) \varepsilon^2 + O(\varepsilon^3), \quad (\text{D1b})$$

for $\dot{u}_e(r)$ and $\dot{u}_e(r)$ and substituting them in Eqs. (15b), (15c), we arrive at

$$R_{l,m}^{s,1}(r) = \frac{1}{2}\varepsilon^2 C_0 e^{i\vec{k}\vec{R}_\alpha} [\ddot{u}_s + \frac{1}{3}\varepsilon \ddot{u}_s + O(\varepsilon^2) + a'_{s,1} u_s + b'_{s,1} \dot{u}_s], \quad (\text{D2a})$$

$$R_{l,m}^{s,2}(r) = \varepsilon C_0 e^{i\vec{k}\vec{R}_\alpha} [\ddot{u}_s + \frac{1}{2}\varepsilon \ddot{u}_s + O(\varepsilon^2) + a'_{s,2} u_s + b'_{s,2} \dot{u}_s]. \quad (\text{D2b})$$

Here

$$a'_{s,1} = \frac{1}{\varepsilon^2}(a_{s,1} + 1), \quad b'_{s,1} = \frac{1}{\varepsilon^2}(b_{s,1} + \varepsilon); \quad (\text{D3a})$$

$$a'_{s,2} = \frac{1}{\varepsilon} a_{s,2}, \quad b'_{s,2} = \frac{1}{\varepsilon} (b_{s,2} + 1). \quad (\text{D3b})$$

The prefactors $\varepsilon^2/2$ and ε in Eqs. (D2a), (D2b) are not very important, because as a consequence of solving secular equations these basis functions will be effectively orthonormalized. Functions $R_{l,m}^{s,1}(r)$ and $R_{l,m}^{s,2}(r)$ have two important features. First, by a linear transformation the two functions, Eqs. (D2a), (D2b), can be transformed to two functions with the following radial dependencies

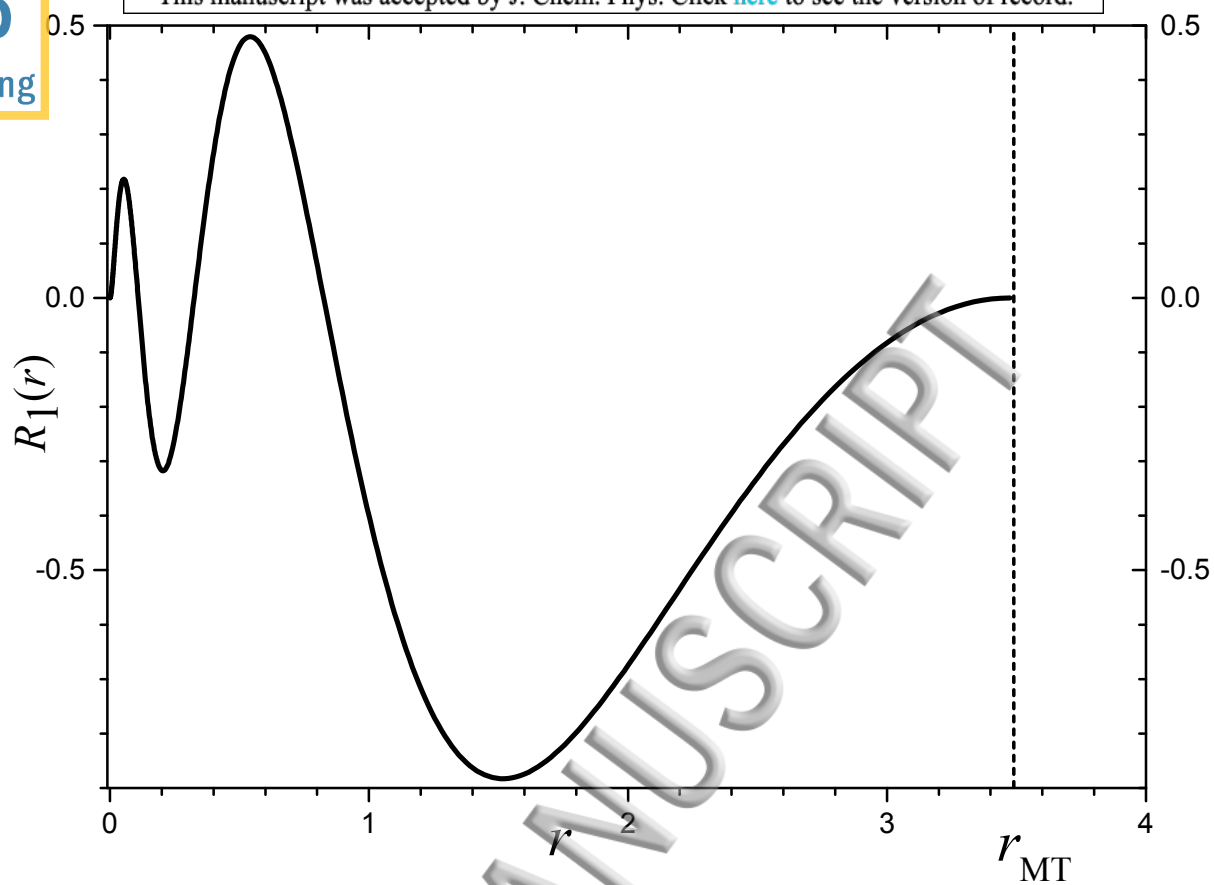
$$U_1(r) = \ddot{u}_s + a''_{s,1} u_s + b''_{s,1} \dot{u}_s, \quad (\text{D4a})$$

$$U_2(r) = \ddot{u}_s + a''_{s,1} u_s + b''_{s,1} \dot{u}_s, \quad (\text{D4b})$$

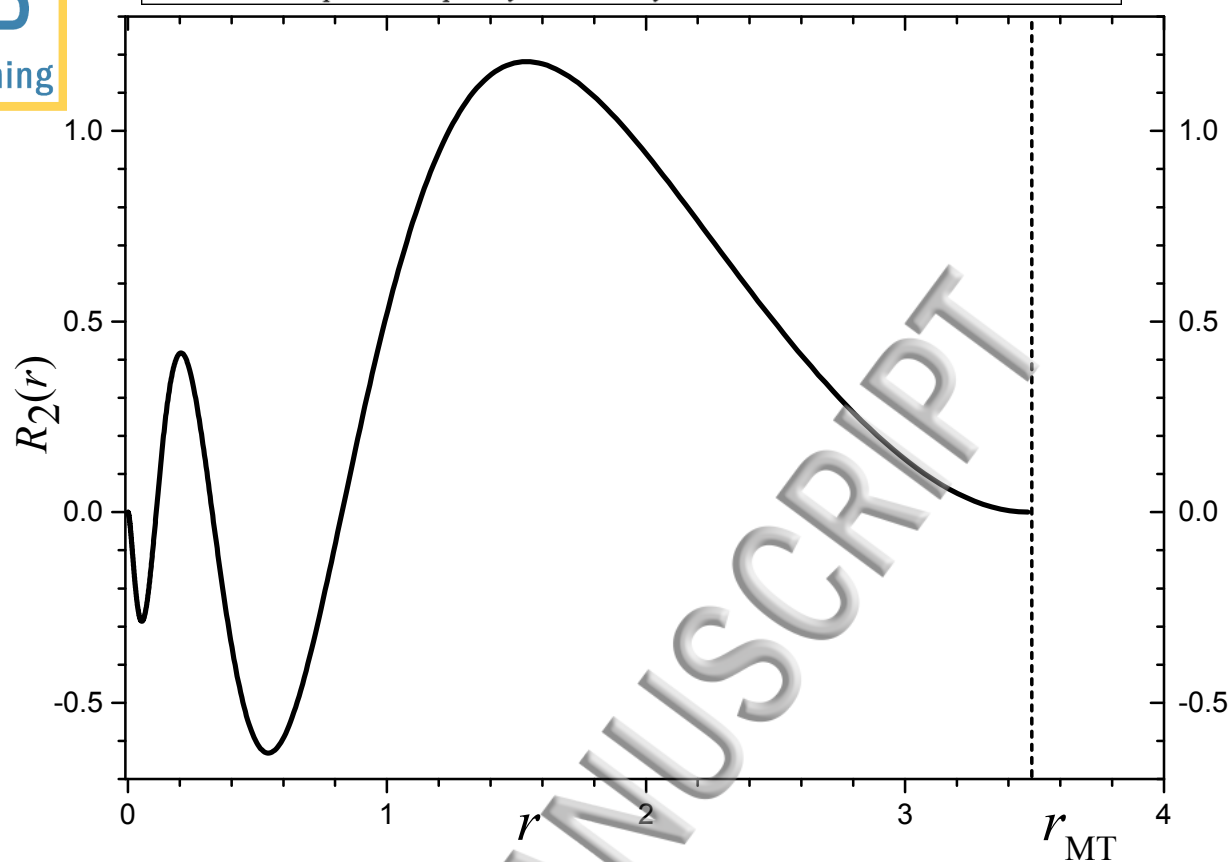
where the coefficients $a''_{s,1}$ etc. can be expressed through $a'_{s,1}$ etc. Since the functions $\dot{u}_s(r)$ and $\ddot{u}_s(r)$ are linear independent, the same property applies to $U_1(r)$ and $U_2(r)$ and, consequently, to $R_{l,m}^{s,1}(r)$ and $R_{l,m}^{s,2}(r)$, although the property deteriorates as $\varepsilon \rightarrow 0$. Second, we still can impose the boundary conditions (18a) and (18b).

However, since the initial functions $R_{l,m}^{s,1}(r)$ and $R_{l,m}^{s,2}(r)$, have almost identical radial dependence (neglecting terms with $\varepsilon \ddot{u}_s$ and the others of high order of ε in Eqs. (D2a), (D2b) make them completely identical), the normalization procedure leads to the appearance of an effective basis state ϕ' , which is orthogonal to other basis states and expressed through the linear combination of initial states, $\phi' = C_1 \psi_{s,1} + C_2 \psi_{s,2}$ with large coefficients C_1 and C_2 (i.e. $|C_1| \gg 1$, $|C_2| \gg 1$). In that case, the partial charges of supplementary basis states can also be very large. Nevertheless, some of these partial charges are of opposite sign and effectively cancel each other in the final answer. We have observed the effect in the calculation of the hexagonal close packed lattice of cadmium reported in Sec. IV C.

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