New treatment of semicore states in the linearized augmented plane wave method (LAPW) using supplemented tight binding basis functions

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We present a new method for the treatment of extended-core states in the linearized augmented plane wave method (LAPW) where the usual LAPW basis set is supplemented by basis functions of the tight binding type, which go to zero with zero derivative at the sphere boundary and are linear independent of the standard LAPW basis functions. These supplemented tight binding basis functions appear as a result of a plane wave augmentation by two different radial wave components constructed at two different energies (referring to valence and semicore states) of linear expansion. We discuss properties of such additional tight binding basis functions and apply the extended basis set for computation of electron energy bands of lanthanum (f ace and body centered structures) and hexagonal close packed lattice of cadmium. We also discuss the relation between the present method and other variational approaches.

I. INTRODUCTION

The linear augmented plane wave (LAPW) method is probably the most precise method for electronic band structure calculations and is widely used for the calculation of materials properties. In the LAPW method space is partitioned in spheres and the interstitial region. The basis functions \( \phi_n(\vec{k}, \vec{R}) \) where \( n = 1, 2, ..., N \) are given by

\[
\phi_n(\vec{k}, \vec{R}) = \left\{ \begin{array}{ll}
V^{-1/2} \exp(i(\vec{k} + \vec{R}_n) \cdot \vec{R}), & \vec{R} \in I \\
\sum_{l,m} R^{n,\alpha}_{l,m}(r, E_i) Y_{l,m}(\vec{r}), & \vec{R} \in MT(\alpha)
\end{array} \right.
\]

with radial parts

\[
R^{n,\alpha}_{l,m}(r, E_i) = A^{n,\alpha}_{l,m} u_l(r, E_i) + B^{n,\alpha}_{l,m} \hat{u}_l(r, E_i).
\]

Here the index \( \alpha \) refers to the type of atom (or \( MT \)-sphere) in the unit cell, the radius \( r \) is counted from the center \( \vec{R}_\alpha \) of the sphere \( \alpha \) (i.e. \( \vec{r} = \vec{R} - \vec{R}_\alpha \)), \( V \) is the volume of the unit cell. Radial functions \( u_{l,m}(r, E_i) \) are solutions of the Schrödinger equation in the spherically averaged crystal potential computed at the linearization energy \( E_i \), and \( \hat{u}_l(r, E_i) \) is the derivative of \( u_{l,m} \) with respect to \( E \) at \( E_i \). The coefficients \( A^{n,\alpha}_{l,m} \) and \( B^{n,\alpha}_{l,m} \) are found from the condition that the basis function \( \phi_n \) is continuous with continuous derivative at the sphere boundary, \( r = R^{\alpha}_{MT} \) (\( R^{\alpha}_{MT} \) is the radius of the \( MT \)-sphere \( \alpha \)). In the following for compactness we omit the index \( \alpha \) and restore it when needed. Linearization energies \( E_i \) are chosen close to average values of corresponding band energies or to the Fermi level. The extended electron basis states defined by Eq. (1) as a rule are orthogonal to the core states. This is a consequence of the relation

\[
\int_0^{R^{MT}} U_c(r) U_r(r)r^2 dr = \frac{R^{MT}}{2(E_c - E_v)} \times \left( U_c(R^{MT}) \frac{\partial U_r(R^{MT})}{\partial r} - U_r(R^{MT}) \frac{\partial U_c(R^{MT})}{\partial r} \right), \tag{3}
\]

applied to a core state with orbital quantum numbers \( l, m \) and the radial wave function \( U_c(r) \), and a partial radial function of valence state, \( U_r(r) = R^{n,\alpha}_{l,m}(r, E_i) \), 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,

\[
\frac{\partial U_c(R^{MT})}{\partial r} = 0, \tag{4a}
\]

\[
\frac{\partial U_r(R^{MT})}{\partial r} = 0. \tag{4b}
\]

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 muffin-tin sphere. Semicore states leaking out of the \( MT \)-regions should be treated as extended states. This in turn requires that the linearization energy \( E_i \) is chosen near the energy of the semicore level, \( E_i \approx E_c \), because the LAPW basis describes only states near \( E_i \) well. However, as \( E_c \) is quite
far from the Fermi energy $E_F$ and the valence band energy, the choice $E_l = E_v$ inevitably gives poor description for partial $l = l_v$ valence states. On the other hand, the option $E_l = E_c$ is not satisfactory for the semicore states situated substantially deeper in energy. As discussed in Refs. [3], [12] 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" [6, 7] 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 [3].

To circumvent the problem and improve the LAPW efficiency Singh put forward a third approach based on local orbitals (LAPW+LO) [2]. In the LAPW+LO approach the same three radial functions as in SLAPW-3 are used (i.e. $u_{l_1}^{(1)}, u_{l_1}^{(2)}$, and $u_{l_2}^{(2)}$), but the coefficient of $u_{l_2}^{(2)}$ is fixed (say, $A_{l_2,m}^{(2),n} = 1$) and the two remaining coefficients ($A_{l_1,m}^{(1),n}$, $B_{l_1,m}^{(1),n}$) 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 [3, 4]. However, conceptually the LAPW+LO method is understood as a procedure giving additional variational freedom through an increase of the number of basis functions. It is not clear why additional basis functions should include these particular components (i.e. $u_{l_1}^{(1)}$, $u_{l_1}^{(2)}$, and $u_{l_2}^{(2)}$) and why they require the proposed zero boundary conditions.

In Ref. [5] Singh has proposed to introduce supplemented tight binding basis functions (see Eqs. (15b) and (15c) below), satisfying Bloch’s theorem.

The paper is organized as follows. In Sec. III we present the method and introduce supplemented tight binding basis functions. In Sec. III we apply the method to electron band structure calculations of the face centered and body centered lattice of lutetium and the hexagonal close packed lattice of cadmium. Our conclusions are summarized in Sec. IV.

II. DESCRIPTION OF THE METHOD

As we discussed in the Introduction, in the case of semicore states we have two types of radial solutions in the MT-region with the same angular dependence $Y_{l,m}(r)$ but different linearization energies $E_l^{(1)}$ and $E_l^{(2)}$: $R_{l,m}^{(1)}(r, E_l^{(1)})$, Eq. (5b), and $R_{l,m}^{(2),n}(r, E_l^{(2)})$, Eq. (5c). One of the radial functions can refer to extended states, i.e. $R_c(r) = R_{l_1,m}^{(1),n}(r, E_l^{(1)})$, while the other can refer to supplementary angular states $R_s(r) = R_{l_2,m}^{(2),n}(r, E_l^{(2)})$. 
As we will see later in Sec. 11, in practice we describe the semicore states as extended states with $E_l = E_{\text{core}}$ and valence states with the same $l$ as supplementary states for which $E_l = E_v$ (For metals one can take $E_l = E_v \approx E_{F_p}$). Since in the interstitial I-region both types of solutions are represented by the plane wave function $\phi_n(\vec{k}, \vec{R})$, Eq. (5a), they become indistinguishable there. In LAPW method there are two matching conditions (for the function and its derivative) on the sphere boundary. Therefore, in our case we have

$$A_c u_e + B_c \dot{u}_e + A_s u_s + B_s \dot{u}_s = \frac{4\pi}{\sqrt{V}} \int_{l} j_l(k_n R_{MT}) Y_{l,m}^*(\vec{k}_n) e^{i\vec{k}_n \cdot \vec{R}_o}$$ (6a)

$$A_c' u'_e + B_c' \dot{u'_e} + A_s' u'_s + B_s' \dot{u'_s} = \frac{4\pi}{\sqrt{V}} \int_{l} j_l'(k_n R_{MT}) Y_{l,m}^*(\vec{k}_n) e^{i\vec{k}_n \cdot \vec{R}_o}.$$ (6b)

Here we adopt short notations $A_c = A_{l,m}^{(1),n}$, $A_s = A_{l,m}^{(2),n}$, $u_e = u_l^{(1)}(R_{MT}, E_l^{(1)})$, $u_s = u_l^{(2)}(R_{MT}, E_l^{(2)})$, $u'_e = \partial u_l^{(1)}(R_{MT}, E_l^{(1)})/\partial r$, $u'_s = \partial u_l^{(2)}(R_{MT}, E_l^{(2)})/\partial r$, and have used the Rayleigh expansion of the plane wave $\phi_n$ on the sphere surface. Since there are four coefficients ($A_c$, $B_c$, $A_s$ 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

$$A_c = \frac{4\pi}{\sqrt{V}} \int_{l} R_{MT}^2 Y_{l,m}^*(\vec{k}_n) e^{i\vec{k}_n \cdot \vec{R}_o} a_c,$$ (7a)

$$B_c = \frac{4\pi}{\sqrt{V}} \int_{l} R_{MT}^2 Y_{l,m}^*(\vec{k}_n) e^{i\vec{k}_n \cdot \vec{R}_o} b_c.$$ (7b)

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

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

$$a_e' u'_e + b_e' \dot{u'_e} + a_s' u'_s + b_s' \dot{u'_s} = j_l'(k_n R_{MT}) \frac{1}{R_{MT}^2}. $$ (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 $a_s = 0$, $b_s = 0$, can be found from the following system

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

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

Defining auxiliary quantities $t_a$ and $t_b$

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

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

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

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

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

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

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

$$\begin{cases}
  a_{s,2} u_e + b_{s,2} \dot{u}_e = -u_e \\
  a_{s,2} u'_e + b_{s,2} \dot{u'}_e = -u'_e.
\end{cases}$$ (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

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

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

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

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

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

$$R_{l,m}^n(r) \sim a_e^0 u_e + b_e^0 \dot{u}_e + t_a (u_e a_{s,1} + b_e b_{s,1} \dot{u}_e) + t_b (u_e a_{s,2} + b_e b_{s,2} \dot{u}_e).$$ (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. $R_{l,m}^{1,0}(r), R_{l,m}^{1,1}(r), R_{l,m}^{1,2}(r)$) instead of the single function $R_{l,m}^n(r) = R_{l,m}^1(r) + t_a R_{l,m}^{1,1}(r) + t_b R_{l,m}^{1,2}(r)$. Explicitly,

$$R_{l,m}^1(r) = C_n e^{i\vec{k}_n \cdot \vec{R}_o} (u_e^0 u_e + b_e^0 \dot{u}_e),$$ (15a)

$$R_{l,m}^{1,1}(r) = C_n e^{i\vec{k}_n \cdot \vec{R}_o} (u_e a_{s,1} + b_e b_{s,1} \dot{u}_e),$$ (15b)

$$R_{l,m}^{1,2}(r) = C_n e^{i\vec{k}_n \cdot \vec{R}_o} (u_e a_{s,2} + b_e b_{s,2} \dot{u}_e).$$ (15c)

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

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

The first function, Eq. (15a), is in fact the standard radial part of the $l$-type, $R_{l,m}^1 = R_{l,m}^{1,0},$ 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. (4a), (4b). Two other functions however
are very different from $\phi_i(\vec{k}, \vec{R})$ and should be included to the LAPW basis set as extra basis states,

$$
\phi_{s,i}(\vec{k}, \vec{R}) = Y_i^m(\hat{r}) R_{s,i}^r(r),
$$

(17)

where $i = 1, 2$. The important things 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). In respect to two new functions $R_{s,i}^r$ Eqs. (12a), (12b) impose the following boundary conditions

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

These relations have a simple interpretation: new supplementary basis functions $\phi_{s,i}(\vec{k}, \vec{R})$ are required to be zero with zero derivative at the sphere boundary. We want to stress here, that the conditions $\partial R_{s,i}^r(r) = 0$ and $R_{s,i}^r(r) = 0$ are not assumed or introduced at our will. 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, $U^{s,i}(r) = u_r + a_{s,1} u_s + b_{s,1} \hat{u}_s$ for $i = 1$, or $U^{s,2}(r) = \hat{u}_r + a_{s,2} u_s + b_{s,2} \hat{u}_s$ 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 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 $C_0 = \pi/V \int R_{s,i}^r(\vec{k})^2$ [compare with Eq. (15)] can be further rationalized by omitting the multiplier $Y_i^m(\vec{k})$ or equivalently, including it in factors $t_a$ and $t_b$, Eq. (10a), (10b). Thus, we substitute $C_0$ with

$$
C_0 = \frac{4\pi}{V} \int R_{s,i}^r(\vec{k})^2 .
$$

(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,

$$
\phi_{s,i}(\vec{k}, \vec{R}) = e^{i\vec{k}\vec{R}} \psi_i^{l,m}(\vec{R} - \vec{R}_0),
$$

(20)

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

$$
\psi_i^{l,m}(\vec{R} - \vec{R}_0) = C_0 U^{s,i}(r) Y_i^m(\hat{r}).
$$

(21)

Notice that each local function $\psi_i^{l,m}(\vec{R} - \vec{R}_0)$ is strictly confined inside the MT-sphere $\alpha$, because both $U^{s,i}(r)$ and $R_{s,i}^r(r)$ 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

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

(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 equations, 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 for 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 $\phi_n$ are listed in Appendix [C]. For briefness 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), (B3a) 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. [IIC].

III. PRACTICAL IMPLEMENTATION

A. FACE CENTERED CUBIC STRUCTURE OF LA

We have applied the method developed in Sec. [I] to electron band structure calculations of face centered cubic (fcc) structure of lanthanum. Atomic lanthanum has
completely filled 5p semicore electron shell lying at -22.47 eV which can slightly mix with valence states (5d, 6s, 4f) at energies from -3 to -2 eV. For lanthanum here and below we have chosen the exchange correlation potential and energy in the form of Vosko-Wilk-Nusair (VWN) (which is a variant of the local density approximation, LDA) and Perdew-Burke-Ernzerhof (PBE) (which is a variant of the generalized gradient approximation, GGA).

We have employed our original version of LAPW code with the potential of general form. Integration in the irreducible part of the Brillouin zone has been performed over 89 $\bar{k}$-points, in the final run over 505 points. Angular expansions for the electron density and wave function inside MT-sphere have been done up to $L_{\text{max}} = 8$. The number of basis functions has been limited by the condition $K_{\text{MT}}a < 8.5$, resulting in 59 basis states. 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. II.

The 5p semicore states have been treated as band states. The LAPW linear expansion energy $E_c$ for them has been found from the condition

$$u_p(r = R_{\text{MT}}, E_c) = 0,$$

which results in $E_c(p) = -8.91$ eV in respect to the self-consistent crystal potential. The linear expansion energy for supplementary tight binding $p$-states has been fixed at the Fermi energy, $E_s(p) = 6.40$ eV. Under these conditions two supplementary radial functions shown in Fig. 1 are given by $R_1(r) = u_e(r) + a_{s,1}u_s(r) + b_{s,1}u_s(r)$ where $a_{s,1} = 0.0228$, $b_{s,1} = 0.4651$, and $R_2(r) = u_e(r) + a_{s,2}u_s(r) + b_{s,2}u_s(r)$ where $a_{s,2} = -2.0916$, $b_{s,2} = 1.2000$. Notice that the number of nodes for both radial functions is three (excluding points with $r = 0$ and $r = R_{\text{MT}}$) 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. The iteration procedure with supplemented tight binding functions has been stable converging to a self consistent solution without additional difficulties.

Partial charges for fcc lanthanum including the supplemented and extended-supplemented $p$-charges are presented in Table II. Notice that the charges related with supplemented basis states are significant, and their sum even exceeds the partial $s$-charge $Q_s$. Therefore, the role of additional $p$-states is at least as important as the role of $s$-states and inclusion of supplementary states is essential for a correct description of the electronic structure. For completeness we quote partial $p$-charges $Q(u_1, u_2)$ which have been used for the construction of electron density according to the relation

$$\Delta\rho_{u_1, u_2}(r) = Q(u_1, u_2) u_1(r) u_2(r),$$

where $\Delta\rho_{u_1, u_2}(r)$ is a radial component of the electron density associated with the pair of functions $u_1$ and $u_2$. The extended charges (in units of $e$) are $Q_p(u_e, u_e) = 5.0404, Q_p(u_e, u_s) = -1.3564, Q_p(u_s, u_e) = 0.1030$; the supplementary charges are $Q_p(u_s, u_s) = 0.1029, Q_p(u_s, u_s) = -0.1330$, $Q_p(u_s, u_s) = 0.0401$; the extended-supplementary charges are $Q_p(u_e, u_s) = 1.0264, Q_p(u_e, u_s) = -0.7425$, $Q_p(u_e, u_s) = -0.1677, Q_p(u_e, u_s) = 0.1185$.

Finally, we notice that the overall description of fcc La is systematically improved by using supplemented basis functions. For example, the equilibrium lattice constant is $a = 5.35$ Å ($a_{\text{exp}} = 5.304$ Å. Ref. 16), whereas without tight binding basis functions it amounts to $a = 5.45$ Å in VWN-LDA calculations. PBE-GGA exchange results in $a = 5.45$ Å and $a = 5.80$ Å for calculations with and without supplementary basis functions, correspondingly. (The LAPW+LO calculation with Hedin-Lundqvist exchange-correlation potential yields $a = 5.15$ Å. 17) We have also found that
We see that while the extended charges to a lesser extent the fcc values, the supplementary tight binding energy ($E$) inside MT-spheres, 91 special points in the irreducible part of the Brillouin zone during the self-consistent procedure and 506 points for the final run.

As for fcc-La the LAPW linear expansion energy for the extended $p$-states has been found from condition [23], giving $E_{c}(p) = -6.47$ eV in the crystal potential. The linear expansion energy for supplementary tight binding $p$-states has been calculated at the Fermi energy ($E_{F}(p) = 8.00$ eV). Then two supplementary radial functions are $R_{1}(r) = u_{c}(r) + a_{s,1}u_{s}(r) + b_{s,1}u_{s}(r)$ where $a_{s,1} = -0.0830$, $b_{s,1} = 0.5795$, and $R_{2}(r) = u_{c}(r) + a_{s,2}u_{s}(r) + b_{s,2}u_{s}(r)$ where $a_{s,2} = -1.8033$, $b_{s,2} = 0.5416$. The partial charges for bcc-La are reported in Table I.

We see that while the extended charges $Q_{s}$, $Q_{p}(e-e)$, and to a lesser extent $Q_{d}$ and $Q_{f}$ decrease in comparison with the fcc values, the supplementary $p$-charges $Q_{p}(s-s)$ and $Q_{p}(e-s)$ become larger, mainly at the expense of $Q_{p}(e-e)$.

**TABLE I**: Partial charges (in units of $e$) $Q_{i}$ for fcc La ($a = 5.35$ Å) and bcc La ($a = 4.10$ Å) with VWN (LDA) exchange [13]. $Q_{p}(e-e)$ refers to the $p$-charge of the extended states, $Q_{p}(s-s)$ to the $p$-charge of the additional supplementary states and $Q_{p}(e-s)$ to the $p$-charge due to the overlap between the extended and supplementary states, $Q_{out}$ to the charge in the interstitial region.

| $Q_{i}$ | fcc La | bcc La |
|--------|--------|--------|
| $Q_{s}$ | 0.4356 | 0.3457 |
| $Q_{p}$ e-e | 5.3019 | 4.7544 |
| s-s | 0.2711 | 0.3375 |
| e-s | 0.4999 | 0.8720 |
| $Q_{d}$ | 1.5314 | 1.4821 |
| $Q_{f}$ | 0.1371 | 0.1363 |
| $Q_{p}$ | 0.0072 | 0.0085 |
| $Q_{b}$ | 0.0020 | 0.0023 |
| $Q_{t}$ | 0.0008 | 0.0006 |
| $Q_{l}$ | 0.0003 | 0.0002 |
| $Q_{out}$ | 0.8128 | 1.0606 |

The total energy of fcc-La ($\beta$-La) is $\sim 0.10$ eV (LDA) and $\sim 0.05$ eV (GGA) lower than the energy of bcc-La ($\gamma$-La), which is in agreement with the fact that the $\gamma$-phase at normal pressure exists only at high temperatures ($>1138$ K) and in a narrow temperature range (53 K) [17]. In both fcc and bcc cases applying supplemented tight binding functions led to a 0.2-0.3 eV lowering of the total energy.

**B. Body centered cubic structure of La**

For the full potential electron band structure calculations of the bcc-phase we have used a plane wave cut off parameter $K_{w}R_{MT} < 8.5$ (55 basis states supplemented by 6 additional tight binding $p$-states). $I_{max} = 8$ for the expansion of the electron density and wave functions inside MT-spheres, 91 special $\vec{k}$-points in the irreducible part of the Brillouin zone along the high symmetry lines of the Brillouin zone ($a = 4.10$ Å). Partial $p$-charges which have been used for the construction of electron density from the wave functions, Eq. (24), are the following: $Q_{p}(u_{c}, u_{c}) = 4.3415$, $Q_{p}(u_{s}, u_{s}) = 2.0726$, $Q_{p}(u_{c}, u_{c}) = 0.2740$ for the extended states; $Q_{p}(u_{s}, u_{s}) = 0.3197$, $Q_{p}(u_{s}, u_{s}) = -0.2270$, $Q_{p}(u_{s}, u_{s}) = 0.0634$ for the supplementary states; $Q_{p}(u_{c}, u_{s}) = 1.5018$, $Q_{p}(u_{c}, u_{s}) = -0.9193$, $Q_{p}(u_{c}, u_{s}) = -0.4181$, $Q_{p}(u_{c}, u_{s}) = 0.2501$ for the extended-supplementary states. The calculated band structure of bcc lattice of lanthanum in LDA (VWN) approximation is shown in Fig. 2.

As for fcc-La the LAPW linear expansion energy for the extended $p$-states has been found from condition [23], giving $E_{c}(p) = -6.47$ eV in the crystal potential. The linear expansion energy for supplementary tight binding $p$-states has been calculated at the Fermi energy ($E_{F}(p) = 8.00$ eV). Then two supplementary radial functions are $R_{1}(r) = u_{c}(r) + a_{s,1}u_{s}(r) + b_{s,1}u_{s}(r)$ where $a_{s,1} = -0.0830$, $b_{s,1} = 0.5795$, and $R_{2}(r) = u_{c}(r) + a_{s,2}u_{s}(r) + b_{s,2}u_{s}(r)$ where $a_{s,2} = -1.8033$, $b_{s,2} = 0.5416$. The partial charges for bcc-La are reported in Table I.

We see that while the extended charges $Q_{s}$, $Q_{p}(e-e)$, and to a lesser extent $Q_{d}$ and $Q_{f}$ decrease in comparison with the fcc values, the supplementary $p$-charges $Q_{p}(s-s)$ and $Q_{p}(e-s)$ become larger, mainly at the expense of $Q_{p}(e-e)$.

This implies that the additional $p$-states for the bcc structure of lanthanum are even more important than for the fcc lattice. This is due to the fact that the MT-sphere and MT-radius are smaller for the bcc case which leads to depleting the population of the 5s semicore states and pushing them to interact more strongly with the extended states.

FIG. 2: Electronic band structure of bcc $\gamma$-La along high symmetry lines of the Brillouin zone ($a = 4.10$ Å). (a) valence bands, (b) semicore ($5p$) band. The horizontal dashed line indicates the Fermi level.

We have found that the equilibrium lattice constant for body centered cubic (bcc) lanthanum is $a = 4.10$ Å with LDA and $a = 4.45$ Å with GGA (the experimental lattice constant of $\gamma$-La is $a_{exp} = 4.25$ Å [17]). Again, we have observed an improvement in the value of lattice constants when calculations with supplemented basis functions have been carried out. Without tight binding functions the lattice constant is 4.50 Å (LDA) and 4.85 Å (GGA).
In that case one can expect that the extended electron density and wave functions inside the MT-spheres, 125 special points in the irreducible part of the Brillouin zone during the self-consistent procedure and 729 points for the final run. The Vosko-Wilk-Nusair exchange correlation contribution has been used, Ref. 13.

The technical parameters of FLAPW calculations were the following: the plane wave cut off parameter $K_{\text{F}}R_{\text{MT}} < 8.5$ (135 basis states and 10 supplemented tight binding $d$-states), $L_{\text{max}} = 8$ for the expansion of electron density and wave functions inside the MT-spheres, 125 special $\vec{k}$-points in the irreducible part of the Brillouin zone during the self-consistent procedure and 729 points for the final run. The Vosko-Wilk-Nusair (VWN) exchange correlation contribution has been used, Ref. 13.

We first describe calculations with supplemented $d$-states. As for lanthanum the LAPW linear expansion energy for the extended $d$-states has been found from the condition \[ E_s(d) = -1.3 \text{ eV}, \] giving $E_s(d) = -1.3 \text{ eV}$. If the linear expansion energy for supplementary tight binding $d$-states is fixed at the Fermi energy ($E_s(d) = E_F = 6.08 \text{ eV}$), then two supplementary radial functions plotted in Fig. 4 are $R_1(r) = u_s(r) + a_{s,1}u_s(r) + b_{s,1}u_s(r)$ where $a_{s,1} = -0.4870$, $b_{s,1} = 0.4254$, and $R_2(r) = u_s(r) + a_{s,2}u_s(r) + b_{s,2}u_s(r)$ where $a_{s,2} = -1.9259$, $b_{s,2} = -0.3713$.

Electronic bands at the $\Gamma$-point of the Brillouin zone and the partial charges $Q_\ell$ calculated with and without supplementary $d$-states are presented in Tables 1 and 11. The band shift between two types of calculations shown in Table 11 is typical for the other points of the Brillouin zone. Therefore filled energy bands with additional $d$-states always lie slightly lower in energy, although the effect in not very pronounced. The total energy of the calculation with additional $d$-states is $\approx 0.15 \text{ eV}$ lower than in FLAPW method.

It is worth noting that the electron density distri-
A and ˚ good correspondence with experimental values, a with our method, quantities gives an improvement even in this case, but the partial important conclusion is that the present method clearly 

tional tight-binding sequence of the approximate linear dependence of additional properties the localized orbitals of the LAPW+LO method. Finally, for correct transforma-

tions 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.

We have demonstrated how the method works for the face centered and body centered phases of lanthanum (β-La and γ-La) with the 5p-semicore shell separated from the valence states and for the hexagonal close packed structure of cadmium, where the semicore 4d-states overlap with the valence 5s-states, Sec. III.

Finally, we remark on the comparison between our approach and the LAPW+LO method [2]. Additional basis functions of the LAPW+LO method called local orbitals, are introduced in the framework of a pure variational consideration whereas our starting point is different – to use two different radial components in a single LAPW plane wave. The boundary conditions for supplemented functions, Eqs. (18a) and (18b), are a consequence of the procedure of finding a general solution. Next, we note that in our treatment for each l, m-component there are two supplemented functions. In particular, there is a radial function of the form (15c), which is absent in the LAPW+LO method. Finally, for correct transformational properties the localized orbitals of the LAPW+LO method are subjected to an additional procedure by attaching them to some (fictitious) plane waves [1,2]. In our approach there is no need for that because the supplemented basis functions are of the tight-binding form, which ensures their correct symmetry and fulfilment of Bloch’s law.

IV. CONCLUSIONS

We have presented a new method for the improvement of the LAPW description of the electronic band structure in the presence of extended-core (semicore) states. Starting with two LAPW radial solutions, Eqs. (15a) and (15c), having the same angular dependence $Y_{l,m}(\hat{r})$ but different linearization energies ($E_{l}(1)$ and $E_{l}(2)$) in the LAPW expansion inside MT-spheres, we have solved the problem by constructing additional basis functions $\phi_{s,i}$ ($i = 1, 2$) in the form of Eq. (17) [two functions, Eqs. (15a) 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 particular, our method with additional tight-binding functions gives $Q_d = 9.8057$. However, the formal distribution between extended and supplemented states, $Q_d(e-e) = 17.2138$, $Q_d(e-s) = -32.6738$, $Q_d(s-s) = 25.2658$ (defined by means of Eq. (21)), is surprising. Such big numbers with opposite signs are a consequence of the approximate linear dependence of additional tight-binding $d$–functions and standard extended LAPW $d$–states. The effect specific for a gapless energy spectrum is discussed in detail in Appendix D. The important conclusion is that the present method clearly gives an improvement even in this case, but the partial quantities $Q(e-e)$, $Q(e-s)$ and $Q(s-s)$ should be considered as technical ones.

The equilibrium lattice constants for hcp Cd found with our method, $a = 3.050$ Å and $c = 5.585$ Å, are in good correspondence with experimental values, $a = 2.98$ Å and $c = 5.62$ Å. The calculated cohesive energy is 1.25 eV, and the electric field gradient at the nucleus is 238.9 · 10$^{13}$ esu/cm$^3$ (218.7 · 10$^{13}$ esu/cm$^3$ in the final run over 729 points) which compares well with the experimental value of 230 · 10$^{13}$ esu/cm$^3$ [18].

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**TABLE II:** Energy band spectrum (in eV) of hexagonal close packed structure of Cd at the Γ-point of the Brillouin zone ($a = 3.050$ Å, $c = 5.585$ Å) with VWN exchange [13]. FLAPW+STBFs stands for the calculation with supplementary tight-binding $d$–functions presented in this work, $E_F$ is the Fermi energy, deg. stands for the bands degeneracy.

| N | deg. | FLAPW+STBFs | FLAPW |
|---|------|-------------|-------|
| 1 |      | -3.3596     | -3.3467 |
| 2 |      | -3.0893     | -3.0722 |
| 3 | (2)  | -2.8177     | -2.8032 |
| 4 | (2)  | -2.7649     | -2.7488 |
| 5 | (2)  | -2.3872     | -2.3713 |
| 6 |      | -2.3229     | -2.2894 |
| 7 | (2)  | -2.1160     | -2.1025 |
| 8 |      | 3.5044      | 3.5515  |
| 9 |      | 3.5700      | 3.6066  |
| $E_F$ | | 6.2794      | 6.3397  |
| 10 |     | 17.1264     | 16.1000 |

**TABLE III:** Partial charges $Q_l$ for hexagonal close packed structure of Cd ($a = 3.050$ Å, $c = 5.585$ Å) with VWN exchange [13]. FLAPW+STBFs stands for the calculation with supplementary tight-binding $d$–functions presented in this work. $Q_{out}$ is the charge in the interstitial region.

| $Q_l$ | FLAPW+STBFs | FLAPW |
|------|-------------|-------|
| $Q_s$ | 0.8136      | 0.8158 |
| $Q_p$ | 0.5562      | 0.5583 |
| $Q_d$ | 9.8057      | 9.8006 |
| $Q_f$ | 0.0196      | 0.0197 |
| $Q_g$ | 0.0041      | 0.0041 |
| $Q_{out}$ | 1.5972 | 1.5804 |
Appendix A

Solution to the system of linear equations, Eq. [12a], is given by

\[
\begin{align*}
    a_{s,1} &= \frac{1}{\Delta}(u_c u'_s - u'_c u_s), \quad \text{(A1a)} \\
    b_{s,1} &= \frac{1}{\Delta}(u'_c u_s - u_c u'_s), \quad \text{(A1b)}
\end{align*}
\]

and the solution to the system [12b] is

\[
\begin{align*}
    a_{s,2} &= \frac{1}{\Delta}(\dot{u}_c u'_s - \dot{u}'_c u_s), \quad \text{(A2a)} \\
    b_{s,2} &= \frac{1}{\Delta}(\dot{u}'_c u_s - \dot{u}_c u'_s). \quad \text{(A2b)}
\end{align*}
\]

Here

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

Appendix B

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

\[
\begin{align*}
    \langle \phi_{s,i} | O | \phi_{s,j} \rangle &= O^i_{j,s}, \quad \text{(B1a)} \\
    \langle \phi_{s,i} | H | \phi_{s,j} \rangle &= H^i_{j,s}. \quad \text{(B1b)}
\end{align*}
\]

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

\[
O^{11}_{s,s}(\vec{k}) = O_{s,s} \left(1 + C^{11}_{s,s} + C^{1}_{s,s}\right), \quad \text{(B2a)}
\]

where \( N_\alpha \) is the number of equivalent spheres \( \alpha \), while

\[
\begin{align*}
    O_{s,s} &= \frac{(4\pi)^2}{V} \left(R_{MT}^2 \right)^4 N_\alpha, \quad \text{(B2b)} \\
    C^{11}_{s,s} &= a_{s,1} a_{s,1} + b_{s,1} b_{s,1} N(u_s, \dot{u}_s), \quad \text{(B2c)} \\
    C^{1}_{s,s} &= a_{s,1} N(u_s, \dot{u}_s) + b_{s,1} N(u_s, \dot{u}_s). \quad \text{(B2d)}
\end{align*}
\]

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

\[
\mathcal{N}(u_1, u_2) = \int_{0}^{R_{MT}} u_1(r) u_2(r) r^2 dr. \quad \text{(B3)}
\]

Notice that \( N(u_c, u_s) = \mathcal{N}(u_s, u_s) = 1 \) and \( \mathcal{N}(u_c, \dot{u}_s) = \mathcal{N}(u_s, \dot{u}_s) = 0. \) 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 \( O_{s,s} \), Eq. [B2b], and \( O_{c,s}(\vec{k}_n) \), Eq. (C2c) should be changed accordingly.

For the block II we obtain

\[
O^{22}_{s,s} = O_{s,s} (\mathcal{N}(\dot{u}_c, \dot{u}_c) + C^{22}_{s,s} + C^{2}_{s,s}), \quad \text{(B4a)}
\]

where

\[
\begin{align*}
    C^{22}_{s,s} &= a_{s,2} a_{s,2} + b_{s,2} b_{s,2} \mathcal{N}(\dot{u}_s, \dot{u}_s), \quad \text{(B4b)} \\
    C^{2}_{s,s} &= a_{s,2} \mathcal{N}(\dot{u}_c, u_s) + b_{s,2} \mathcal{N}(\dot{u}_c, \dot{u}_s). \quad \text{(B4c)}
\end{align*}
\]

Finally, for the block III we get

\[
O^{12}_{s,s} = O_{s,s} \left( C^{12}_{s,s} + C^{1}_{s,s} + C^{2}_{s,s} \right), \quad \text{(B5a)}
\]

where

\[
C^{12}_{s,s} = a_{s,1} a_{s,2} + b_{s,1} b_{s,2} \mathcal{N}(\dot{u}_s, \dot{u}_s), \quad \text{(B5b)}
\]

and \( C^{1}_{s,s} \) is given by Eq. (B2d), while \( C^{2}_{s,s} \) by Eq. (B4c).

For the matrix elements of the Hamiltonian \( H^{11}_{s,s}(\vec{k}) \), Eq. (B1a), we also obtain three blocks. For the first block (I) we have

\[
H^{11}_{s,s} = O_{s,s} \left( E_s + E_s C^{11}_{s,s} + a_{s,1} b_{s,1} \right) + (E_c + E_s) C^{1}_{s,s} + b_{s,1} \mathcal{N}(u_c, u_s)). \quad \text{(B6)}
\]

Here \( E_c \) and \( E_s \) are energies at which the radial wave functions \( u_c(r) \) and \( u_s(r) \) are evaluated in the \( MT \)-sphere \( \alpha \).

For the second block (II) we get

\[
H^{22}_{s,s} = O_{s,s} \left( E_s \mathcal{N}(\dot{u}_c, \dot{u}_c) + E_s C^{22}_{s,s} + a_{s,2} b_{s,2} \right) + (E_c + E_s) C^{2}_{s,s} + \gamma_{s,s}, \quad \text{(B7a)}
\]

where

\[
\gamma_{s,s} = a_{s,2} \mathcal{N}(u_c, u_s) + b_{s,2} \left( \mathcal{N}(u_c, \dot{u}_s) + \mathcal{N}(\dot{u}_c, u_s) \right). \quad \text{(B7b)}
\]

For the third block (III) we have

\[
H^{12}_{s,s} = O_{s,s} \left( E_s (C^{12}_{s,s} + C^{1}_{s,s}) + a_{s,2} b_{s,1} \right) + E_c C^{2}_{s,s} + b_{s,1} \mathcal{N}(u_c, u_s)). \quad \text{(B8)}
\]

Appendix C

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

\[
\begin{align*}
    \langle \phi_{s,i} | O | \phi_{n} \rangle &= O^i_{s, e}(\vec{k}), \quad \text{(C1a)} \\
    \langle \phi_{s,i} | H | \phi_{n} \rangle &= H^i_{s, e}(\vec{k}). \quad \text{(C1b)}
\end{align*}
\]

The extended states here are the usual LAPW basis functions, Eq. [11], 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. [15a], [15c], [17].

For the matrix of overlap we get

\[
O^{1n}_{s,e}(\vec{k}) = O_{e,s}(\vec{k}_n) S^{1n}_{s,e}, \quad \text{(C2a)}
\]
where
\[ S_{\pi e}^{1n} = a_\pi + a_{s,1} a_\pi N(u_\pi, u_\pi) + a_{s,1} b_\pi N(\dot{u}_\pi, \dot{u}_\pi) + b_{s,1} a_\pi N(u_\pi, \dot{u}_\pi) + b_{s,1} b_\pi N(\dot{u}_\pi, \dot{u}_\pi), \] (C2b)
and the structure factor is
\[ O_{c,s}(\vec{k}_n) = \frac{(4\pi)^2}{V} (R_{MT}^c)^4 Y_{lm}^{*}(\vec{k}_n), \]
\[ \times \sum_\nu \exp[i(\vec{k}_n - \vec{k}) \vec{r}_{\nu,\alpha}]. \] (C2c)
Here, \( \vec{r}_{\nu,\alpha} \) stands for the coordinates of all \( \nu \) centers of \( MT \)-spheres of the type \( \alpha \) in the primitive unit cell. The factors \( N(u_1, u_2) \) in (C2b) are integrals between two functions given by Eq. [153].

The quantities \( a_\pi \) and \( b_\pi \) in Eq. (C2b) and below are standard LAPW expansion coefficients for the component with \( l, m \), defined by Eq. [285] and [295], i.e. \( a_\pi = a_\pi^{0} \) and \( b_\pi = b_\pi^{0} \). Since they depend on \( \vec{k}_n \), \( l \), and \( \alpha \), we can write \( a_\pi = a_\pi^{0}(\vec{k}) \), \( b_\pi = b_\pi^{0}(\vec{k}) \). Explicit expressions for them can be found in Ref. [23].

The matrix element for the second case \((i = 2)\) reads as
\[ O_{c,s}^{2n}(\vec{k}) = O_{c,s}(\vec{k}_n) S_{\pi e}^{2n}, \] (C3a)
where
\[ S_{\pi e}^{2n} = b_\pi N(u_\pi, \dot{u}_\pi) + a_{s,2} a_\pi N(u_\pi, u_\pi) + a_{s,2} b_\pi N(\dot{u}_\pi, \dot{u}_\pi) + b_{s,2} a_\pi N(u_\pi, \dot{u}_\pi) + b_{s,2} b_\pi N(\dot{u}_\pi, \dot{u}_\pi). \] (C3b)

Below we quote the matrix elements for the Hamiltonian,
\[ H_{e,s}^{1n}(\vec{k}) = O_{e,s}(\vec{k}_n) (E_e S_{\pi e}^{1n} + b_\pi + a_{s,1} a_\pi N(u_\pi, u_\pi) + b_{s,1} b_\pi N(u_\pi, \dot{u}_\pi)), \] (C4)
\[ H_{e,s}^{2n}(\vec{k}) = O_{e,s}(\vec{k}_n) (E_e S_{\pi e}^{2n} + a_{s,2} a_\pi N(u_\pi, u_\pi) + b_{s,2} b_\pi N(u_\pi, \dot{u}_\pi)). \] (C5)

Here \( O_{e,s} \) is given by Eq. (C2c), while \( S_{\pi e}^{1n} \) 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. [171], 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
\[ u_\varepsilon(r) = u_s(r) + \dot{u}_s(r) \varepsilon + \frac{1}{2} \ddot{u}_s(r) \varepsilon^2 + \frac{1}{6} \dddot{u}_s(r) \varepsilon^3 + O(\varepsilon^4), \] (D1a)
\[ \dot{u}_\varepsilon(r) = \dot{u}_s(r) + \ddot{u}_s(r) \varepsilon + \frac{1}{2} \dddot{u}_s(r) \varepsilon^2 + O(\varepsilon^3), \] (D1b)
for \( u_\varepsilon(r) \) and \( \dot{u}_\varepsilon(r) \) and substituting them in Eqs. [15b], [15c], we arrive at
\[ R_{i,m}^{11}(r) = \frac{1}{2} \varepsilon^2 C_0 e^{i\vec{k}_n \vec{R}_e} \left[ \dddot{u}_s + \frac{1}{3} \varepsilon \ddot{u}_s + O(\varepsilon^2) \right] + C_1 \dddot{u}_s + b_{s,1} \dddot{u}_s, \] (D2a)
\[ R_{i,m}^{s2}(r) = \varepsilon C_0 e^{i\vec{k}_n \vec{R}_e} \left[ \dddot{u}_s + \frac{1}{2} \varepsilon \ddot{u}_s + O(\varepsilon^2) \right] + C_2 \dddot{u}_s + b_{s,2} \dddot{u}_s. \] (D2b)
Here
\[ a_{s,1} = \frac{1}{\varepsilon^2}(a_{s,1} + 1), \quad b_{s,1} = \frac{1}{\varepsilon}(b_{s,1} + \varepsilon); \] (D3a)
\[ a_{s,2} = \frac{1}{\varepsilon} a_{s,2}, \quad b_{s,2} = \frac{1}{\varepsilon}(b_{s,2} + 1). \] (D3b)

The prefactors \( \varepsilon^2/2 \) and \( \varepsilon \) in Eqs. (D2a), (D2b) are not very important, because as a consequence of solving secular equations these basis functions will be effectively orthonormalized. Functions \( R_{i,m}^{11}(r) \) and \( R_{i,m}^{s2}(r) \) 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
\[ U_1(r) = \dddot{u}_s + a_{s,1} \dddot{u}_s + b_{s,1} \dddot{u}_s, \] (D4a)
\[ U_2(r) = \dddot{u}_s + a_{s,2} \dddot{u}_s + b_{s,2} \dddot{u}_s, \] (D4b)
where the coefficients \( a_{s,1} \) etc. can be expressed through \( a_{s,1}, \) etc. Since the functions \( \dddot{u}_s(r) \) and \( \dddot{u}_s(r) \) are linear independent, the same property applies to \( U_1(r) \) and \( U_2(r) \) and, consequently, to \( R_{i,m}^{11}(r) \) and \( R_{i,m}^{s2}(r) \), although the property deteriorates as \( \varepsilon \to 0 \). Second, we still can impose the boundary conditions (15a) and (15b).

However, since the initial functions \( R_{i,m}^{11}(r) \) and \( R_{i,m}^{s2}(r) \), have almost identical radial dependence (neglecting terms with \( \varepsilon \) \( \dddot{u}_s \) and the others of high order of \( \varepsilon \) in Eqs. (D2a), (D2b) make them completely identical), the normalization procedure leads to the appearance of an effective basis state \( \phi' \), which is orthogonal to other basis states and expressed through the linear combination of initial states, \( \phi' = C_1 \phi_{s,1} + C_2 \phi_{s,2} \) 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. [11C].
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