

# DFTB<sup>+</sup> and lanthanides

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**Abstract.** DFTB<sup>+</sup> is a recent general purpose implementation of density-functional based tight binding. One of the early motivators to develop this code was to investigate lanthanide impurities in nitride semiconductors, leading to a series of successful studies into structure and electrical properties of these systems. Here we describe our general framework to treat the physical effects needed for these problematic impurities within a tight-binding formalism, additionally discussing forces and stresses in DFTB. We also present an approach to evaluate the general case of Slater-Koster transforms and all of their derivatives in Cartesian coordinates. These developments are illustrated by simulating isolated Gd impurities in GaN.

## 1. Introduction

The Kohn-Sham density functional theory (DFT) can be approximated to give a family of semi-empirical methods with much lower computational costs than full DFT. The Density Functional based Tight binding method (DFTB) [1] is a non-orthogonal method derived from an approximate second-order expansion of DFT with respect to fluctuations in the density [2]. This gives a transparent and parameter-free technique where all terms can be readily pre-calculated using DFT. This method has been applied with some success to a range of solid state, molecular and biological systems.

The study of systems like rare-earth or transition metal containing compounds and solids requires somewhat different techniques beyond charge self-consistent DFTB [3]. Spin polarisation [4] is essential, and for the strongly correlated  $d$  and  $f$  electrons, methods like LDA+U [5] or pseudo-SIC [6] also become necessary. Additionally lanthanide atomic numbers are between 57 and 70, hence relativistic effects start becoming important. The latest version of the DFTB<sup>+</sup> code [7] includes extensions to address all of this additional complexity in the treatment of lanthanides, the DFTB method having been substantially extended by adapting LDA+ $U$  and pseudo-SIC into a common framework [8] and adopting Russel-Saunders  $L \cdot S$  coupling [4]. Here we describe the approach used to include these disparate effects within an common computational framework.

### 1.1. non-SCC DFTB and Slater-Koster transforms

In the present case, Slater-Koster type tight binding [9] requires geometrical transformations for two centre terms between orbitals with angular momentum of up to  $f$ . Closed form expressions for these transforms to arbitrary angular momentum [10] and their analytical derivatives [11] are available. However, in the spherical-polar coordinate systems used, there are spurious

singularities at the poles, leading to these points being presented as separate special cases without a continuous functional form over the whole coordinate range. The transformations are written in terms of directional cosines between atomic pairs ( $N$ ,  $M$  and  $L$ ) and depend on products of the general form  $\exp(i\phi|m|)d_{m,m'}^l(\theta)$  where  $l$ ,  $m$  and  $m'$  are the usual angular labels,  $\theta$  and  $\phi$  are the polar and azimuthal angles (see Ref. [10] for details). The apparently problematic part of the Wigner- $d$  matrices in these terms is

$$d_{m,m'}^l \propto \sum_{t=0, \text{non-neg}}^{2 \times l + 1} (1 - N)^{t+m/2+m'/2} (1 + N)^{l-t-m/2+m'/2} \times \frac{(-1)^t}{(l+m'-t)!(l-m-t)!t!(t+m-m')!}$$

where the summation over  $t$  is such that the factorial terms in the denominator are all  $\geq 0$ . This summation constraint leads to the  $(1 \pm N)$  terms being well-behaved even at the poles ( $|N| = 1$ ). This holds from  $t \geq 0$  and  $t \geq m' - m$ ,  $\therefore t + m/2 + m'/2 \geq 0$  and similarly,  $l + m' - t \geq 0$  and  $l - m - t \geq 0$ ,  $\therefore l - m/2 + m'/2 - t \geq 0$ .

However the problem of the azimuthal angle, which becomes undefined at either pole, remains. This can be partially alleviated by defining this angle using  $\phi = \text{atan2}(M, -L)$ , but care is required since  $\text{atan2}(0, 0)$  is again undefined (but in specific machine implementations, Intel's FPATAN [12] for example, it is defined as the required case of  $\pm 0$  for sign choices of  $\text{atan2}(\pm 0, +0)$ ). The overall exponential term is then of the form  $\left( (M + iL) / \sqrt{M^2 + L^2 + \delta} \right)^{|m|}$  where delta is infinitesimally positive, and again the  $M = L = 0$  case requires a convention that the function gives +1.

Since the system as a whole is invariant under the rotation group  $O_3$ , a simpler option is to perform the calculation in a global coordinate system rotated, for example, in the  $xz$  plane and chosen such that no inter-atomic vectors align exactly along the  $z$  axis (in all cases  $|N| \neq 0$ ). This allows the original rotation expressions and any order of their derivatives to be used. In the situation that a change in geometry brings an atomic pair into exact alignment with  $\pm z$ , the stable Wigner  $d$ -matrix form given above can then be used to rotate any orientationally dependent terms in the Hamiltonian away from the problematic alignment by an additional application of Eqns. 5-6 of Ref [10] with the azimuthal change,  $\gamma$ , chosen as 0. However, in practice, DFTB<sup>+</sup> currently uses explicitly coded cases of the geometrical transformations up to  $f$ .

### 1.2. Potential shifts

The total energy for spin-polarised SCC DFTB is the following functional of the density matrix  $\rho$ :

$$E = \sum_{\mu\nu} H_{\mu\nu}^0 \rho_{\nu\mu} + \frac{1}{2} \sum_{ab} (\delta q_a[\rho] \gamma_{ab} \delta q_b[\rho] + \delta m_a[\rho] W_{ab} \delta m_b[\rho])$$

where  $\delta q$  and  $\delta m$  are fluctuations in the charge and magnetisation respectively from the reference system used to construct the non-self-consistent Hamiltonian,  $H^0$ . The domains  $a$  and  $b$  are Mulliken populations constructed from the density and overlap ( $S$ ) matrices,  $q_\mu = \frac{1}{2} \sum_\nu S_{\mu\nu} \rho_{\nu\mu}$ , where  $q_\mu$  is additionally summed over either whole atoms or atomic shells with a given value of  $l$  to give  $q_a$ . The couplings  $\gamma$  and  $W$  are derived from either an approximation to the Hartree and exchange correlation or an on-site Stoner-like exchange contribution respectively between the fluctuations. The reference system chosen is a superposition of neutral and spin-free atomic densities (or potentials, see Ref. [2] for more details of conventional DFTB).

The Hamiltonian for the system, derived using the usual approach of minimising the total energy subject to orthonormality of the resulting single particle states, is then of the general form

$$H_{\mu\nu}^{\sigma} = H_{\mu\nu}^0 + \frac{1}{2}S_{\mu\nu} (\Omega_{\mu}^{\sigma} + \Omega_{\nu}^{\sigma})$$

where the spin dependent shifts are defined as  $\Omega_{\mu}^{\sigma} = \sum_b \gamma_{\mu b} \delta q_b[\rho] + \sigma \sum_b W_{\mu b} \delta m_b[\rho]$  for spins  $\sigma = \pm 1$ . More general Hamiltonian contributions can also be cast into this form. An example would be the constrained density method of Dederichs *et al.* [13] where the ground state density matrix is found for a chosen charge distribution (so similar to the Levy–Lieb constrained search method), by finding the ground state of the system in a (carefully chosen) external potential. Wu and Van Voorhis [14] formulated this as a maximisation problem for integral constraints using undetermined multipliers, by defining a new functional:

$$W[n(\mathbf{r}), \mathbf{V}] = E[n(\mathbf{r})] + \sum_i V_i \left( \int w_i(\mathbf{r})n(\mathbf{r})dr - N_i \right)$$

to constrain  $N_i$  electrons to match the weighting envelope  $w_i(\mathbf{r})$  over the density or magnetisation within region that the  $i$ -th constraint is formulated.  $W$  is convex in  $n(\mathbf{r})$  and concave in  $\mathbf{V}$ . This then also gives a contribution to the DFT potential. To write these constraints for DFTB’s Mulliken-charge based tight-binding populations is straight forward, and again gives a stationary energy structure, as with DFT.

$$W[\rho, \mathbf{V}] = E_{\text{DFTB}}[\rho] + \sum_i V_i \left( \sum_{\mu} w_{i\mu} q_{\mu}[\rho] - N_i \right)$$

where  $\mu$  are basis function labels for the  $i^{\text{th}}$  constraint, giving an equivalent shift contribution of the form

$$\Omega_{\mu} = \sum_i V_i \sum_{\nu} w_{i\nu} S_{\mu\nu}$$

More general constraints of the form  $U_i (w_{i\mu} q_{\mu}[\rho] - N_i)^{\kappa}$  can also be used, where in the case that  $\kappa$  is odd the constraint is enforced by the choice of  $U$  as a Lagrange undetermined multiplier, while for even values of  $\kappa$  this constraint is approximately enforced as  $U \rightarrow \infty$ .

### 1.3. Generalisations for orbital potentials and $L \cdot S$

Instead of choosing Mulliken populations as our basic variable, the more general on-site occupation matrix [15] can be used for assorted semi-local non-mean field potentials. These matrices are defined as

$$n_{\mu\nu} = \frac{1}{2} \sum_{\tau} (S_{\mu\tau} \rho_{\tau\nu} + \rho_{\mu\tau} S_{\tau\nu}); \mu\nu \in a$$

where the matrix diagonal is the conventional Mulliken charge for atom  $a$ . Further generalising, the Hamiltonian and occupation matrices can be projected onto the orthogonal Pauli matrices, giving charge and non-collinear vectoral magnetisation in the system. The spin-block Hamiltonian and density matrix can then be written as coefficients of Pauli matrices ( $\sigma_{I,x,y,z}$ ):

$$H_{\mu\nu} = H_{\mu\nu}^0 \sigma_I + \frac{1}{2} S_{\mu\nu} \sum_{j=x,y,z} (\Omega_{\mu}^j + \Omega_{\nu}^j) \sigma_j$$

$$\rho = \sum_{j=I,x,y,z} \rho_{\nu\mu}^j \sigma_j$$

for the corresponding generalised vectorial shifts. In the case of Russel-Saunders spin-orbit coupling (or Complex Absorbing Potentials [16]) these Pauli-matrix coefficients become complex.

#### 1.4. Forces and stresses

First derivatives of the band-structure part of the total energy can similarly be written in terms of the shift components, using the Hellman-Feynman theorem and the Pulay correction for the change of basis (using the energy weighted density matrix,  $\rho^E$ ). The  $i^{\text{th}}$  component of the derivative of energy with respect to the position of atom  $a$  due to atom  $b$  is

$$\left. \frac{\partial E}{\partial x_{ai}} \right|_b = \sum_{\mu \in a} \sum_{\nu \in b} \frac{\partial H_{\mu\nu}^0}{\partial x_{ai}} \rho_{\nu\mu} + \sum_{\mu \in a} \sum_{\nu \in b} \frac{\partial S_{\mu\nu}}{\partial x_{ai}} ((\Omega_\mu + \Omega_\nu) \rho_{\nu\mu} - \rho_{\nu\mu}^E)$$

where the  $i^{\text{th}}$  Cartesian component of the force on atom  $a$  is then

$$F_{ai} = - \sum_b \left. \frac{\partial E}{\partial x_{ai}} \right|_b$$

and the summation is calculated using the real-space matrices of Ref. [7]. The stress tensor is also of similar form, with band-structure contributions of

$$\sigma_{ij} = - \frac{1}{2V_{\text{cell}}} \sum_{ab} \left. \frac{\partial E}{\partial x_{ai}} \right|_b (x_{aj} - x_{bj})$$

where  $V_{\text{cell}}$  is the unit cell volume. For the total stress and forces, the repulsive energy and also long range interactions such as the electrostatic double counting and the dispersive interactions introduce other terms into the total expressions, but these are of standard forms from the literature.

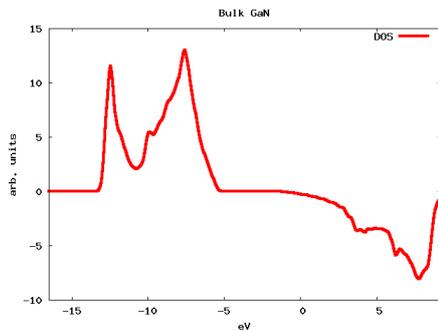
The two main advantages of using the shift contributions formulation of the forces are that firstly it simplifies the implementation of the majority of the force terms (since the code is then common for many distinct contributions) using the already calculated shift contributions from the Hamiltonian. Secondly it provides a semi-independent test for the correctness of any new extension to DFTB, since while the Hamiltonian and the band-structure part of the forces depend on the shifts, it is generally not possible to calculate the total energy from the total shift, due to the differing functional forms of the various contributions. Therefore agreement between the numerical and analytical derivatives of the energy signify that the independent shift and total energy terms agree (and therefore the shift is the derivative of the energy with respect to the eigenstates of the system).

## 2. Gd doped GaN

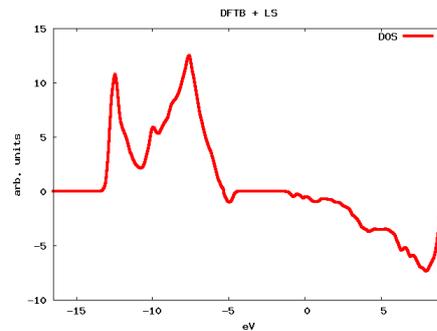
Focussing on a specific application of this formalism we now consider treatment a specific substitutional rare-earth impurity in gallium nitride. RE<sub>Ga</sub> substitutionals are the simplest stable lanthanide defects in GaN [17, 18, 19, 20, 21, 22, 23]. From experimental studies we know that the ions prefer the Ga position [24], occur in the 3+ valence state [25] and possess  $C_{3v}$  symmetry [26] with relatively short distances to the surrounding N-ligands [27]. Gadolinium doped GaN has been suggested to [28] have an extraordinarily large magnetic moment per dopant atom.

The local structure of the substitutional is insensitive as to whether the Ga-3d orbitals are treated as valence or core. The results here use a parameterization where the Ga-3d states are not included in the valence, but these do not differ substantially from results obtained by including them [17]. Supercells containing 192 atoms and a 6<sup>3</sup> Monkhorst-Pack  $k$ -point sampling [29] were

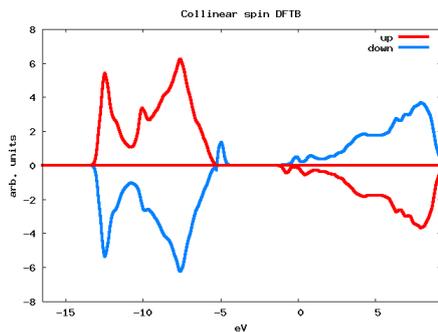
used to calculate the results reported here, with the density of states for the bulk GaN supercell used shown in Fig. 1, with the density inverted in sign above the Fermi energy (this convention is also used in other plots where two spin channels are shown). The substitutional  $\text{Gd}_{\text{Ga}}$  in the lowest energy configuration is found to have  $C_{3v}$  symmetry as expected with Gd–N distances of 2.246 and 2.242 Å for the axial and 3 fold surrounding bonds respectively.



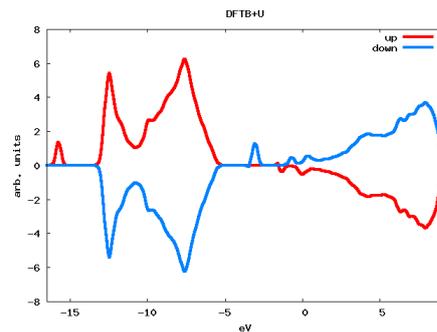
**Figure 1.** Bulk DOS of GaN, empty states are marked below 0.



**Figure 2.** Non-collinear z-aligned density of states for Gd doped GaN including spin-orbit coupling.



**Figure 3.** Collinear density of states for Gd doped GaN.



**Figure 4.** DFTB+U collinear density of states for Gd doped GaN.

The conventional spin polarised DFTB calculation leads to 7 unpaired spins primarily localised on the Gd (6.77) with 96 % of that localized on the  $4f$  shell. As shown in figure 3 the presence of the Gd ions splits the spin degeneracy of the bottom of the conduction band and would provide ferromagnetic coupling in the case of strong  $n$ -type doping [30], however this does not explain the observed moment in the experimental conditions of highly resistive material [28].

The collinear ( $z$ ) spin-polarized and non-collinear calculations are degenerate in energy. The system is, as expected, degenerate with respect to rotation of the spin direction in the non-collinear case. The addition of spin orbit coupling splits this degeneracy (values of the screened atomic spin-orbit constants,  $\xi$ , are taken from Refs. [31, 32]), but by less than 1 meV. The  $4f$  shell is strongly spin polarized with  $6.5 \mu_B$  unpaired spin and a parallel orbital momentum of  $0.28 \mu_B$ , yielding a total moment of  $6.8 \mu_B$ , all similar to the expected  $^8S_{7/2}$  ground state. As shown in Fig. 2 this does not lead to a substantial change in the density of states compared to the collinear spin polarised case.

The  $4f$  states of Gd are present around the valence band maximum for the spin-polarised calculations, due to the incorrect treatment of the self-interaction of these states. Applying LDA+U type potentials [18] shifts this type feature, moving the occupied states downwards in

energy, and depending on the potential, the unoccupied states upwards.

Previous application of DFTB+U to other rare-earths and their complexes [33] have demonstrated the applicability of this method to these systems. In the specific case of Gd<sub>Ga</sub> the “FLL” LDA+U functional has been applied with a choice of 7.43 eV for ( $U - J$ ) in accordance with Ref. [8]. This leads to the an increase in the total energy by  $\sim 0.8$  eV, consisting primarily of an increase of 1.4 and 0.3 eV in the band structure and additional LDA+U energy terms, but a reduction of 0.9 eV in the spin polarization energy, due primarily to the increased localization of the unpaired spin on the Gd 4*f* shell. This is evident between Figs. 3 and 4 where the empty 4*f* states are lifted clear from the valence band, while the filled states drop below the region of the valence band.

### 3. Acknowledgements

We thank Simone Sanna for making available his unpublished parameterization of Gd doped GaN. This work was partly funded by the FP7 ITN “RAINBOW” (PITN-GA-2008-213238)

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