Precise Kohn-Sham total-energy calculations at reduced cost

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Abstract

The standard way to calculate the Kohn-Sham orbitals utilizes an approximation of the potential. The approximation consists in a projection of the potential into a finite subspace of basis functions. The orbitals, calculated with the projected potential, are used to evaluate the kinetic part of the total energy, but the true potential is used to evaluate the interaction energy with the electron density. Consequently, the Kohn-Sham total-energy expression loses its stationary behaviour as a functional of the potential. It will be discussed that this stationarity is important for the calculation of precise total energies at low computational cost and an approach will be presented that practically restores stationarity by perturbation theory. The advantage of this approach will be illustrated with total-energy results for the example of a disordered CrFeCoNi high entropy alloy.

1 Introduction

The standard way to solve the Kohn-Sham density-functional equations is based on the variational principle of the total energy. The Kohn-Sham orbitals are expanded into a finite set of basis functions and the total energy is minimized with respect to the expansion coefficients. In practice, this means that the Kohn-Sham effective potential, defined as the sum of external, Hartree and exchange-correlation potentials, is approximated by a projection into a finite subspace of basis functions. This approximation leads to first order errors for the orbitals, the density and the potential. For precise total-energy calculations, these first order errors do not represent a problem because the Kohn-Sham total-energy expression can be written in a form [1, 2], which is stationary with respect to orbitals, density and potential. This means that these first order errors lead to only second order errors for the total energy.

Unfortunately, however, the approximation of the potential by projection into a finite subspace of basis functions introduces another important error that is associated with the evaluation of the total-energy functional. While
the kinetic part of the total energy is evaluated with the projected potential, the true potential is used for the evaluation of the interaction energy between the potential and the electronic density. As a consequence of the two different potentials, the total-energy expression loses its stationarity as a functional of the potential and total-energy calculations are considerably more expensive than they should be. It is important to note that this problem is not removed if the quality of the basis set is improved. The use of more basis functions or the choice of better basis functions can reduce the size of the evaluation error, but cannot change its fundamental unfavourable property that it destroys the stationarity with respect to the potential.

In present article it is shown how the error arising from the use of two different potentials can be determined and that this information can be used to obtain corrections which considerably improve the calculated total energies. Because the corrections must be used only once after the density-functional self-consistency steps, only a small overhead of computing time is required to obtain precise total energies. For the example of projection into finite subspaces of spherical harmonics it is shown that almost as precise total energies are obtained by perturbation theory. Because perturbation theory is computationally inexpensive, it can be used during the self-consistency steps to modify the projected potential such that density, potential and total energy are obtained in a consistent manner.

The outline of the article is as follows. In section 2 the total-energy functional and its stationarity properties are discussed. In section 3 non-local potentials are introduced, which describe projection into subspaces of spherical harmonics, and it is explained that for these angular projection potentials the density and the kinetic energy can be determined numerically practically exactly. Section 3 also provides two expressions that can be used to determine the total-energy error either from the single-particle energies or from the interaction energy between density and potential. In section 4 it is shown how perturbation theory can be used to obtain precise total energies with considerably reduced computational resources. Section 5 contains a summary and an outlook. In the appendix the evaluation error is discussed for plane wave methods in order to motivate further work beyond the present article for projection potentials which correspond to other basis functions than spherical harmonics.

2 Total-energy functional

The total-energy of Kohn-Sham density-functional theory is usually written as

\[ E_{\text{tot}}[n(r)] = T_s[n(r)] + \int \text{d}V_{\text{ext}}(r)n(r) + E_{\text{hxc}}[n(r)] + E_{\text{nn}}. \]  

(1)

Here \( n(r) \) is the electron density, \( V_{\text{ext}}(r) \) the external potential provided by the nuclei, \( E_{\text{nn}} \) the interaction energy of the nuclei and

\[ E_{\text{hxc}}[n(r)] = \frac{c^2}{2} \int \int \frac{n(r)n(r')}{|r-r'|} \text{d}r \text{d}r' + E_{\text{xc}}[n(r)] \]  

(2)
the sum of Hartree and exchange-correlation energy. $T_s[n(r)]$ is the kinetic energy of the non-interacting Kohn-Sham reference system, which in Rydberg atomic units $\hbar^2/2m = 1$ is given by

$$T_s[n(r)] = \sum_i n_i \int d\mathbf{r} \, \phi_i^*(\mathbf{r}) \left[ -\nabla^2 + V(\mathbf{r}) \right] \phi_i(\mathbf{r}).$$  \hspace{1cm} (3)

Here $\phi_i(\mathbf{r})$ are the Kohn-Sham orbitals and $n_i$ are occupation numbers which are one for occupied orbitals and zero for unoccupied orbitals. It is well known that $E_{\text{tot}}[n(r)]$ is stationary with respect to $n(r)$ and that the minimum energy $E_0^{\text{tot}}$ is obtained for the ground-state density $n_0(\mathbf{r})$.

Haydock and Heine have shown [1, 2] that the functional (1) can be generalized into a functional which is stationary with respect to density, potential and orbitals. This functional can be written as

$$E_{\text{tot}}[n(r)] = \sum_i n_i \int d\mathbf{r} \, \phi_i^*(\mathbf{r}) \left[ -\nabla^2 + V(\mathbf{r}) \right] \phi_i(\mathbf{r})$$

$$- \int d\mathbf{r} V(\mathbf{r}) n(\mathbf{r}) + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{hxc}}[n(\mathbf{r})] + E_{\text{nn}} - \sum_i n_i \epsilon_i \left[ \int d\mathbf{r} \, \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) - 1 \right]$$

where Lagrange multipliers $\epsilon_i$ are used to enforce the normalization of the orbitals. Variation of (4) with respect to the orbitals leads to the Kohn-Sham equation

$$\left[ -\nabla^2 + V(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$  \hspace{1cm} (5)

for the orbitals, variation with respect to the density leads to the standard expression

$$V(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \frac{\delta E_{\text{hxc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$  \hspace{1cm} (6)

for the effective potential and variation with respect to the potential leads to the standard expression

$$n(\mathbf{r}) = \sum_i n_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})$$  \hspace{1cm} (7)

for the density. If (5-7) are solved self-consistently, the functional (4) gives the usual density-functional total energy for the ground state. Furthermore, if $\phi_i(\mathbf{r})$, $V(\mathbf{r})$, $n(\mathbf{r})$ are approximated, the total-energy error is of second order in $\delta \phi_i(\mathbf{r})$, $\delta V(\mathbf{r})$, $\delta n(\mathbf{r})$.

For the example of projection into a finite subspace of spherical harmonics it has been shown recently [3, 4] that the Green function for the differential equation (5) can be calculated practically exactly. This means that no approximation must be made for the orbitals and the density. Thus, the relevant error arises from $\delta V(\mathbf{r})$ while errors arising from $\delta \phi_i(\mathbf{r})$ and $\delta n(\mathbf{r})$ are negligible. If,
as suggested in [1, 2], the total-energy error is of second order in $\delta V(r)$, the calculated total energy should rapidly improve with an increasing subspace of spherical harmonics and only small subspaces should be necessary for precise results. This rapid improvement, however, is not found. This implies that the error is not of second order and that the stationarity of (4) with respect to $\delta V(r)$ is not fulfilled. The reason for this deficiency is that the second term in the total-energy functional (4) must contain the true potential in order that the condition (6) is satisfied whereas the first term of (4) contains the approximated projected potential.

3 Angular projection potentials

The approximation of the potential by a finite number of matrix elements can be understood as a projection of the potential into a finite subspace of basis functions. The projected potential is non-local which complicates the mathematical and numerical treatment because the single-particle Schrödinger equation is transformed from a differential equation into an integro-differential equation, formally by the replacement

$$V(r)\varphi_i(r) \Rightarrow \int V(r,r')\varphi_i(r')dr'.$$

This means that the local potential, which acts as multiplicative factor, is replaced by the non-local potential which acts as an integral operator.

For projection into subspaces of spherical harmonics the non-local potential has the form

$$V(r,r') = \frac{\delta(r-r')}{r^2}V(r,\hat{r},\hat{r}')$$

with

$$V(r,\hat{r},\hat{r}') = \sum_{LL'} Y_L(\hat{r})V_{LL'}(r)Y_{L'}(\hat{r}).$$

where $L = (l, m)$ is a combined index for the angular quantum numbers. For systems which are described by a sum of such angular projection potentials, centred at the atomic positions $\mathbf{R}^n$, the integro-differential Schrödinger equation can be solved [5] by a generalization of the Koringa-Kohn-Rostoker Green-function (KKR-GF) method. The important advantage of using non-local projection potentials instead of local potentials is that the matrix elements

$$V_{LL'}(r) = \int d\hat{r} \int d\hat{r}' Y_L(\hat{r})V(r,\hat{r},\hat{r}')Y_{L'}(\hat{r})$$

for the projection potential are exactly zero for $l > l_{\text{max}}$ and for $l' > l_{\text{max}}$ because of the orthogonality of the spherical harmonics. In contrast to this, a local potential $V(r)$ is described by a infinite number of matrix elements

$$V_{LL'}(r) = \int d\hat{r} Y_L(\hat{r})V(r)Y_{L'}(\hat{r}).$$
and thus can be treated only approximately. An important consequence of the exact description of the non-local angular projection potentials by a finite number of matrix elements is that the density and the Green function can be expressed by a finite number of terms with analytically known dependence on the angular variables \([3, 4]\). Only the radial dependence must be treated numerically. With the present computer capabilities this can be done practically exactly. This means that the precision of the total energies is essentially determined by the single parameter \(l_{\text{max}}\) and that an increase of \(l_{\text{max}}\), which improves the agreement between the projection potential and the true effective potential, should increase the precision.

### 3.1 Green function

The Green function \(G(\mathbf{r}, \mathbf{r}'; \epsilon)\) for the integro-differential Schrödinger equation can be obtained by solving the integral equation

\[
G(\mathbf{r}, \mathbf{r}'; \epsilon) = g(\mathbf{r}, \mathbf{r}'; \epsilon) + \int d\mathbf{r}'' g(\mathbf{r}, \mathbf{r}''; \epsilon) \int d\mathbf{r}''' V(\mathbf{r}'', \mathbf{r}''') G(\mathbf{r}''', \mathbf{r}'; \epsilon).
\]  

(13)

Here \(g(\mathbf{r}, \mathbf{r}'; \epsilon)\) is the analytically known Green function of free space (with zero potential), which is defined by the differential equation

\[
[-\nabla^2 - \epsilon] g(\mathbf{r}, \mathbf{r}'; \epsilon) = -\delta(\mathbf{r} - \mathbf{r}').
\]  

(14)

As shown in detail in [5], for a sum of angular projection potentials of type (10), centred at the atomic positions, the Green function can be written as

\[
G(\mathbf{r} + \mathbf{R}^n, \mathbf{r}' + \mathbf{R}^{n'}; \epsilon) = \sum_{L} \delta_{nn'} S^n_L(\mathbf{r}'; \epsilon) R^n_L(\mathbf{r}'; \epsilon)
\]  

(15)

\[
+ \sum_{LL'} R^n_L(\mathbf{r}; \epsilon) G_{LL'}^{nn'}(\epsilon) R^{n'}_{L'}(\mathbf{r}'; \epsilon)
\]

with matrix elements

\[
G_{LL'}^{nn'}(\epsilon) = g_{LL'}^{nn'}(\epsilon) + \sum_{n''} \sum_{L''L'''} g_{LL'}^{nn''}(\epsilon) t_{L''L'''}^{n''n'''}(\epsilon) G_{L''L'''}^{n''n'''}(\epsilon)
\]  

(16)

that can be obtained by solving this linear matrix equation either directly or by iterative techniques [6]. Here \(g_{LL'}^{nn''}(\epsilon)\) are the analytically known matrix elements of the free-space Green function \(g(\mathbf{r}, \mathbf{r}'; \epsilon)\). Note that the symbols \(\mathbf{r}\) and \(\mathbf{r}'\) in (15), as well as below in (17) and (24-28), denote coordinates originating at the atomic positions \(\mathbf{R}^n\) (with \(\mathbf{r}_<\) and \(\mathbf{r}_>\) being defined as the ones with larger and smaller length), while elsewhere they denote coordinates in all space.

The functions \(R^n_L(\mathbf{r})\) and \(S^n_L(\mathbf{r})\) are simple products of spherical Bessel or Hankel functions with spherical harmonics for \(l > l_{\text{max}}\), while for \(l \leq l_{\text{max}}\) they are given by finite expansions in spherical harmonics [3]. As a consequence of
this fact, the angular dependence of the Green function (15) is also analytically known \([5]\) as
\[
G(r + R^n, r' + R^{n'}; \epsilon) = \sum_{LL'} Y_L(\hat{r}) Y_{L'}(\hat{r}') G^{nn'}_{LL'}(r, r'; \epsilon),
\]
a formula which will be used in the next subsection.

### 3.2 Kinetic energy

For the evaluation of the total-energy functional one needs the density
\[
n(r) = -\frac{2}{\pi} \lim_{r' \to r} \int_{-\infty}^{E_F} \text{Im} \, \text{d}G(r, r'; \epsilon + i0^+) \tag{18}
\]
and the kinetic energy
\[
T_s[n(r)] = -\frac{2}{\pi} \int \text{d}r \lim_{r' \to r} \int_{-\infty}^{E_F} \text{d} \epsilon \left[ -\nabla_r^2 - \epsilon \right] G(r, r'; \epsilon + i0^+). \tag{19}
\]

\(E_F\) is the Fermi level and \(0^+\) an infinitesimally small positive quantity which indicates that the integral must be performed in the complex \(\epsilon\) plane just above the real \(\epsilon\) axis. The factor two in these equations, which is valid for non-spin-polarized systems, simplifies the notation. Generalization to spin-polarized systems is straightforward. With the density of states
\[
n(\epsilon) = -\frac{2}{\pi} \int \text{d}r \lim_{r' \to r} \text{Im} G(r, r'; \epsilon + i0^+), \tag{20}
\]
the kinetic energy can be expressed as
\[
T_s[n(r)] = \int_{-\infty}^{E_F} \text{d} \epsilon \epsilon n(\epsilon) \tag{21}
\]
\[
-\frac{2}{\pi} \int \text{d}r \lim_{r' \to r} \int_{-\infty}^{E_F} \text{d} \epsilon \left[ -\nabla_r^2 - \epsilon \right] G(r, r'; \epsilon + i0^+).
\]

Here insertion of
\[
\left[ -\nabla_r^2 - \epsilon \right] G(r, r'; \epsilon) = -\delta(r - r') - \int \text{d}r'' V(r, r'') G(r'', r'; \epsilon), \tag{22}
\]
which is obtained from (15) by application of the operator \([-\nabla_r^2 - \epsilon]\) and by use of (14), leads to
\[
T_s[n(r)] = \int_{-\infty}^{E_F} \text{d} \epsilon \epsilon n(\epsilon) + \frac{2}{\pi} \int \text{d}r \int \text{d}r'' V(r, r'') \text{Im} \int_{-\infty}^{E_F} \text{d}\epsilon G(r'', r; \epsilon + i0^+) \tag{23}
\]
because the delta function as a real quantity gives no contribution to the imaginary part.
The last term in (23) can be simplified by writing the integrals over the spatial coordinates as a sum of integrals over the atomic cells and by inserting (9), (10) and (17). This leads to

\[
\frac{2}{\pi} \sum_n \int_n \int_n \int_{-\infty}^{E_F} d\epsilon \delta(r - r') \sum_{L'L''} Y_{L''}(\hat{r}) V_{L''}^n(r') Y_L(\hat{r}'') \text{Im} \int_{-\infty}^{E_F} d\epsilon G_{L''}^{nn}(r', r; \epsilon + i0^+) \tag{24}
\]

\[
= -2\pi \sum_n \int_n \int_0^{l_{\text{max}}} r^2 dr \sum_{L'L'} \sum_{L''}^{l_{\text{max}}} V_{L'L'}^n(r)n_{L'L'}^n(r) \tag{25}
\]

For the last result the integrals over \(r''\), \(\hat{r}''\) and \(\hat{r}\) were evaluated by the help of the delta function and by the orthogonality of the spherical harmonics and the integral over \(\epsilon\) was written in terms of the matrix elements

\[
n_{L'L'}^n(r) = -\frac{2}{\pi} \text{Im} \int_{-\infty}^{E_F} d\epsilon G_{L'L'}^{nn}(r, r; \epsilon + i0^+) \tag{26}
\]

Expression (26) is an important result. First, it shows how the kinetic energy for non-local potentials of type (10) can be evaluated without numerical differentiation using the Laplace operator. Second it shows that only \(L, L'\) components with \(l \leq l_{\text{max}}\) and \(l' \leq l_{\text{max}}\) are needed in the second term. Because also only these \(L, L'\) components are needed to evaluate the first term as explained in section 4.3 of [5], the computing time increases as \(N_{\text{at}}^3(l_{\text{max}} + 1)^6\), where \(N_{\text{at}}\) is the number of atoms in the system, which provides considerable savings for low values of \(l_{\text{max}}\). Third, in comparison to

\[
T_s[n(r)] = \int_{-\infty}^{E_F} d\epsilon \text{en}(\epsilon) - \sum_n \int_0^{l_{\text{max}}} r^2 dr \sum_{L'L'} V_{L'L'}^n(r)n_{L'L'}^n(r), \tag{27}
\]

which is the kinetic energy for the true effective potential, expression (26) shows that the use of a finite number of matrix elements changes the kinetic energy in two ways, implicitly by the dependence of the density of states, the potential and the density on \(l_{\text{max}}\) and explicitly by limiting the sums to terms with \(l \leq l_{\text{max}}\) and
\[ l' \leq l_{\text{max}}. \] Finally, it should be remarked that \( \text{(20)} \) and \( \text{(27)} \) are stationary with respect to changes of the potential as a result of standard first order perturbation theory.

The essential problem for obtaining precise total energies at low computational cost is the incompatibility of the second term in \( \text{(4)} \) with the second term in \( \text{(26)} \). These terms differ by

\[
\Delta E_{\text{tot}} = \sum_n \int_n r^2 dr \sum_{LL'} V_{LL'}^n(r)n_{LL'}^n(r) - \sum_n \int_n r^2 dr \sum_{LL'} l_{\text{max}} V_{LL'}^n(r)\hat{n}_{LL'}^n(r) \tag{28}
\]

which is the main error made in the evaluation the total energy if a finite number of potential matrix elements is used. If \( \Delta E_{\text{tot}} \) is neglected, the stationarity condition \( \text{(6)} \) is violated and a large number of potential matrix elements must be used if precise total energies are desired. If, however, \( \Delta E_{\text{tot}} \) is properly taken into account, much less computational resources are needed as the numerical investigation in the next section illustrates.

4 Numerical investigation

In \( \text{(5)} \) it was found for the face-centred-cubic (fcc) metals Al, Cu and Pd that excellent total-energy results are obtained if the calculated total energies are corrected according to the single-particle expression

\[
\Delta E_{\text{tot}} = \int_{-\infty}^{E_F} d\epsilon \epsilon n(\epsilon) - \int_{-\infty}^{E_F} d\epsilon \hat{n}(\epsilon), \tag{29}
\]

which is consistent with \( \text{(28)} \) because both \( \text{(20)} \) and \( \text{(27)} \) are stationary with respect to the potentials. In these calculations with the screened Korringa-Kohn-Rostoker method \( \text{(7, 8)} \) the effective potential was expanded in spherical harmonics as

\[
V(\mathbf{r}) = \sum_{L} V_{L}(r)Y_{L}(\hat{\mathbf{r}}) \tag{30}
\]

using \( l_{\text{pot}} = 16 \). In principle, according to \( \text{(12)} \) this leads to an infinite number of matrix elements which are obtained by

\[
V_{LL'}(r) = \sum_{L''} C_{LL'L''} V_{L}(r) \tag{31}
\]

where \( C_{LL'L''} = \int d\hat{\mathbf{r}} Y_{L'}(\hat{\mathbf{r}})Y_{L}(\hat{\mathbf{r}})Y_{L''}(\hat{\mathbf{r}}) \) are Gaunt coefficients. In the self-consistency steps a finite number of the matrix elements \( \text{(31)} \) was used which is equivalent to the use of non-local projection potentials. The total energies calculated in this way for different choices of \( l_{\text{max}} \) showed large deviations from the reference energies obtained with \( l_{\text{max}} = 8 \). The deviations were as large as dozens of millielectron-volts for the standard values \( l_{\text{max}} = 3 \) and \( l_{\text{max}} = 4 \). If,
however, a correction as given in \cite{29} was applied, the deviations of the corrected total energies from the reference energies amount to about one millielectron-volt or less.

In the present investigation a disordered CrFeCoNi alloy is considered because it is a more complex system than the fcc systems studied in \cite{5}. Whereas many matrix elements $V_{LL'}$ vanish for the highly symmetric fcc systems, all matrix elements are non-zero for CrFeCoNi. This system is a so-called high-entropy alloy, which belongs to a relatively new class of materials which are technologically important because they can show high hardness, wear, oxidation and corrosion resistance. In a recent large-scale study with up 1372 atoms per unit cell it was found \cite{9} that CrFeCoNi tends to form an L_{12} structure with Cr atoms ordered on one fcc sublattice and Fe, Co, and Ni atoms randomly distributed on the three other sublattices. For the present investigation this structure was simulated by periodically repeating simple-cubic unit cells with 32 atoms per cell.

As in \cite{5}, different choices of $l_{\text{max}}$ were used for the projection potentials defined in \cite{10}, while all other computational parameters were kept fixed. At the end of the converged self-consistency steps the calculated effective potential, the density, the density of states and the total energy depend on the parameter $l_{\text{max}}$. The total-energy results calculated in this way are shown in figure 1 as full squares for different numbers $N_{\text{sph}} = (l_{\text{max}} + 1)^2$ of spherical harmonics used in \cite{10}. They are given as deviations from the reference result obtained with $l_{\text{max}} = 8$. The deviations decrease only slowly with increasing $N_{\text{sph}}$ and are as large as about 100 millielectron-volts per atom and −30 millielectron-volts per atom for the standard values $l_{\text{max}} = 3$ and $l_{\text{max}} = 4$ which correspond to projection into subspaces containing $N_{\text{sph}} = 16$ and $N_{\text{sph}} = 25$ spherical harmonics. Results for fcc Cu, shown in figure 1 as open squares, exhibit the same trend and are of similar size, which indicates that symmetry is of minor importance for the precision of total energies.

The slow improvement of the results shown by squares in figure 1 arises from the error made by implicitly neglecting that the exact expression \cite{26} for the kinetic energy contains an interaction term between potential and density which does not agree with the term $-\int d\mathbf{r} V(\mathbf{r}) n(\mathbf{r})$ in the total energy functional \cite{4}. The slow improvement is not caused by the approximate calculation of the effective potential using a restricted number of potential matrix elements in the self-consistency steps. This can be seen if the total energy is evaluated for the different effective potentials in a post-processing step according to \cite{27} where both the density of states and the density are calculated using all potential matrix elements up to $l_{\text{max}} = 8$. The total energies calculated in this way are shown in figure 1 as circles. They are much better than the results shown as squares and deviate from the reference value by about 1.5 millielectron-volts per atom for $N_{\text{sph}} = 16$, corresponding to $l_{\text{max}} = 3$, and and by less than 0.5 millielectron-volts per atom for larger values of $N_{\text{sph}}$. This good agreement achieved in the post-processing step is a direct consequence of the stationarity of \cite{27} with respect to the potential. First order changes arising from different effective potentials, which are determined by using different numbers of potential
matrix elements in the self-consistency steps, are cancelled because they equally contribute to both terms in (27) and only second order effects remain, which are of the order of millielectron-volts per atom.

A technical detail should be mentioned here. The results shown by the circles in figure 1 are obtained in a non-self-consistent way by using a larger number of potential matrix elements $V_{LL'}$ in the post-processing step than in the self-consistency steps. This leads to densities of states and densities which, in metallic systems as studied here, do not satisfy the condition of charge neutrality. To first order the error in the density of states is compensated by applying a modified single-particle expression

$$E_{\text{sp}} = \int_{-\infty}^{E_F} d\epsilon n(\epsilon) - E_F \left[ \int_{\text{cell}} d\mathbf{r} n(\mathbf{r}) - N \right], \quad (32)$$

where $N$ is the total number of electrons in the unit cell of the periodic crystal and the second term ensures the stationarity of the total-energy functional also for non-particle-conserving densities [10], and the error in density is compensated by renormalizing the density with the help of $\text{Im} G(\mathbf{r}, \mathbf{r}; E_F)$.

4.1 Perturbation theory for the potential

Considerable computing time is saved for the calculation of the results shown as circles in figure 1 because the $V_{LL'}$ components in (10) are used only for small subspaces of spherical harmonics during the self-consistency steps and a
larger subspace is needed only once in the post-processing step. A drawback of this procedure is that it does not save computer memory. The memory increases proportionally to \( N^2_{at} N^2_{sph} \) where \( N_{at} \) is the number of atoms in the system. Because a large value of \( N_{sph} \) is required in the post-processing step, this quadratic increase can represent a bottleneck for systems with many atoms.

Here the question arises whether this bottleneck can be avoided if \( \Delta E_{tot} \) given by (29) is not treated exactly, but in approximations which take into account only first order effects arising from the different number of matrix elements in the self-consistency and post-processing steps. A simple and inexpensive procedure is provided by first order perturbation theory which gives the approximation

\[
\Delta E^{(1)}_{tot} = \sum_n \int_n r^2 dr \sum_{LL'} \hat{V}_{nLL'}(r) \hat{n}_{nL',L}(r) - \sum_n \int_n r^2 dr \sum_{LL'}^{l_{max}} \hat{V}_{nLL'}(r) \hat{n}_{nL',L}(r). \tag{33}
\]

Here in contrast to (28) only the density matrix elements \( \hat{n}_{LL'}(r) \) are needed which are obtained for the effective potentials calculated by using a small value of \( l_{max} \) during the self-consistency steps. Total-energy results corrected with \( \Delta E^{(1)}_{tot} \) are shown in figure 2 by full squares. Note that vertical axis in figure 2 is magnified by a factor three compared to figure 1. Thus first order perturbation theory removes about two thirds of the evaluation error which is nice but not really satisfactory because deviations of about 20 millielectron-volts per atom remain even for \( l_{max} = 6 \) corresponding to \( N_{sph} = 36 \). The reason for these still large deviations is that (33) removes only first order errors arising from the change of the potential but not first order errors arising from the change of the density.

One way to improve the density is to apply the correction (33) in a self-consistent manner. Instead of using (33) in a post-processing step to update the total energy, it can be used to modify the projection potential during the self-consistency steps so that the difference \( \Delta E^{(1)}_{tot} \) vanishes. This can be done in several ways. For instance, the matrix elements \( \hat{V}_{LL'}(r) \) can be adjusted for lower values of \( l \) and \( l' \) so that the integrands in both terms of (33) have equal values for all \( r \) or they can be adjusted in an \( r \)-independent way by the requirement that both integrals have equal values. It is also possible to modify only the \( l = 0, l' = 0 \) component of the projection potential so that \( \Delta E^{(1)}_{tot} \) vanishes in the self-consistency steps. As the numerical investigation has shown, all these modifications lead to minor changes of the calculated total energy which are less than a millielectron-volt per atom. Thus using (33) to modify the matrix elements of the projection potential does not really improve the calculated total energies, but has the conceptual advantage that density and total energy are obtained in consistent manner without the necessity to apply charge-neutrality corrections as discussed above.

Another way to improve the density at modest increase of computational resources is based on the observation that the Green function expression (15) contains quantities as \( R^L_n, S^L_n \) and \( t_{LL'} \), for which the calculation requires computing times that increase linearly with \( N_{at} \), and the Green function matrix
Figure 2: Total-energy deviations from the reference value for different numbers of spherical harmonics used for the projection potential. The results have been obtained by using first order perturbation theory for the potential. Full and open squares differ by using the projection potential for the calculation of the functions $R_L$ and $S_L$ and the Green function matrix elements $G_{LL'}$ or by using the projection potential only for the calculation of $G_{LL'}$.

elements, $G_{nn'}^{LL'}$, for which the calculation requires computing times that increase cubically with $N_{at}$. Thus, for all but the smallest systems the calculation of $R^n_L$ and $S^n_L$ can be done without $l_{\text{max}}$ cutoff and nevertheless the main computational effort can be saved by restricting the sums in (16) to terms with $l'' \leq l_{\text{max}}$ and $l''' \leq l_{\text{max}}$. The improved calculation of $R^n_L$ and $S^n_L$ should lead to better densities, potential and total energies and to a smaller size of the first order correction (33). This is indeed true as the calculated open squares in figure 2 show, but only for $N_{\text{sph}}$ up to $N_{\text{sph}} = 25$ the improvement is appreciable. For higher values of $N_{\text{sph}}$ the deviations are only slightly reduced which indicates that the second term in (15) dominates the total-energy evaluation error.

### 4.2 Perturbation theory for the density

While standard first order perturbation theory for the potential apparently reduces the total-energy evaluation error, it does not provide results which are comparable in precision to the ones shown as circles in figure 1. The reason for this is that (33) only compensates the error arising from the finite sums in (28), but not the error which is caused by calculating the density using potential matrix elements limited by $l_{\text{max}}$. This limitation can be relaxed by using more matrix elements in an approximate manner. In the KKR-GF method this can be done by recognizing that (11) can be solved in two steps. First the auxiliary Green function matrix elements $G_{LL'}^{nn'}$ are calculated by solving $G = g + g G$


and then the matrix elements $G_{LL'}^{nn'}$ are calculated by solving $G = \bar{G} + \bar{G} \Delta t \bar{G}$. Here, $t^0$ has matrix elements limited by $l_{\text{max}}$ and $\Delta t = t - t^0$ contains the matrix elements neglected in $t^0$. The advantage of $G = \bar{G} + \bar{G} \Delta t \bar{G}$ is that it can be approximated by $G = \tilde{G} + \tilde{G} \Delta t \tilde{G}$ if the assumption is used that $\Delta t$ must be treated only to first order. Total energies calculated in this way are shown in figure 3 as squares. For $N_{\text{sph}} \geq 16$ they deviate from the value for $N_{\text{sph}} = 81$ only by a few millielectron-volts per atom. Thus, total energies, which are calculated by using $\Delta t$ in first order perturbation theory, are almost as good as the ones shown as circles, which are calculated without this approximation. The big advantage of using $G = \bar{G} + \bar{G} \Delta t \bar{G}$ instead of $G = \tilde{G} + \tilde{G} \Delta t \tilde{G}$ is that only matrix multiplications are needed and that the computing time is reduced by a factor $N_{\text{lat}}$, because only on-site ($n = n'$) Green function matrix elements are needed to calculate the density. Thus, total energies can be calculated essentially by using $l_{\text{max}} = 3$ in the time-consuming parts of the calculations if deviations of a few millielectron-volts per atom are tolerated. Moreover, because the solution of $G = \bar{G} + \bar{G} \Delta t \bar{G}$ is fast, it can be afforded in each self-consistency step so that effective potential, density and total energy are obtained in a consistent manner without the need to apply total-energy or density corrections in a post-processing procedure.
4.3 Numerical details

The calculations were done with the standard Jülich KKR code and partly also with KKRnano [6] which is a newly developed linear-scaling code suitable for large systems with up to tens of thousands of atoms. Both codes are based on the tight-binding (screened) KKR method [7, 8] and lead to identical results. The screened structure constants were determined in real space by using clusters of 55 repulsive muffin-tin potentials with a constant height of 8 Ryd. The disordered CrFeCoNi alloy was described by a simple-cubic unit cell with lattice constant 712.91 pm with 32 atoms on ideal fcc positions. The assumption of ideal positions is justified because the chemical composition is mainly responsible for disorder effects and additional disorder effects arising from the small atomic relaxations are not important. This assumption is also convenient because highly accurate shape functions can be calculated for the fcc geometry [11]. The core electrons up to 3s and 3p states were calculated in atomic fashion as described as in [5]. Monkhorst-Pack grids [12] were used for the Brillouin-zone integration with 64 points for CrFeCoNi and 8000 points for Cu. The Fermi level was chosen at 5 eV by appropriately adjusting the average value of the potential in the interstitial region outside the inscribed muffin-tin spheres as discussed in [5], where also other details, which are not mentioned here, can be found.

5 Summary and outlook

In the present article the problem of calculating precise density-functional total energies at low cost has been considered from the viewpoint of non-local projection potentials. It has been discussed that such potentials can be described exactly by finite numbers of matrix elements in contrast to local potentials for which an exact description requires an infinite number of matrix elements. A consequence of the finite number of matrix elements is that the orbitals and the density can be calculated practically exactly, which means that only the approximation of using non-local potentials defined by (10) is decisive for the precision of the calculated total energies. It has been explained that the errors made by approximating the potential lead to second order errors for the total energy if the generalized Haydock-Heine total-energy functional is used, but only if the potential, which appears at two places in the functional, is treated in a consistent manner. Unfortunately, this means that a large number of potential matrix elements must be used for precise calculations of total energies.

For the example of angular projection potentials, which describe projection into subspaces of spherical harmonics, it has been demonstrated that precise total energies can be obtained if the self-consistent density and effective potential are calculated with a relatively small number of matrix elements and a large number of matrix elements is used only afterwards to calculate the total energy, which leads to considerable savings of computing time. It also has been demonstrated that, at even lower computational cost, almost as precise results
can be obtained if the effect of the large number of matrix elements is taken into account in first order perturbation theory for the density.

The presented analysis of the Haydock-Heine total-energy functional and the observation that the usual approximation of the potential by a finite number of matrix elements is harmful for the stationarity properties of this functional might be useful in other contexts than the one studied here. For instance, the insight gained might be used in other ways than by first order perturbation theory. Furthermore, it might be used in other electronic-structure methods than the KKR-GF method by recognizing that the use of a finite number of potential matrix elements can be understood as working with a non-local potential which arises from projection into finite subspaces of the chosen basis functions.

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7 Appendix

7.1 Projection into subspace of plane waves

In plane wave methods the orbitals are expanded, in simplified notation without indicating the wave vector $k$, as

$$\varphi_i(r) = \sum c_i(G) \exp(iGr)$$

where $G$ are reciprocal lattice vectors and $c_i(G)$ expansion coefficients. The disadvantage of local potentials is that they can be described without approximation only by an infinite number of potential matrix elements

$$V(G, G') = \int \exp(-iGr)V(r)\exp(iG'r).$$

The neglect of matrix elements with $|G| > G_{\text{cut}}$ and $|G'| > G_{\text{cut}}$ means that only expansion coefficients $c_i(G)$ with $|G| \leq G_{\text{cut}}$ are calculated and only approximate orbitals are obtained. In contrast to this, non-local potentials can be defined such that only a finite number of matrix elements are non-zero. For projection potentials given by

$$\hat{V}(r, r') = \sum_{G \leq G_{\text{cut}}}^{G| \leq G_{\text{cut}}} \exp(-iGr)\hat{V}(G, G')\exp(iG'r')$$

the matrix elements

$$\hat{V}(G, G') = \int \exp(-iGr)\hat{V}(r, r')\exp(iG'r)$$
are naturally zero for $|G| > G_{\text{cut}}$ and for $|G'| > G_{\text{cut}}$ because of the orthogonality of the plane waves. Because of that, the orbitals for potentials of type $G^1$ are exactly given by finite sums and the algebraic eigenvalue problem for the determination of the expansion coefficients $c_i(G)$ is by construction of finite dimension which means that it can be solved practically exactly. Thus, except for limiting the sums in $G^1$, essentially no other approximation must be made. According to the Haydock-Heine functional the total energy error should depend only to second order in the potential approximation if errors arising from evaluation of the functional using two different potentials are avoided. Similarly as presented in section 4 for projection into subspaces of spherical harmonics, this might be possible by using first order perturbation theory for the orbitals and by properly exploiting the stationarity properties of the total energy functional. Work in this direction should lead to improved total energies at reduced cost. In fact, an example of such work was recently published by Cancès et al. [13], where a post-processing method based on first and second order perturbation theory was presented.

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