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## Forces, muffin-tin orbitals, and helical polymers

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**Abstract.** We derive formulae for calculating forces within density-functional methods whereby we specifically take it into account that different parts of space may be treated differently. Special emphasis is put on correcting for various approximations, such as incomplete basis sets and approximative descriptions of electron densities and of Coulomb and exchange–correlation potentials. In particular, we apply the formulae for the full-potential linear muffin-tin orbital method for helical polymers. After discussing general results obtained for various finite and infinite systems, we apply the method in optimizing all structural degrees of freedom for undimerized and dimerized *trans*-polyacetylene as well as determining the energy gain upon dimerization.

### 1. Introduction

First-principles calculations of the electronic structure of materials provide information that can be used to get a better understanding of the properties of the materials. For some properties (e.g., band structures, densities of states, the total electron density or that of selected orbitals, charge transfers, and chemical bonding) a calculation for a single ‘realistic’ structure will give the required information. Others, however, require that the structure with the lowest total energy is found. This is obviously the case for structural information but, e.g., also for vibrational spectra, and it is needed when one wants to compare the stability of different systems (e.g., isomers) to one another.

In calculating the electronic properties, the single-particle eigenfunctions are in most cases expanded in some basis, and most methods differ in their choice. Gaussians and plane waves are common choices, since a large proportion of the required expressions can be evaluated analytically. There are, however, other methods that utilize the fact that electrons in different parts of space behave differently; i.e., they are strongly bound by an approximately spherically symmetric potential close to the nuclei, whereas they are more delocalized in the bonding region where the potential is only slowly varying. Using this leads to methods that are conceptually more transparent but which become more complicated to implement—mainly due to this separation of space into more parts that are treated differently.

Most first-principles calculations are performed within the Born–Oppenheimer approximation and by carrying a full self-consistent calculation on each structure through separately. For systems with just a few atoms (per unit cell for extended periodic systems, or in total for finite molecules) it is very difficult to optimize the structure when using only the total energy. In general only through knowledge of the forces may this task be transformed into a manageable one. It is the purpose of the present work to show how the forces can be calculated

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for general methods that treat different parts of space differently. Explicitly we shall discuss a first-principles density-functional LMTO (linearized muffin-tin orbitals) method for helical polymers but we stress that most of our results are not restricted to that particular method.

There exist many descriptions of procedures for calculating forces within parameter-free methods for electronic structure calculations. However, to the present authors' knowledge there have been only very few other presentations of methods for calculating forces within LMTO or related methods, which moreover differ in several important aspects from the present one and in some cases invoke extra approximations. In other cases, when treating three-dimensional periodic structures, parts of space are treated with plane waves which also leads to significant simplifications.

The first of these methods is due to Harris *et al* [1], who, however, only calculated the Hellmann–Feynman forces plus an extra term due to the frozen-core approximation. Savrasov and Savrasov [2] recently presented formulae for forces within a full-potential LMTO method, which, though, was explicitly constructed for closely packed solids. Methfessel and van Schilfhaarde [3] suggested replacing the Kohn–Sham density-functional total energy by the expression due to Harris [4]. Since the latter has extrema for the same densities and geometries as the former, the forces obtained by using the form of Harris agree with those obtained using the Kohn–Sham expression, at least in the neighbourhood of the total-energy minimum. This method has the very important advantage of being computationally much simpler than what we present, but it works only well when the Kohn–Sham equations are solved accurately. Finally, Blöchl [5] has discussed formulae for a full-potential LMTO method that is constructed explicitly for crystalline materials for which, furthermore, the ASA (atomic sphere approximation) is a good approximation.

Soler and Williams [6], Yu *et al* [7, 8], Goedecker and Maschke [9], and Kohler *et al* [10] have all presented formulae for forces within the LAPW (linearized augmented-plane-wave) method. Being based on plane waves as basis functions, it is restricted to three-dimensional periodic structures and can thereby avoid some of the general problems that we shall discuss here. The PAW (projector augmented-wave) method, developed by Blöchl [11], has also been used in treating isolated, molecular systems by employing a supercell approximation.

In the present work we shall calculate forces that are consistent with the calculated total-energy hypersurface as independently as possible of the accuracy with which the latter is obtained, and the approach will therefore not be restricted to special (classes of) systems. As extensions of previous works we shall explicitly include the corrections to the forces due to incomplete sets of basis functions that, furthermore, are represented differently in different parts of space (a larger part of these corrections are absent within the augmented-plane-wave methods) and due to different, more or less accurate, descriptions of the potential in different parts of space (other studies have only considered the case where the potentials are approximated in the complete space; see below in sections 3.5 and 3.6). Our approach is accordingly the first one that treats the Kohn–Sham total-energy expression, that completely takes into account the separation of space into more parts, that is not restricted to plane waves and three-dimensional crystalline systems, and that corrects for essentially all approximations made in the calculations. Our specific first-principles method has been described in detail elsewhere [12, 13] and section 2 contains therefore only a brief account, sufficient for the subsequent sections. The formulae for the forces are derived in section 3. The special case of helical polymers is discussed in section 4. In section 5 we give some general results obtained from a number of test calculations on some finite molecules and helical polymers and subsequently we apply the method for obtaining a complete, parameter-free optimization of the structural degrees of freedom of undimerized and dimerized *trans*-polyacetylene. This study also gives the energy gain upon dimerization. Finally, we conclude in section 6.

## 2. The first-principles method

We make use of the Born–Oppenheimer approximation and apply the density-functional formalism of Hohenberg and Kohn [14]. The resulting Kohn–Sham single-particle equations [15]

$$\hat{H}_{\text{eff}}\psi_i(\vec{r}) \equiv [-\nabla^2 + V_{\text{Nc}}(\vec{r}) + V_{\text{C}}(\vec{r}) + V_{\text{xc}}(\vec{r})]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \quad (1)$$

are solved by expanding the eigenfunctions  $\psi_i$  in a basis of linearized muffin-tin orbitals (LMTOs). In equation (1) we have used Rydberg atomic units,  $V_{\text{Nc}}$  is the Coulomb potential of the nuclei and of the (frozen-) core electrons,  $V_{\text{C}}$  is that of the valence electrons, and  $V_{\text{xc}}$  is the exchange–correlation potential. For the latter we shall in our calculations use the local approximation of von Barth and Hedin [16], but it will be stressed that for our general discussion we may use any (local or non-local) form.

Inside any of the atom-centred, non-overlapping (muffin-tin) spheres (at  $\vec{R}'$ ) an LMTO (centred at  $\vec{R}$  and having the angular dependence defined by  $L \equiv (l, m)$ ) is described as linear combinations

$$\sum_{\vec{R}', L'} S_{L, L'}(\kappa, \vec{R} - \vec{R}') [\phi_{\vec{R}', L', \kappa}(\vec{r} - \vec{R}') + \omega_{\vec{R}, \vec{R}', L'}(\kappa) \dot{\phi}_{\vec{R}', L', \kappa}(\vec{r} - \vec{R}')] \quad (2)$$

and outside all spheres analytically as

$$c_{\vec{R}, L}(\kappa) K_L(\kappa, \vec{r} - \vec{R}) \quad (3)$$

with

$$K_L(\kappa, \vec{r} - \vec{R}) \equiv \frac{i\kappa^{l+1}}{(2l-1)!!} h_l^{(1)}(\kappa|\vec{r} - \vec{R}|) Y_L(\widehat{r - R}) \equiv K_l(\kappa, |\vec{r} - \vec{R}|) Y_L(\widehat{r - R}). \quad (4)$$

Here,  $|\kappa|$  is the decay constant of the Hankel functions  $h_l^{(1)}$  and  $\kappa$  is purely imaginary. The numerical functions  $\phi$  of equation (2) are obtained by replacing the full potential in equation (1) by its spherically symmetric component and the eigenvalue  $\epsilon_i$  by the (chosen) energy  $\epsilon_v$ .  $\dot{\phi} \equiv \partial\phi/\partial\epsilon_v$  and the constants  $S$ ,  $\omega$ , and  $c$  are determined such that the function is continuous and differentiable everywhere in space. For  $\vec{R} = \vec{R}'$ , we have  $S_{L, L'} = \delta_{L, L'}$ .

Not too far from the nuclei the potential is close to spherical symmetry, such that the functions  $\phi_{\vec{R}, L, \kappa}$  in that region (where a large part of the total energy originates) represent accurate approximations to the exact solutions to the Kohn–Sham equations.

By applying the variational principle the eigenfunctions of equation (1) are accordingly approximated by a linear combination of the LMTOs,  $\chi$ , i.e.

$$\psi_i(\vec{r}) \simeq \tilde{\psi}_i(\vec{r}) = \sum_{\vec{R}, L, \kappa} u_{\vec{R}, L, \kappa}^i \chi_{\vec{R}, L}(\kappa, \vec{r} - \vec{R}). \quad (5)$$

Only for a complete basis set is  $\psi_i = \tilde{\psi}_i$ .

The potential depends on the solutions to equation (1) that in turn depend on the potential; i.e. an iterative process is necessary. We shall here assume that self-consistency has been reached.

Inside the muffin-tin spheres we decompose the total electron density into one component from the valence electrons and one from the core electrons,

$$\rho(\vec{r}) = \rho_v(\vec{r}) + \rho_c(\vec{r}) \quad (6)$$

with  $\rho_c$  being the core electron density. Within the frozen-core approximation  $\rho_c$  is assumed to be a sum of spherically symmetric core densities of the free atoms that are each confined to the corresponding muffin-tin sphere.

Inside the spheres we expand the valence-electron density as

$$\rho_v(\vec{r}) = \sum_L \rho_{v,L}(|\vec{r} - \vec{R}|) Y_L(\widehat{r - \vec{R}}) \quad (7)$$

where the  $L$ -summation can in principle be carried through to any desired accuracy. Thereby similar expressions for the Coulomb potential and the exchange–correlation potential can then be found for inside the spheres.

In the interstitial region neither the exchange–correlation potential nor the Coulomb potential can be calculated directly from the density. This is not the case when the method is based on a plane-wave basis set in the interstitial region. Here, however, we approximate the electron density in the interstitial region,

$$\rho_v(\vec{r}) \simeq \tilde{\rho}_v(\vec{r}) = \sum_{\lambda} \sum_L \sum_{\vec{R}} r_{\vec{R},L,\lambda} K_L(\lambda, \vec{r} - \vec{R}) \quad (8)$$

where the coefficients  $r_{\vec{R},L,\lambda}$  are determined from a least-squares fit. The Coulomb potential in the interstitial region is then expressed in a closely related form

$$V_C(\vec{r}) = \sum_{\lambda} \sum_L \sum_{\vec{R}} v_{C;\vec{R},L,\lambda} K_L(\lambda, \vec{r} - \vec{R}) \quad (9)$$

with the difference that the sum in equation (9) includes  $\lambda = 0$ , whereas that in equation (8) does not.

The exchange–correlation potential  $V_{xc}$  and the corresponding energy density  $\epsilon_{xc}$  are in the interstitial region approximated in an equivalent way:

$$\begin{aligned} V_{xc}(\vec{r}) &\simeq \tilde{V}_{xc}(\vec{r}) = \sum_{\lambda} \sum_L \sum_{\vec{R}} v_{xc;\vec{R},L,\lambda} K_L(\lambda, \vec{r} - \vec{R}) \\ \epsilon_{xc}(\vec{r}) &\simeq \tilde{\epsilon}_{xc}(\vec{r}) = \sum_{\lambda} \sum_L \sum_{\vec{R}} \epsilon_{xc;\vec{R},L,\lambda} K_L(\lambda, \vec{r} - \vec{R}) \end{aligned} \quad (10)$$

excluding, however,  $\lambda = 0$ .

It will be important to specify the fits. The electron-density fit is performed by minimizing

$$\int \int_{i.r.} [\rho_v(\vec{r}_1) - \tilde{\rho}_v(\vec{r}_1)][\rho_v(\vec{r}_2) - \tilde{\rho}_v(\vec{r}_2)] f(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (11)$$

including the ‘electron-conservation’ constraint

$$\int_{i.r.} \rho_v(\vec{r}) d\vec{r} = \int_{i.r.} \tilde{\rho}_v(\vec{r}) d\vec{r}. \quad (12)$$

Here, ‘i.r.’ denotes integrals over the interstitial region, and

$$f(\vec{r}_1, \vec{r}_2) = \begin{cases} \delta(\vec{r}_1 - \vec{r}_2) \\ \text{or} \\ \frac{1}{|\vec{r}_1 - \vec{r}_2|}. \end{cases} \quad (13)$$

The first choice corresponds to minimizing the error in the electron density and the second to minimizing that of the Coulombic electron–electron interaction energy.

The exchange–correlation fits are performed equivalently by minimizing the square of the error but with the integral replaced by a sum over a larger number of selected points in the interstitial region and without any constraint. Moreover we use  $\tilde{\rho}_v(\vec{r})$  of equation (8) instead of  $\rho_v(\vec{r})$ . Accordingly, we minimize

$$\sum_i \{ \tilde{V}_{xc}(\vec{r}_i) - V_{xc}[\tilde{\rho}_v(\vec{r}_i)] \}^2 \quad (14)$$

with  $i$  running over the finite number of points in the interstitial region.

At self-consistency we may finally write the total valence energy as [13]

$$\begin{aligned}
 E_{\text{val}} = & \sum_{i=1}^{\text{occ}} \langle \tilde{\psi}_i | -\nabla^2 | \tilde{\psi}_i \rangle + \int_{\text{MTS}} \rho_v(\vec{r}) \left\{ \frac{1}{2} V_C(\vec{r}) + V_{\text{Nc}}(\vec{r}) + \epsilon_{\text{xc}}[\rho(\vec{r})] \right\} d\vec{r} \\
 & + \int_{\text{MTS}} \rho_c(\vec{r}) \{ \epsilon_{\text{xc}}[\rho(\vec{r})] - \epsilon_{\text{xc}}[\rho_c(\vec{r})] \} d\vec{r} \\
 & + \int_{\text{i.r.}} \rho_v(\vec{r}) \left[ V_C(\vec{r}) + V_{\text{Nc}}(\vec{r}) + \frac{4}{3} \tilde{\epsilon}_{\text{xc}}(\vec{r}) \right] d\vec{r} \\
 & + \int_{\text{i.r.}} \tilde{\rho}_v(\vec{r}) \left[ -\frac{1}{2} V_C(\vec{r}) - \frac{1}{3} \tilde{\epsilon}_{\text{xc}}(\vec{r}) \right] d\vec{r} + \sum_{i \neq j} \frac{Z_{ci} Z_{cj}}{|\vec{R}_i - \vec{R}_j|}. \quad (15)
 \end{aligned}$$

‘MTS’ denotes integrals over the muffin-tin spheres. Moreover,  $Z_{ci}$  is the effective charge (i.e., nuclear minus core) of the  $i$ th nucleus, and  $\vec{R}_i$  its position. The valence energy excludes terms of the total energy that are constants (i.e., independent of the structure and deposition) within the frozen-core approximation.

This expression is general for most density-functional methods. Whenever fitting strategies are used, first-order errors in the difference between exact and approximate quantities are largely removed when using the ‘i.r.’ expressions in those parts of space where the fits are employed. In the remaining parts, where no fits are used, the ‘MTS’ terms should be used. In many density-functional methods one uses only one strategy, but whenever both strategies are used in different parts of space (most notably in the augmented-wave and multiple-scattering methods) it is important to be aware of the fact that there may be (small) discontinuities on the boundaries between the two parts. Furthermore, the number of electrons in the fit regions may not be constant. The existence of the boundaries leads to a number of extra terms when calculating derivatives of  $E_{\text{val}}$ .

### 3. Forces

#### 3.1. Surface terms

The forces are obtained by differentiating the total valence energy of equation (15) with respect to a nuclear coordinate  $R_{\alpha}$ , with  $\alpha = x, y, \text{ or } z$ . This means that we shall indirectly assume that one of the nuclei (at  $\vec{R}_k$ ) is displaced infinitesimally. This displacement will lead to an infinitesimal change in all quantities entering equation (15), but will moreover also result in a shift of the muffin-tin sphere centred at  $\vec{R}_k$ . Therefore, any derivative of an integral with respect to  $R_{\alpha}$  contains both a term from the derivative of the integrand as well as a surface term from the sphere at  $\vec{R}_k$ .

We shall use the fact that the surface is that of a sphere, such that an  $\alpha$ -projection of a normal to the surface pointing away from the integration region can be written as

$$\pm n_{\alpha} = \pm \sqrt{\frac{4\pi}{3}} Y_{p_{\alpha}}(\widehat{r - \vec{R}_k}) \quad (16)$$

where the sign depends on whether the integration region is the sphere (+) or the interstitial region (–).

Therefore, assuming that the integrand of interest is

$$f(\{\vec{R}_i\}, \vec{r}) = \begin{cases} f_1(\vec{R}_i, \vec{r}) & \text{inside the sphere at } \vec{R}_i \\ f_2(\vec{r}) & \text{in the interstitial region} \end{cases} \quad (17)$$

we have

$$\begin{aligned} \frac{\partial}{\partial R_\alpha} \int f(\{\vec{R}_i\}, \vec{r}) d\vec{r} &= \int_{|\vec{r}-\vec{R}_k|=s_k} s_k^2 [f_1(\vec{R}_k, \vec{r}) - f_2(\vec{r})] \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) d(\widehat{r - R_k}) \\ &+ \int \frac{\partial}{\partial R_\alpha} f(\{\vec{R}_i\}, \vec{r}) d\vec{r} \end{aligned} \quad (18)$$

with  $s_k$  being the radius of the muffin-tin sphere at  $\vec{R}_k$ .

### 3.2. Hellmann–Feynman forces

The Hellmann–Feynman force is the exact force when no approximation is made in solving the Kohn–Sham equations (i.e., when  $\psi_i$  and  $\tilde{\psi}_i$  of equation (5) are identical, no fits in the interstitial region have been made, all expansions are carried through to convergence, and the core electrons are not kept frozen). It is the partial derivative of the total energy with respect to the nuclear coordinate. The total energy (which also contains terms from the core electrons) may be obtained from equation (15) by setting  $\rho_c = 0$  and replacing  $\rho_v$  by  $\rho = \rho_v + \rho_c$ . When the fits in the interstitial region are exact, the total energy contains only two terms that explicitly depend on the nuclear coordinates, i.e., the potential generated by the nuclei and the nuclear–nuclear repulsion. Therefore, the Hellmann–Feynman force is

$$-F_{R_\alpha}^{\text{HF}} = \frac{\partial E_{\text{tot}}}{\partial R_\alpha} = \frac{\partial}{\partial R_\alpha} \left\{ - \sum_i \int \frac{2Z_i}{|\vec{r} - \vec{R}_i|} \rho(\vec{r}) d\vec{r} + \sum_{i \neq j} \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \right\}. \quad (19)$$

The second term on the right-hand side is easily evaluated as

$$2Z_k \sum_{i \neq k} \frac{Z_i}{|\vec{R}_i - \vec{R}_k|^2} \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{R_i - R_k}). \quad (20)$$

For the first term on the right-hand side of equation (20) one may use two different expressions, as pointed out by Harris *et al* [1]:

$$\begin{aligned} \int \frac{\partial}{\partial R_\alpha} \sum_i \frac{-2Z_i}{|\vec{r} - \vec{R}_i|} \rho(\vec{r}) d\vec{r} &= -Z_k \frac{\partial}{\partial R_\alpha} [V_C(\vec{r})]_{\vec{r}=\vec{R}_k} \\ &= -2Z_k \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{R}_k|^2} \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) d\vec{r}. \end{aligned} \quad (21)$$

Note that we here have interchanged integration and differentiation compared with equation (19) and thereby neglected surface terms.

The first expression in equation (21) involves the derivative of the potential at the site of the nucleus and is thus very sensitive to an accurate description here. The second expression may be numerically and computationally more stable since it is a one-dimensional integral of the  $p_\alpha$ -projected electron density over the whole space. We have implemented both methods and found that for the present method they yield identical results, and we shall therefore use the first expression that is the simplest one. In both cases we have, however, used the approximate electron density in the interstitial region in defining the Coulomb potential. The correction term for this error will be discussed in subsection 3.5.

Independently of which expression in equation (21) is used, we also have to include a surface term, i.e.

$$\begin{aligned} \frac{\partial}{\partial R_\alpha} \sum_i \int \frac{-Z_i}{|\vec{r} - \vec{R}_i|} \rho(\vec{r}) d\vec{r} &= \int \frac{\partial}{\partial R_\alpha} \frac{-Z_k}{|\vec{r} - \vec{R}_k|} \rho(\vec{r}) d\vec{r} \\ &+ \int_{|\vec{r}-\vec{R}_k|=s_k} s_k^2 \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) \frac{-2Z_k}{|\vec{r} - \vec{R}_k|} [\rho^-(\vec{r}) - \rho^+(\vec{r})] d(\widehat{r - R_k}) \end{aligned} \quad (22)$$

where  $\rho^-$  ( $\rho^+$ ) is the exact electron density just inside (outside) the muffin-tin sphere. Since, however, the basis functions are continuous everywhere,  $\rho^- = \rho^+$ , and the surface term vanishes.

### 3.3. Pulay forces

In order to calculate the forces such that they become the gradients to the calculated total-energy surface we need explicitly to take three effects into account that are neglected when considering only the Hellmann–Feynman forces. These effects arise from the fact that the wavefunctions  $\psi_i$  (cf. equation (5)) are not the exact solutions to the Kohn–Sham equations, from the frozen-core approximation, and from the fits of the potentials and densities in the interstitial region. The first effect leads to the so-called Pulay forces [17], whereas the second has been treated by Harris *et al* [1]. For the last effect we shall closely follow a procedure of Fournier *et al* [18], but with some important modifications, as well as one due to Dunlap *et al* [19]. Both for the Pulay forces and for the fit corrections, our separation of space into muffin-tin spheres and the interstitial region leads to extra complications.

Considering first the Pulay forces and neglecting for the moment their surface terms it is relatively straightforward (see, e.g., [20]) to obtain

$$\begin{aligned}
 -F_{R_\alpha}^{\text{Pulay}} = & \sum_{i=1}^{\text{occ}} \sum_{\vec{R}_1, \vec{R}_2} \sum_{L_1, L_2} \sum_{\kappa_1, \kappa_2} (u_{\vec{R}_1, L_1, \kappa_1}^i)^* u_{\vec{R}_2, L_2, \kappa_2}^i \\
 & \times \int \left[ \frac{d\chi_{\vec{R}_1, L_1, \kappa_1}^* (\vec{r} - \vec{R}_1)}{dR_\alpha} (\hat{H}_{\text{eff}} - \epsilon_i) \chi_{\vec{R}_2, L_2, \kappa_2} (\vec{r} - \vec{R}_2) \right. \\
 & \left. + \chi_{\vec{R}_1, L_1, \kappa_1}^* (\vec{r} - \vec{R}_1) (\hat{H}_{\text{eff}} - \epsilon_i) \frac{d\chi_{\vec{R}_2, L_2, \kappa_2} (\vec{r} - \vec{R}_2)}{dR_\alpha} \right] d\vec{r}. \tag{23}
 \end{aligned}$$

For the basis functions  $\chi$  we insert the LMTOs of section 2. The integrals split them up into two terms, one over the muffin-tin spheres and one over the interstitial region. By considering each part of the space separately we have to take into account that  $\hat{H}_{\text{eff}}$  then is no longer Hermitian. Since

$$\hat{H}_{\text{eff}} = -\nabla^2 + V(\vec{r}) \tag{24}$$

only  $-\nabla^2$  leads to non-Hermiticity (this is due to the separation of space into the spheres and the interstitial region so that the wavefunctions do not vanish on some of the borders of the integration regions, i.e., on the sphere boundaries). For  $-\nabla^2$  we use Green's theorem,

$$- \int_{\Xi} f(\vec{r}) \nabla^2 g(\vec{r}) d\vec{r} = - \int_{\Xi} g(\vec{r}) \nabla^2 f(\vec{r}) d\vec{r} - \int_{\delta\Xi} [f(\vec{r}) \vec{\nabla} g(\vec{r}) - g(\vec{r}) \vec{\nabla} f(\vec{r})] \cdot \vec{n} d\vec{r}. \tag{25}$$

Here,  $\Xi$  is the volume of integration (either the muffin-tin spheres or the interstitial region) and  $\delta\Xi$  its boundary. Moreover,  $\vec{n}$  is a normal to  $\delta\Xi$  pointing away from  $\Xi$  (cf. equation (16)). Identifying  $f = \chi_{\vec{R}_1, L_1, \kappa_1}^*$  and

$$g = \frac{d}{dR_\alpha} \chi_{\vec{R}_2, L_2, \kappa_2}$$

in equation (23) we can evaluate the complete expression in equation (23). As above, the continuity and differentiability of the basis functions make the surface term in equation (25) vanish.



A further surface term for the Pulay forces that was neglected in equation (23) can be written as

$$\sum_{i=1}^{\text{occ}} \left[ \int \tilde{\psi}_i^*(\vec{r}) \nabla^2 \tilde{\psi}_i(\vec{r}) d(\widehat{r - R_k}) \Big|_{|\vec{r} - \vec{R}_k| = s_k^+} - \int \tilde{\psi}_i^*(\vec{r}) \nabla^2 \tilde{\psi}_i(\vec{r}) d(\widehat{r - R_k}) \Big|_{|\vec{r} - \vec{R}_k| = s_k^-} \right] + \int_{|\vec{r} - \vec{R}_k| = s_k} s_k^2 \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) [V(\vec{r})\rho(\vec{r}) - \tilde{V}(\vec{r})\rho(\vec{r})] d(\widehat{r - R_k}) \quad (26)$$

where the first part is due to the kinetic energy operator and the second part to the potential. This term does not vanish.

### 3.4. The frozen-core approximation

Harris *et al* [1] have shown that when applying a frozen-core approximation it is not sufficient to correct the Hellmann–Feynman force simply by replacing the total density by the valence density, but an extra term turns up due to the implicitly assumed rigid shift of both nucleus and corresponding core. This term is (including surface terms)

$$F_{R_\alpha}^{\text{core}} = \int \rho'_c(|\vec{r} - \vec{R}_k|) \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) [V_C(\vec{r}) + V_{xc}(\vec{r})] d\vec{r} - \int_{|\vec{r} - \vec{R}_k| = s_k} s_k^2 \rho_c(s_k) \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) [V_C(\vec{r}) + \epsilon_{xc}(\vec{r})] d(\widehat{r - R_k}) \quad (27)$$

where we have assumed that the core density is spherically symmetric. In our calculations we renormalize the core density by including an additional (small) constant density such that it is confined to the corresponding muffin-tin sphere. Therefore, the integral in equation (27) is only over the corresponding sphere and is easily evaluated using the  $p$ -components of the angular expansions of the potentials  $V_C$  and  $V_{xc}$ .

Despite the frozen-core approximation, the nuclear charge in equation (21) has to remain the true one, and *not* the effective one, whereas those in equation (20) are to be replaced by the effective ones.

### 3.5. Corrections due to the charge-density fit

The third set of correction terms mentioned in section 3.3 is due to the approximate description of densities and potentials in the interstitial region. We shall first discuss corrections due to the fit of the Coulomb potential and follow closely an approach of Fournier *et al* [18]. There will, however, be some important modifications, which is the reason for the more detailed description here.

Fournier *et al* use the fit of equation (11) with  $f(\vec{r}_1, \vec{r}_2) = |\vec{r}_1 - \vec{r}_2|^{-1}$ , as suggested by Dunlap *et al* [21]. In addition, they have no separation of space into muffin-tin spheres and interstitial region, so all integrals are over the whole space.

Due to the fit of the interstitial charge density, we need to include two more terms in the calculation of the forces. The first one is

$$\sum_{\vec{R}L\lambda} \frac{\delta E_{\text{val}}}{\delta r_{\vec{R},L,\lambda}} \frac{dr_{\vec{R},L,\lambda}}{dR_\alpha} \quad (28)$$

Using equation (15) and neglecting the fact that the exchange–correlation energy also has a dependence on  $r_{\vec{R},L,\lambda}$ , it is straightforward to rewrite this as

$$\sum_{\vec{R}L\lambda} \frac{dr_{\vec{R},L,\lambda}}{dR_\alpha} \int \int \frac{2[\rho_v(\vec{r}_1) - \tilde{\rho}_v(\vec{r}_1)]K_L(\lambda, \vec{r}_2 - \vec{R})}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2. \quad (29)$$

This term vanishes as a consequence of equation (34) if we use  $f(\vec{r}_1, \vec{r}_2) = |\vec{r}_1 - \vec{r}_2|^{-1}$  and if the area of integration is the whole space. However, when the fit is performed only in parts of space where the number of electrons may not be constant, and/or when using  $f(\vec{r}_1, \vec{r}_2) = \delta(\vec{r}_1 - \vec{r}_2)$ , this is not the case. Instead the coefficients  $r'_{\vec{R},\lambda,L} \equiv dr_{\vec{R},\lambda,L}/dR_\alpha$  have to be obtained as follows.

Equation (11) together with the constraint of equation (12) can be written as

$$\frac{\partial}{\partial r_{\vec{R},L,\lambda}} \left\{ \int \int [\rho_v(\vec{r}_1) - \tilde{\rho}_v(\vec{r}_1)] f(\vec{r}_1, \vec{r}_2) [\rho_v(\vec{r}_2) - \tilde{\rho}_v(\vec{r}_2)] d\vec{r}_1 d\vec{r}_2 - \gamma \int \tilde{\rho}_v(\vec{r}) d\vec{r} \right\} = 0. \quad (30)$$

$\gamma$  is a Lagrange multiplier, and the region of integration is the interstitial region in our approach but the whole space in the approach of Fournier *et al.*

By introducing

$$\begin{aligned} A_{\vec{R}'\lambda'L',\vec{R}\lambda L} &= 2 \int \int K_{L'}(\lambda', \vec{r}_1 - \vec{R}') f(\vec{r}_1, \vec{r}_2) K_L(\lambda, \vec{r}_2 - \vec{R}) d\vec{r}_1 d\vec{r}_2 \\ B_{\vec{R}\lambda L} &= \int K_L(\lambda, \vec{r} - \vec{R}) d\vec{r} \\ D_{\vec{R}\lambda L} &= 2 \int \int \rho_v(\vec{r}_1) f(\vec{r}_1, \vec{r}_2) K_L(\lambda, \vec{r}_2 - \vec{R}) d\vec{r}_1 d\vec{r}_2 \end{aligned} \quad (31)$$

we have in matrix form

$$\frac{\partial}{\partial r_{\vec{R},L,\lambda}} (\underline{A} \underline{r} + \gamma \underline{B}) = \frac{\partial}{\partial r_{\vec{R},L,\lambda}} \underline{D}. \quad (32)$$

Due to the constraint, equation (13), we have in addition

$$\underline{r}^\dagger \underline{B} = \underline{B}^\dagger \underline{r} = N_e \quad (33)$$

with  $N_e$  being the number of electrons in the region of integration. Representing the derivatives with primes, this leads to

$$\underline{A} \underline{r}' + \gamma' \underline{B} = \underline{D}' - \underline{A}' \underline{r} - \gamma \underline{B}' \quad (34)$$

and

$$(\underline{r}')^\dagger \underline{B} = N'_e - \underline{r}^\dagger \underline{B}'. \quad (35)$$

These equations have the same forms as equations (32) and (33) and, accordingly, they can be solved in an equivalent way, once the right-hand sides are known. These can, in turn, be calculated from the definitions in equation (31) with proper inclusion of surface terms.

The other term that will be included in the calculation of the forces is related to the functional derivative of the valence energy with respect to the fit functions  $K_L(\lambda, \vec{r} - \vec{R})$  of the electron density. We shall focus on the two terms

$$\int_{\text{MTS}} \rho_v(\vec{r}) \frac{1}{2} V_C(\vec{r}) d\vec{r} + \int_{\text{i.r.}} \left[ \rho_v(\vec{r}) V_C(\vec{r}) - \frac{1}{2} \tilde{\rho}_v(\vec{r}) V_C(\vec{r}) \right] d\vec{r} \quad (36)$$

and accordingly neglect the fact that the exchange–correlation terms also contain some dependences on the fit functions of the electron density (cf. equation (14)).

Then,

$$\begin{aligned} & \int \sum_{\vec{R}\lambda L} \frac{\delta E_{\text{val}}}{\delta K_L(\lambda, \vec{r} - \vec{R})} \frac{\partial K_L(\lambda, \vec{r} - \vec{R})}{\partial R_\alpha} d\vec{r} \\ &= 2 \sum_{\lambda L} r_{\vec{R}_k,L,\lambda} \int \int_{\text{i.r.}} \frac{\partial K_L(\lambda, \vec{r}_1 - \vec{R}_k)}{\partial R_\alpha} [\rho_v(\vec{r}_2) - \tilde{\rho}_v(\vec{r}_2)] \frac{1}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2. \end{aligned} \quad (37)$$

The right-hand side can be interpreted as the Coulomb energy for the interaction between the charge densities  $\rho_v - \tilde{\rho}_v$  and  $\sum r dK/dR_\alpha$ . We may thus, alternatively, write this term as an integral over the product of the charge density  $\rho_v - \tilde{\rho}_v$  and a potential, where the potential is the Coulomb potential of the charge density  $\sum r dK/dR_\alpha$ . The latter can be written as a closed form (i.e., by using the properties of the fitting functions).

It turns out that the surface term corresponding to equation (37) vanishes. In showing this we use

$$2 \int_{\text{MTS}} \frac{\rho_v(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 + 2 \int_{\text{i.r.}} \frac{\tilde{\rho}_v(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 = V_C(\vec{r}). \quad (38)$$

Differentiating this with respect to  $R_\alpha$  gives

$$\begin{aligned} \frac{dV_C}{dR_\alpha} &= 2 \int_{\text{MTS}} \frac{d\rho_v(\vec{r}_1)}{dR_\alpha} \frac{1}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 + 2 \int_{\text{i.r.}} \frac{d\tilde{\rho}_v(\vec{r}_1)}{dR_\alpha} \frac{1}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 \\ &+ 2 \int_{|\vec{r}_1 - \vec{R}_k| = s_k} s_k^2 \frac{\rho_v^-(\vec{r}_1) - \tilde{\rho}_v(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) d(\widehat{r - R_k}). \end{aligned} \quad (39)$$

Differentiating now equation (36) and using equation (39) results in the following surface terms:

$$\begin{aligned} &\int_{\text{MTS}} \rho_v(\vec{r}) \int_{|\vec{r}_1 - \vec{R}_k| = s_k} s_k^2 \frac{\rho_v^-(\vec{r}_1) - \tilde{\rho}_v(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) d(\widehat{r - R_k}) d\vec{r} \\ &+ \int_{\text{i.r.}} [2\rho_v(\vec{r}) - \tilde{\rho}_v(\vec{r})] \\ &\times \int_{|\vec{r}_1 - \vec{R}_k| = s_k} s_k^2 \frac{\rho_v^-(\vec{r}_1) - \tilde{\rho}_v(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) d(\widehat{r - R_k}) d\vec{r} \\ &+ \int_{|\vec{r} - \vec{R}_k| = s_k} s_k^2 [-2\rho_v^+(\vec{r}) + \rho_v^-(\vec{r}) + \tilde{\rho}_v(\vec{r})] \\ &\times \frac{1}{2} V_C(\vec{r}) \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) d(\widehat{r - R_k}). \end{aligned} \quad (40)$$

Neglecting second-order terms in  $\rho_v - \tilde{\rho}_v$  gives

$$\int_{|\vec{r} - \vec{R}_k| = s_k} s_k^2 [\rho_v^-(\vec{r}) - \rho_v^+(\vec{r})] V_C(\vec{r}) \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(\widehat{r - R_k}) d(\widehat{r - R_k}) \quad (41)$$

which vanishes since the basis functions are continuous on the sphere boundaries.

### 3.6. Corrections due to the exchange–correlation fits

Dunlap *et al* [19] have discussed a correction term due to the fits of the exchange–correlation functions  $\epsilon_{xc}$  and  $V_{xc}$ . Since their discussion is directly applicable here we shall only give the final formulae for this correction term with, however, the modification that we have to include extra surface terms.

The least-squares fit of equation (10) corresponds to solving the equations

$$\sum_{\vec{R}_2 L_2 \lambda_2} v_{xc; \vec{R}_2, L_2, \lambda_2} \sum_i K_{L_1}(\lambda_1, \vec{r}_i - \vec{R}_1) K_{L_2}(\lambda_2, \vec{r}_i - \vec{R}_2) = \sum_i K_{L_1}(\lambda_1, \vec{r}_i - \vec{R}_1) V_{xc}(\vec{r}_i) \quad (42)$$

for all  $\vec{R}_1, L_1, \lambda_1$ .  $i$  labels the points used in the fit. According to Dunlap *et al* we define the quantities  $t_{\vec{R}_2, L_2, \lambda_2}$  (replacing  $v_{xc; \vec{R}_2, L_2, \lambda_2}$ ) as the solutions to equation (42) obtained by replacing the right-hand sides by

$$\int_{\text{i.r.}} \rho_v(\vec{r}) K_{L_1}(\lambda_1, \vec{r} - \vec{R}_1) d\vec{r}$$

(for the sake of completeness we add that using  $\tilde{\rho}_v(\vec{r})$  instead of  $\rho_v(\vec{r})$  leads to only negligible changes in the final results). Subsequently, we introduce

$$T(\vec{r}) = \sum_{\vec{R}, L, \lambda} t_{\vec{R}, L, \lambda} K_L(\lambda, \vec{r} - \vec{R}). \quad (43)$$

The correction term has then the following form:

$$\begin{aligned} & \sum_{\lambda L} e_{\text{xc}; \vec{R}_k, \lambda, L} \int_{\text{i.r.}} \tilde{\rho}_v(\vec{r}) \frac{\partial K_L(\lambda, \vec{r} - \vec{R}_k)}{\partial R_\alpha} d\vec{r} \\ & + \sum_{\vec{R}, \lambda L} (e_{\text{xc}; \vec{R}, L, \lambda} - v_{\text{xc}; \vec{R}, L, \lambda}) \int_{\text{i.r.}} K_L(\lambda, \vec{r} - \vec{R}) \frac{\partial \tilde{\rho}_v(\vec{r})}{\partial R_\alpha} d\vec{r} \\ & + \sum_{\lambda L} t_{\vec{R}_k, L, \lambda} \sum_i [\epsilon_{\text{xc}}(\vec{r}_i) - \tilde{\epsilon}_{\text{xc}}(\vec{r}_i)] \frac{\partial K_L(\lambda, \vec{r}_i - \vec{R}_k)}{\partial R_\alpha} \\ & - \sum_i T(\vec{r}_i) \frac{\epsilon_{\text{xc}}(\vec{r}_i) - V_{\text{xc}}(\vec{r}_i)}{\tilde{\rho}_v(\vec{r}_i)} \frac{\partial \tilde{\rho}_v(\vec{r}_i)}{\partial R_\alpha} \\ & - \sum_{\lambda L} e_{\text{xc}; \vec{R}_k, L, \lambda} \sum_i T(\vec{r}_i) \frac{\partial K_L(\lambda, \vec{r}_i - \vec{R}_k)}{\partial R_\alpha} \\ & - \int_{|\vec{r} - \vec{R}_k| = s_k} s_k^2 \sqrt{\frac{4\pi}{3}} Y_{p_\alpha}(r - R_k) \\ & \times \left[ \rho_v(\vec{r}) \epsilon_{\text{xc}}(\vec{r}) - \rho_v(\vec{r}) \frac{4}{3} \tilde{\epsilon}_{\text{xc}}(\vec{r}) + \tilde{\rho}_v(\vec{r}) \frac{1}{3} \tilde{\epsilon}_{\text{xc}}(\vec{r}) \right] d(\widehat{r - R_k}). \end{aligned} \quad (44)$$

We have here used  $\tilde{\rho}_v$  instead of  $\rho_v$  since we determine  $\tilde{\epsilon}_{\text{xc}}$  and  $\tilde{V}_{\text{xc}}$  from  $\tilde{\rho}_v$ . Moreover, the last term is a surface term which is absent in the original expression of Dunlap *et al* [19].

#### 4. Helical polymers

For infinite, periodic systems we may use the formulae of the preceding section in obtaining the forces related to equivalent displacements of all equivalent atoms simultaneously. The only modifications will be that the orbital summation has to be extended with a  $\vec{k}$ -space integration and that the wavefunctions and basis functions are Bloch waves, i.e., sums over equivalent atom-centred basis functions of different unit cells multiplied with Bloch phase factors. The forces are, however, not able to give information on the variations of the total energy as a function of the size of the unit cell.

A special case is the helical polymers for which our full-potential LMTO method has been explicitly developed [12]. These systems are assumed to be infinite, helical, isolated, periodic chains with straight helical axes. The interactions between different chains are supposed to be negligible so that only one chain needs to be considered.

The helical symmetry is utilized by defining all quantities (basis functions, fit functions, potentials, etc) in local atom-centred right-handed coordinate systems that each have the  $z$ -axis parallel to the helical axis and the  $x$ -axis pointing away from this. Moreover, the size of the unit cell is described by the two parameters  $h$  and  $v$ , that describe the primitive symmetry operation (i.e., a translation of  $h$  and a rotation of  $v$ ).

## 5. Applications to molecules and helical polymers

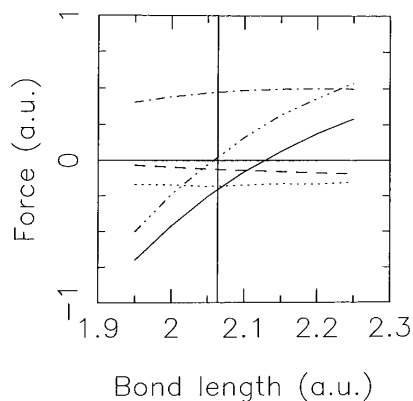
We have implemented the ideas presented in sections 3 and 4 in the full-potential LMTO method for helical polymers and tested the results for some simple systems. The general findings of these test calculations will now be discussed. Subsequently, we shall apply the method in optimizing all structural degrees of freedom of *trans*-polyacetylene as well as calculating the energy gain due to the dimerization.

However, we first give a few technical details. The basis sets consist of two sets of functions each containing s, p, and d functions on all sites. The two sets differ only in the value of  $\kappa$ .

In calculating the Pulay forces we notice that this leads to matrix elements for functions of s, p, d, and f symmetry. The f functions are only included explicitly inside the spheres, whereas it is assumed that these functions are so localized that their effects in the interstitial region can be neglected. For atoms at the beginning of the 3d and 4d series this may be a problem. Exchange and correlation effects were included using the local approximation of von Barth and Hedin [16].

All our test calculations showed one general result: in deriving the formulae for the forces we have started with the Hellmann–Feynman forces and those due to the frozen-core approximation and assumed that all other contributions are due to small inaccuracies in solving the Kohn–Sham equations. In agreement with this, the test calculations showed that only when the calculation is done ‘well’ (i.e., when the approximate wavefunctions  $\tilde{\psi}_i$  are close to the exact ones  $\psi_i$ , and the fits are accurate) are the calculated forces actually the derivatives of the total-energy surface and, consequently, only then does the structure of vanishing forces equal that of the lowest total energy.

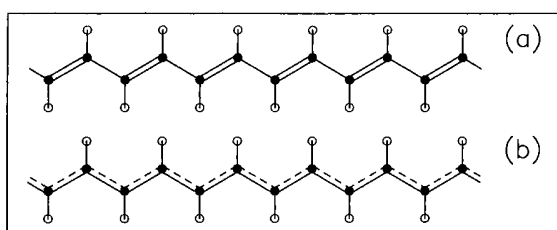
In order to illustrate the importance of the various contributions to the forces we show in figure 1 those for the  $N_2$  molecule. The Hellmann–Feynman forces and the frozen-core corrections are in principle exact under the assumption that no other approximation is made in the calculation. On the other hand, the Pulay forces and those due to the fits are corrections and as such calculated under the assumption that they are only small. Nevertheless, as figure 1 shows, these corrections are certainly not vanishing and without them the forces would vanish



**Figure 1.** Various contributions to the forces on a single atom of a  $N_2$  molecule as functions of the bond length. The solid curve is the sum of the Hellmann–Feynman and the frozen-core contributions, the dashed curve the Pulay forces, the dashed–dotted curve the corrections due to the charge-density fits, and the dotted curve those due to the exchange–correlation fits. The last curve is the total force. Finally, the vertical line marks the position of the total-energy minimum.

for a bond length very different from that of the lowest total energy.

We have, in addition to the  $N_2$  molecule, tested the quality of the present approach on a number of smaller molecules as well as on some helical polymers. Here, we shall only report results on one system, *trans*-polyacetylene. This polymer contains a zigzag backbone of carbon atoms that are bonded via  $sp^2$  hybrids, forming  $\sigma$ -bonds and  $\pi$ -bonds. In addition, there is one hydrogen atom per carbon atom; cf. figure 2. The lowest total energy is found for a structure where the C–C bond lengths alternate, but the structure without this alternation has a total energy only slightly above that of the former. It is a critical test to be able to describe this bond-length alternation as well as the energy gain related to this. We have optimized all structural degrees of freedom for this using the forces and thereby obtained C–C bond lengths of 2.520 and 2.636 au, C–C–C bond angles of  $123.6^\circ$ , C–H bond lengths of 2.065 au, and, finally, C–C–H and C=C–C bond angles of  $119.7^\circ$  and  $116.7^\circ$ , respectively. Assuming that the C–C bond lengths are constant, but keeping the unit-cell length unchanged leads to C–C bond lengths of 2.576 au, C–C–C bond angles of  $123.7^\circ$ , C–H bond lengths of 2.064 au, and C–C–H bond angles of  $118.2^\circ$ . In addition, the total energy is increased by 0.037 eV per CH unit compared with that of the structure with alternating C–C bond lengths.



**Figure 2.** The structure of *trans*-polyacetylene with (a) alternating and (b) non-alternating C–C bond lengths. Black and white circles represent carbon and hydrogen atoms, respectively.

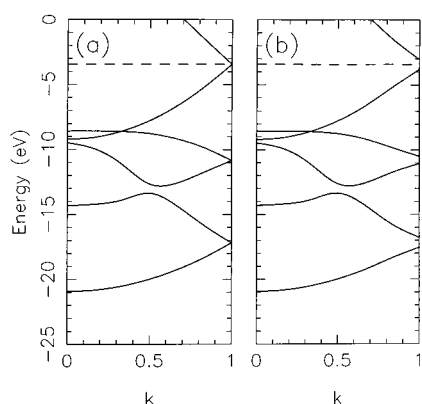
Only recently there have been other reports of full structure optimizations for this polymer [22–27]. These give C–C single-bond lengths between 2.67 and 2.76 au, C–C double-bond lengths between 2.46 and 2.60 au, C–H bond lengths from 2.06 to 2.08 au, C–C–C bond angles of  $124$ – $125^\circ$ , and C–C–H bond angles of  $117$ – $119^\circ$ . Experimentally, the C–C bond lengths are 2.57 and 2.72 au, the C–H bond lengths are 2.05–2.10 au, and the C–C–C bond angles  $123^\circ$  [28, 29] which agrees well with our values as well as with those from the other theoretical approaches. Finally, with the other theoretical approaches, the energy gain upon the bond-length alternation has been estimated to be between 0.019 and 0.067 eV per CH unit, also in excellent agreement with our value.

The existence of the bond-length alternation is often ascribed to a Peierls distortion that leads to a gap at the Fermi level, which is confirmed by the band structures for the optimized structures shown in figure 3. These band structures are very similar to those obtained earlier with the present computational method but for a slightly different geometry [13] and which were shown to agree well with experimental information. Therefore, the band structures of figure 3 will not be discussed further here.

In total we see that our results agree well with those of other theoretical studies. Therefore, we believe that this critical test shows that our calculation of the forces is correct.

## 6. Conclusions

In the present work we have derived closed formulae for the calculation of forces within general density-functional methods, where we also considered methods that treat different parts of space differently. We discussed in particular a full-potential LMTO method. LMTO



**Figure 3.** Band structures for (a) the optimized structure of *trans*-polyacetylene and (b) the structure with non-alternating C–C bond lengths but the same unit-cell length as in (a).

and related methods have the advantage that the basis functions are constructed so as to be good approximations to the exact solutions to the Kohn–Sham equations. In order to achieve this, space is divided into two parts, i.e. muffin-tin spheres and the interstitial region. This separation makes the calculation of matrix elements more cumbersome since any integration over the whole space has to be split into two terms, of which one is an integral over all spheres and the other is an integral over a ‘Swiss cheese’. In deriving the formulae for the forces, i.e. the changes in the total energy due to small shifts of the nuclei and their corresponding spheres, this separation leads to extra complications including that of the occurrence of surface terms, as we have seen.

Our general strategy has been to calculate forces that are consistent with the calculated total-energy hypersurface partly independently of the accuracy with which the latter is obtained. This meant correcting for various approximations in describing single-particle eigenfunctions, electron densities, and potentials. Our test results demonstrated that we have achieved this goal as long as one may consider the calculations ‘realistic’. In order to do so we relied on earlier works for corrections due to not fully converged expansions, notably those of Pulay [17], Fournier *et al* [18], and Dunlap *et al* [19], but modified in order to suit the present LMTO approach.

Finally, we have applied the method in optimizing the structure of *trans*-polyacetylene as well as in calculating the energy gain upon bond-length alternation. By comparing with results of experimental and other theoretical studies on this material, we were able to show that our method is reliable.

### Acknowledgments

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