First-principles pseudopotential calculations for hydrogen in 4d transition metals. I. Mixed-basis method for total energies and forces

First-principles pseudopotential calculations for hydrogen in 4d transition metals: I. Mixed-basis method for total energies and forces

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Abstract. A first-principles study of hydrogen in transition metals within the framework of the Born–Oppenheimer and local density-functional approximations using a mixed-basis pseudopotential method is presented in this work, which consists of two parts. In this first part our computational techniques are outlined. The features of the norm-conserving ionic pseudopotentials, the mixed basis and the calculation of total energies are summarized. A mixed-basis formalism for the calculation of forces on atoms in crystals, using the Hellmann–Feynman theorem and including contributions originating from the atom-centred localized functions in the mixed basis, is described in detail and applied to the example of restoring forces in PdH. An application to a study of vibrational properties of hydrogen isotopes in Pd and Nb will follow in the second part.

1. Introduction

The calculation of electronic, structural or magnetic properties of crystals from first principles, i.e. with only knowledge of the constituent elements as input, has become a very successful field of solid state physics during the last 15 years. Several efficient computational methods based on the local density-functional approximation (LDA) (Hohenberg and Kohn 1964, Kohn and Sham 1965, for a recent review see e.g. Jones and Gunnarsson 1989) as well as powerful electronic computers are available nowadays to calculate complex properties of single crystals and compounds across the periodic system of elements in a quantitative manner (see e.g. the reviews of Srivastava and Weaire 1987 or Pickett 1989).

Ideal single crystals or compounds are described by their unit cells with periodic boundary conditions. For the treatment of localized defects like vacancies or interstitial atoms, two different strategies have been developed (see e.g. Dederichs and Zeller 1981): the Green function method and the supercell approach.

In the Green function method the defect is embedded into the ideal host structure. The Green function of the crystal with the defect can be calculated from the Green function of the ideal crystal and the scattering potential of the defect by solving the Dyson equation.

In the supercell approach a single defect in a crystal is replaced by a periodic superlattice of defects, which need to be separated sufficiently to make their mutual

interaction negligible. Thus the crystal is described by a large unit cell with periodic boundary conditions containing one defect and several host-lattice atoms.

Conceptually the Green function method is very appealing, but it is technically demanding and difficult to achieve sufficient numerical accuracy for total energies. With the supercell approach the same computational techniques are used for the system with and without the defect. But one has to be careful that the size of the supercell, which is commonly limited by the computer memory and time, is sufficiently large to avoid spurious effects of the artificially periodic defect structure.

Our present contribution, which consists of two parts, is a first-principles study of the vibrational states of interstitial hydrogen isotopes in transition metals by means of a supercell approach. In this first part we present our computational techniques for the calculation of total energies and forces in crystals. The paper is organized in the following way: Section 2 introduces the two basic assumptions of our method: the Born–Oppenheimer approximation (BOA) (Born and Oppenheimer 1927) allows the formal separation of electronic and ionic motion in a quantum-mechanical system for the calculation of static and dynamic properties of crystals, and the electronic ground-state structure for a given ionic configuration is calculated by means of the LDA (Hohenberg and Kohn 1964, Kohn and Sham 1965). The calculation of electron densities, total energies and forces for transition metals using a mixed-basis pseudopotential method (Louie *et al* 1979) is outlined in sections 3 and 4. The non-local norm-conserving ionic pseudopotentials (Hamann *et al* 1979, Bachelet and Schlüter 1982), the mixed-basis method (Louie *et al* 1979, Elsässer *et al* 1990) and the Fourier-space total-energy formalism (Ihm *et al* 1979, Yin and Cohen 1982) used for our study are already described extensively in the literature. Therefore we restrict ourselves to giving only the basic relations. But the mixed-basis force formalism (Ho *et al* 1983), which has already been applied successfully several times (see e.g. Ho and Bohnen 1987, Ho and Harmon 1990), was only explained concisely. It will be discussed in detail in section 5, and applied to an example in section 6. To obtain accurate results for the electronic forces, it is necessary to take into account contributions originating from the atom-centred basis functions in the mixed basis (Ho *et al* 1983).

An application of the mixed-basis method to a study of vibrational properties of hydrogen isotopes in Pd and Nb (Elsässer 1990, Elsässer *et al* 1991a,b) will be given in the second part (Elsässer *et al* 1992, denoted by II).

2. Born–Oppenheimer approximation

The Born–Oppenheimer approximation for the many-particle system of atomic nuclei and electrons assumes that, owing to the large mass difference between nuclei and electrons ($M_j \gg m_e$), the many-body states can be approximated by product states:

$$\Psi(X_1, \ldots, X_{N_n}, x_1, \ldots, x_{N_e}) = \phi(X_1, \ldots, X_{N_n}) \cdot \psi(x_1, \ldots, x_{N_e}; \{X_j\}) \qquad (1)$$

where the electrons are adiabatically following the nuclei and are always in their ground state with respect to the instantaneous nuclear configuration. X_j or x_j denote space and spin coordinates of a nucleus or an electron, respectively. Then the total energy of the whole system can be calculated in two steps:

$$E = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle = \langle \phi | \langle \psi | \hat{\mathcal{H}} | \psi \rangle | \phi \rangle. \qquad (2)$$

$\hat{\mathcal{H}}$ is the many-body Hamiltonian for the N_n nuclei and the N_e electrons. In the first step the ground-state energy $E_0^e = \langle \psi_0 | \hat{\mathcal{H}} | \psi_0 \rangle$ of the electrons is calculated for given nuclear positions using the density-functional formalism (Hohenberg and Kohn 1964):

$$E_0^e(\{R_j\}) = E_0^e[\rho] = \min\{E^e[\tilde{\rho}]\} \tag{3}$$

where the total energy E^e is a unique functional of the electron density $\tilde{\rho}$, and its minimum E_0^e is obtained for the correct ground-state density ρ. In the second step the dynamics of the nuclei is calculated:

$$E^{ad} = \left\langle \phi \left| \sum_{j=1}^{N_n} \frac{\hat{P}_j^2}{2m_j} + E_0^e(\{R_j\}) \right| \phi \right\rangle . \tag{4}$$

The nuclei are moving in an adiabatic potential which is given by the energy hyperface E_0^e in the configuration space $\{R_j\}$ of the nuclear positions.

Equation (4) is the starting point for both statics (relaxations) and dynamics (local or collective vibration modes) of atoms in a crystal. Static relaxation means the search for the minimum of $E_0^e(\{R_j\})$ with respect to the nuclear positions R_j. For the dynamics of the nuclei their kinetic energies $\hat{P}_j^2/2m_j$ have to be taken into account.

In our case of hydrogen in transition metals the Born–Oppenheimer approximation is invoked once again for a separation of the motion of the light interstitial hydrogen atoms and the motion of the heavy host-metal atoms. The relatively slow motions of the metal atoms are neglected, so that the hydrogen atoms are moving in a stiff metal lattice. By choosing crystal unit cells containing just one hydrogen atom, the total energy in equation (4) is obtained by solving a one-particle Schrödinger equation for the eigenstates $|\phi\rangle$ in a periodic potential. This will be described in detail in II.

3. Ionic pseudopotentials and mixed basis

In the density-functional formalism the density of the valence electrons in a crystal is given by

$$\rho(r) = \sum_{n,k} w_{nk} |\psi_{nk}(r)|^2 . \tag{5}$$

The sum is over all n occupied one-particle states calculated on a cubic mesh of k-points in the first Brillouin zone. The sum can be restricted to the irreducible part (IBZ), but then the density additionally needs to be symmetrized (see appendix B in Elsässer *et al* 1990). The symmetry weights of the k-points and the band occupations are contained in the weights w_{nk}, which are calculated using a Gaussian smearing scheme (Fu and Ho 1983; see also appendix 1 here).

Wavefunctions $\psi_{nk}(r)$ and eigenvalues ε_{nk} are given as solutions of a Schrödinger-like equation:

$$\hat{H}\psi_{nk}(r) = (-\nabla^2 + \hat{V})\psi_{nk}(r) = \varepsilon_{nk}\psi_{nk}(r) \tag{6}$$

for a fictitious system of non-interacting electrons, which move in an effective potential

$$\hat{V} = \hat{V}_{HX} + \hat{V}_{ion} \tag{7}$$

and have the same density $\rho(r)$ as the interacting electrons of the real system. In this work atomic Rydberg units are used: $\hbar^2 = 2m_e = e^2/2 = 1$. Energies are given in Rydbergs (1 Ryd = 13.606 eV), lengths in Bohr radii (1 au = 0.529 Å).

$\hat{V}_{ion}$ represents the external potential exerted by the ions on the electrons and is given by the superposition of ionic pseudopotentials. $\hat{V}_{HX}$ represents the screening potential of the electrons and contains two terms: the electrostatic Hartree potential $V_H(r)$, which is a solution of Poisson's equation

$$\nabla^2 V_H(r) = -8\pi\rho(r) \tag{8}$$

and the exchange–correlation potential $V_{xc}(r)$, which is given in the LDA as a function of the local electron density $\rho(r)$ by the derivative $d(\rho\epsilon_{xc}(\rho))/d\rho$, where $\epsilon_{xc}(\rho)$ represents the exchange–correlation energy density of a homogeneous electron gas of density ρ in real space. For a periodic crystal the Hartree potential is given in Fourier space by $V_H = 8\pi\rho(G)/|G|^2$. The singular component $V_H(G=0)$ causes an infinite energy shift in the eigenvalue problem (equation (10) below), which is exactly compensated in the total energy formula (equation (11) below). Thus it can be set to zero arbitrarily. The set of equations (5)–(8), usually called the *Kohn–Sham* equations, is iterated to find the self-consistent ground-state density and effective potential.

The electronic structures, densities and total energies are calculated in the LDA. The parametrization of Hedin and Lundqvist (1971) for the exchange–correlation energy was used for this work.

In the pseudopotential theory the interaction of the valence electrons with the closed-shell core electrons and the nuclei is taken into account by ionic pseudopotentials. We used non-local norm-conserving pseudopotentials for the Pd^{10+} and Nb^{5+} ion cores. They were constructed from relativistic atomic LDA eigenstates following the scheme of Hamann, Schlüter and Chiang (Hamman *et al* 1979, Bachelet and Schlüter 1982). For H^+ a local norm-conserving pseudopotential derived from the Coulomb potential of a proton and its analytic 1s state was chosen. For its construction Kerker's (1981) scheme was used, which was modified to avoid edges and kinks in the potential in real space and thus to give a rapid decay in Fourier space. The angular-momentum dependent components of the ionic pseudopotentials are shown in figure 1. As a test of their transferability the eigenvalues and excitation energies of several atomic configurations from all-electron and pseudopotential calculations are compared in the tables 1–3. In our calculations of crystalline properties Fourier components $V_{j,l}(q)$ were taken into account up to $q_{max} = 16$ au^{-1}.

To solve the Schrödinger equation (6) for crystals the wavefunctions $\psi_{nk}(r)$ are represented by an energy-independent mixed basis of plane waves and localized functions (Louie *et al* 1979, Elsässer *et al* 1990):

$$\psi_{nk}(r) = \sum_G \alpha_G^{nk} \frac{1}{\sqrt{\Omega}} e^{i(k+G)\cdot r} + \sum_{j,l,m} \beta_{jlm}^{nk} \phi_{jlm}^k(r). \tag{9}$$

The expansion coefficients α_G^{nk} and β_{jlm}^{nk} are then obtained as eigenvectors ψ^{nk} of the generalized eigenvalue problem:

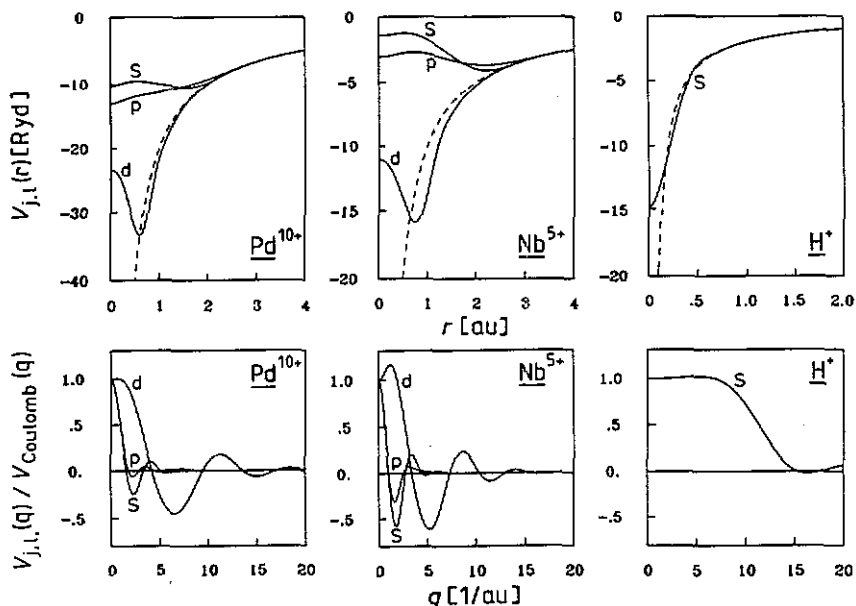$$\mathbf{H}^k \psi^{nk} = \varepsilon_{nk} \mathbf{S}^k \psi^{nk} \tag{10}$$

Figure 1. Radial parts of the angular-momentum dependent ionic pseudopotentials of Pd (left) and Nb (middle) and of the local pseudopotential of H (right) in real space (upper panels) and in Fourier space (lower panels); the corresponding ionic Coulomb potentials are drawn by broken curves.

Table 1. Comparison of atomic valence-state eigenvalues and excitation energies of Pd from pseudopotential (reference configuration $[Kr]4d^{9.5}5s^{0.25}5p^{0.25}$) and (in parentheses) all-electron calculations in the LDA.

Atomic configurations	Valence-state eigenvalues (Ryd)			Excitation energies (Ryd)
	d	s	p	
$[Kr]4d^{10}5s^{0}5p^{0}$	−0.3227	−0.2718	−0.0311	0
	(−0.3238)	(−0.2710)	(−0.0308)	(0)
$[Kr]4d^{9}5s^{1}5p^{0}$	−0.5160	−0.3462	−0.0713	0.1076
	(−0.5143)	(−0.3476)	(−0.0724)	(0.1074)
$[Kr]4d^{9}5s^{0}5p^{1}$	−0.6466	−0.4377	−0.1421	0.3916
	(−0.6447)	(−0.4386)	(−0.1429)	(0.3917)
$[Kr]4d^{8}5s^{2}5p^{0}$	−0.7411	−0.4220	−0.1078	0.3498
	(−0.7316)	(−0.4252)	(−0.1106)	(0.3420)
$[Kr]4d^{8}5s^{1}5p^{1}$	−0.8646	−0.5050	−0.1704	0.6737
	(−0.8531)	(−0.5070)	(−0.1727)	(0.6660)
$([Kr]4d^{9}5s^{0}5p^{0})^{+}$	−1.0999	−0.8394	−0.4737	0.6956
	(−1.1007)	(−0.8407)	(−0.4750)	(0.6967)
$([Kr]4d^{8}5s^{1}5p^{0})^{+}$	−1.3510	−0.9434	−0.5494	1.0271
	(−1.3441)	(−0.9473)	(−0.5541)	(1.0229)
$([Kr]4d^{8}5s^{0}5p^{1})^{+}$	−1.4539	−1.0116	−0.6086	1.4250
	(−1.4452)	(−1.0150)	(−0.6129)	(1.4201)

where H^{k} and S^{k} are the Hamiltonian and overlap matrix, respectively (see appendix 2).

Table 2. Comparison of atomic valence-state eigenvalues and excitation energies of Nb from pseudopotential (reference configuration $[Kr]4d^{3.45}5s^{1.45}5p^{0.1}$) and (in parentheses) all-electron calculations in the LDA.

Atomic configurations	Valence-state eigenvalues (Ryd)			Excitation energies (Ryd)
	d	s	p	
$[Kr]4d^3 5s^2 5p^0$	−0.3600	−0.3625	−0.1198	0
	(−0.3586)	(−0.3630)	(−0.1207)	(0)
$[Kr]4d^4 5s^1 5p^0$	−0.2414	−0.3148	−0.0962	0.0398
	(−0.2428)	(−0.3141)	(−0.0955)	(0.0396)
$[Kr]4d^5 5s^0 5p^0$	−0.1594	−0.2809	−0.0813	0.1390
	(−0.1605)	(−0.2779)	(−0.0786)	(0.1356)
$[Kr]4d^4 5s^0 5p^1$	−0.3230	−0.3737	−0.1447	0.2630
	(−0.3253)	(−0.3741)	(−0.1445)	(0.2632)
$[Kr]4d^3 5s^1 5p^1$	−0.4455	−0.4207	−0.1662	0.2483
	(−0.4432)	(−0.4214)	(−0.1672)	(0.2479)
$([Kr]4d^4 5s^0 5p^0)^+$	−0.7037	−0.7193	−0.4411	0.5535
	(−0.7086)	(−0.7202)	(−0.4403)	(0.5532)
$([Kr]4d^3 5s^1 5p^0)^+$	−0.8593	−0.7965	−0.4969	0.5754
	(−0.8603)	(−0.7987)	(−0.4989)	(0.5766)
$([Kr]4d^3 5s^0 5p^1)^+$	−0.9354	−0.8468	−0.5423	0.8771
	(−0.9355)	(−0.8501)	(−0.5451)	(0.8786)

Table 3. Comparison of the eigenvalues ε_{nl} of the hydrogen problem and of the eigenvalues ε_{nl}^{LDA} and total energies $E_{0,nl}^{LDA}$ of self-consistent LDA calculations for H with the local pseudopotential (reference configuration $1s^1$) and (in parentheses) with the protonic Coulomb potential.

State nl	ε_{nl} (Ryd)	ε_{nl}^{LDA} (Ryd)	$E_{0,nl}^{LDA}$ (Ryd)
1s	−1.000002	−0.473547	−0.898060
	(−1)	(−0.473550)	(−0.898091)
2s	−0.249997	−0.148348	−0.253346
	$(-\frac{1}{4})$	(−0.148354)	(−0.253355)
2p	−0.249993	−0.118529	−0.241612
	$(-\frac{1}{4})$	(−0.118530)	(−0.241618)
3s	−0.111110	−0.076265	−0.121168
	$(-\frac{1}{9})$	(−0.076265)	(−0.121171)
3p	−0.111109	−0.071471	−0.120195
	$(-\frac{1}{9})$	(−0.071472)	(−0.120198)
3d	−0.111111	−0.056884	−0.115350
	$(-\frac{1}{9})$	(−0.056884)	(−0.115350)

Our mixed-basis method, which was originally developed by Louie *et al* (1979), has since been improved and was described in detail recently (Elsässer *et al* 1990). An important feature of the method is that the localized basis functions are restricted to single atomic sites. This avoids the necessity for calculations of two-and three-centre integrals between different sites in real space, and it enables the accurate calculation of forces (Ho *et al* 1983) in an efficient way.

4. Total energy and forces

From the electron density calculated with the mixed-basis scheme in real space and transformed into Fourier space by means of fast Fourier-transform techniques (see e.g. chapter 12 in Press *et al* 1986), the total energy of a crystal can be calculated according to a Fourier-space formalism (Ihm *et al* 1979, 1980, Yin and Cohen 1982). The total energy per unit cell is given by the formula (Fu and Ho 1983)

$$
E_0^e = E_{\text{Ewald}} + \Omega_c \sum_{nk} w_{nk}\varepsilon_{nk} - \Omega_c \sum_G \rho^*(G) V_{\text{HX}}^{\text{in}}(G)
$$

$$
+ \tfrac{1}{2}\Omega_c \sum_{G \neq 0} 8\pi |\rho(G)|^2 / |G|^2 + \Omega_c \sum_G \rho^*(G)\epsilon_{xc}(G)
$$

$$
+ \left(\sum_j Z_j\right)\left(\sum_j \alpha_j\right)
\tag{11}
$$

where E_{Ewald} gives the total-energy contribution from the interactions between the ionic cores calculated according to Ewald's method, Ω_c is the unit-cell volume, Z_j are the charges of the ion cores, $V_{\text{HX}}^{\text{in}}(G)$ are the Fourier components of the input screening potential of the Schrödinger equation for one iteration step, $\epsilon_{xc}(G)$ are the Fourier components of the exchange–correlation energy density calculated from $\rho(r)$, and α_j contains the difference between the local part ($l = 0$ component) of the ionic pseudopotential and the corresponding ionic Coulomb potential for the jth atom:

$$
\alpha_j = \frac{4\pi}{\Omega_c} \int_0^\infty \left(V_{j,0}(r) + \frac{2Z_j}{r}\right) r^2 \, dr.
\tag{12}
$$

The $\rho^*(G)$ are complex conjugate to the Fourier components $\rho(G)$ of the electronic charge density.

As mentioned in the introduction, equilibrium configurations of the crystal can be found via static relaxations by seeking the minimum of the energy hyperface $E_0^e(r_j)$ (r_j denote the atomic positions within one unit cell of a crystal; $R_j = r_j + R$; R is a lattice translation vector of the crystal lattice). The shape of the energy hyperface can be mapped out by calculating E_0^e for a number of different sets of $\{r_j\}$. For simple crystals with few atoms in the unit cell the relaxation paths of the atomic cores are found relatively easily using geometrical considerations. With increasing complexity of the unit cell the many degrees of freedom of the atoms lead to more and more complicated relaxation patterns requiring the calculation of E_0^e for many coordinate sets. For such cases knowledge of the gradients of the energy hyperface at the atomic sites is of considerable help. They indicate the directions along which the atoms have to be shifted to reach the equilibrium configuration.

The forces as negative gradients of the total energy can be calculated directly with the *ab initio* pseudopotential method. For a pure plane-wave basis the force calculation using the Hellmann–Feynman theorem is simple because the plane waves are independent of the atomic positions (Ihm *et al* 1979, Yin and Cohen 1982). But the application of this formalism is more or less restricted to crystals built from principal-group elements (simple metals or semiconductors), because transition-metal

or rare-earth elements require too many plane waves to represent the d or f valence states.

For all kinds of basis sets with atom-centred functions, which are better adapted to localized d or f systems, changes in the total energy due to virtual displacements of the basis functions lead to additional contributions to the forces, which have to be taken into account (Ho *et al* 1983). For basis functions centred at atomic sites with extensions over several neighbouring sites, e.g. Gaussians or augmented functions (augmented plane waves (APW) or muffin-tin orbitals (MTO)), the force calculation is a very difficult problem, which is not yet completely overcome in the most common first-principles methods, for example, the (linear) LMTO and LAPW methods (Andersen 1975).

The mixed-basis force formalism will be outlined in the following section, and its accuracy will be demonstrated by an example in section 6.

5. Force formalism

At self-consistency, the energy change due to virtual displacements of the atoms can be derived (Ho *et al* 1983) from the total-energy expression (11):

$$\delta E_0^e = \delta E_{\mathrm{Ewald}} + \Omega_c \sum_{nk} \delta w_{nk} \varepsilon_{nk} + \Omega_c \sum_{nk} w_{nk} \delta \varepsilon_{nk} - \Omega_c \sum_G \rho^*(G) \, \delta V_{\mathrm{HX}}(G). \tag{13}$$

The last term in equation (11) is independent of the atomic positions. Therefore it has no contribution to the energy change. The change of the interaction energy between the ion cores is given by

$$\delta E_{\mathrm{Ewald}} = -\sum_j F_j^{\mathrm{Ewald}} \cdot \delta r_j \tag{14}$$

and the F_j^{Ewald} are the negative gradients of Ewald's formula with respect to r_j.

Energy changes due to incomplete self-consistency of the effective potential can be taken into account in principle if one makes an efficient estimate of $\delta \rho$. Such a correction is not included in the present calculations.

Thus,

$$\delta E_0^e = \delta E_{\mathrm{Ewald}} + \Omega_c \sum_{nk} \delta w_{nk} \varepsilon_{nk} + \Omega_c \sum_{nk} w_{nk} \delta \varepsilon_{nk} - \Omega_c \sum_{nk} w_{nk} \langle \psi_{nk} | \delta \hat{V}_{\mathrm{HX}} | \psi_{nk} \rangle. \tag{15}$$

We now consider the change in the effective potential $\hat{V}$, due to the atomic displacements. The change $\delta \hat{V}$ can be divided in the following ways:

$$\delta \hat{V} = \delta \hat{V}_{\mathrm{HX}} + \delta \hat{V}_{\mathrm{ion}} = \delta \hat{V}_{\mathrm{HX}} + \delta \hat{V}_{\mathrm{ion}}^{\mathrm{loc}} + \delta \hat{V}_{\mathrm{ion}}^{\mathrm{nl}} = \delta \hat{V}^{\mathrm{loc}} + \delta \hat{V}^{\mathrm{nl}}. \tag{16}$$

The superscripts loc and nl stand for local and non-local parts, respectively, of the effective potential. The local part contains both $\hat{V}_{\mathrm{ion}}^{\mathrm{loc}}$ and $\hat{V}_{\mathrm{HX}}$ and the non-local

part comes only from the ionic pseudopotentials. With this separation, δE_0^e can be regrouped into the following expression:

$$\delta E_0^e = \delta E_{\text{Ewald}} + \Omega_c \sum_{G \neq 0} \rho^*(G) \delta V_{\text{ion}}^{\text{loc}}(G)$$

$$+ \Omega_c \sum_{nk} w_{nk} (\delta \varepsilon_{nk} - \langle \psi_{nk} | \delta \hat{V}^{\text{loc}} | \psi_{nk} \rangle) + \Omega_c \sum_{nk} \delta w_{nk} \varepsilon_{nk} \tag{17}$$

$$= - \sum_j F_j \cdot \delta r_j. \tag{18}$$

The first term arises from the interaction between the ionic cores, the second and third terms contain the change in electronic states due to virtual displacements of the atoms, and the fourth term comes from changes of the band occupations close to the Fermi energy in metallic systems.

It is convenient to calculate the forces according to equation (17). From the local part of the ionic pseudopotential in Fourier space, which is given by (see equation (A2) in Elsässer *et al* 1990):

$$V_{\text{ion}}^{\text{loc}}(G) = \sum_j \exp(-iG \cdot r_j) V_{j,0}(G) \tag{19}$$

its change (second term in equation (17)) can be derived easily as

$$\delta V_{\text{ion}}^{\text{loc}}(G) = \sum_j -i(G \cdot \delta r_j) \exp(-iG \cdot r_j) V_{j,0}(G). \tag{20}$$

Taking together the changes of the non-local part of the ionic pseudopotential and of the mixed basis (third term in equation (17)) several matrix elements, which are difficult to calculate, mutually cancel, as will become clear below. By applying the Gaussian smearing method the calculation of changes in the weights δw_{nk} can be traced back to the calculation of changes in the eigenvalues $\delta \varepsilon_{nk}$, as described in appendix 1.

The next task is the calculation of the matrix elements for the third term in equation (17). In the mixed-basis representation they are given by (see equation (7) in Ho *et al* 1983)

$$\delta \varepsilon_{nk} = \sum_{G',G} \left(\alpha_{G'}^{nk} \right)^* \alpha_G^{nk} (\delta \langle k + G' | \hat{H} | k + G \rangle - \varepsilon_{nk} \delta \langle k + G' | k + G \rangle)$$

$$+ \sum_{G',jlm} \left(\alpha_{G'}^{nk} \right)^* \beta_{jlm}^{nk} (\delta \langle k + G' | \hat{H} | \phi_{jlm}^k \rangle - \varepsilon_{nk} \delta \langle k + G' | \phi_{jlm}^k \rangle)$$

$$+ \sum_{j'l'm',G} \left(\beta_{j'l'm'}^{nk} \right)^* \alpha_G^{nk} (\delta \langle \phi_{j'l'm'}^k | \hat{H} | k + G \rangle - \varepsilon_{nk} \delta \langle \phi_{j'l'm'}^k | k + G \rangle)$$

$$+ \sum_{j'l'm',jlm} \left(\beta_{j'l'm'}^{nk} \right)^* \beta_{jlm}^{nk} (\delta \langle \phi_{j'l'm'}^k | \hat{H} | \phi_{jlm}^k \rangle - \varepsilon_{nk} \delta \langle \phi_{j'l'm'}^k | \phi_{jlm}^k \rangle)$$

$$\tag{21}$$

and

$$\langle \psi_{nk} | \delta \hat{V}^{\text{loc}} | \psi_{nk} \rangle = \sum_{G',G} \left(\alpha_{G'}^{nk} \right)^* \alpha_G^{nk} \langle k + G' | \delta \hat{V}^{\text{loc}} | k + G \rangle$$

$$+ \sum_{G',jlm} \left(\alpha_{G'}^{nk} \right)^* \beta_{jlm}^{nk} \langle k + G' | \delta \hat{V}^{\text{loc}} | \phi_{jlm}^k \rangle$$

$$+ \sum_{j'l'm',G} \left(\beta_{j'l'm'}^{nk} \right)^* \alpha_G^{nk} \langle \phi_{j'l'm'}^k | \delta \hat{V}^{\text{loc}} | k + G \rangle$$

$$+ \sum_{j'l'm',jlm} \left(\beta_{j'l'm'}^{nk} \right)^* \beta_{jlm}^{nk} \langle \phi_{j'l'm'}^k | \delta \hat{V}^{\text{loc}} | \phi_{jlm}^k \rangle. \tag{22}$$

For the overlap matrix elements (see equations (15) in Elsässer *et al* 1990) the changes are given by

$$\delta S_{G',G}^k = \delta \langle k + G' | k + G \rangle = 0 \tag{23}$$

$$\delta S_{jlm,G}^k = \delta \langle \phi_{jlm}^k | k + G \rangle = iG \cdot \delta r_j \, S_{jlm,G}^k \tag{24}$$

$$\delta S_{j'l'm',jlm}^k = \delta \langle \phi_{j'l'm'}^k | \phi_{jlm}^k \rangle = 0 \tag{25}$$

and for the Hamiltonian matrix elements (see equations (16)–(18) in Elsässer *et al* 1990) by

$$\delta H_{G',G}^k = \delta \langle k + G' | - \nabla^2 + \hat{V}^{\text{nl}} | k + G \rangle + \delta \langle k + G' | \hat{V}^{\text{loc}} | k + G \rangle$$

$$= \langle k + G' | \delta \hat{V}^{\text{nl}} | k + G \rangle + \langle k + G' | \delta \hat{V}^{\text{loc}} | k + G \rangle \tag{26}$$

$$\delta H_{jlm,G}^k = \delta \langle \phi_{jlm}^k | - \nabla^2 + \hat{V}^{\text{nl}} | k + G \rangle + \delta \langle \phi_{jlm}^k | \hat{V}^{\text{loc}} | k + G \rangle$$

$$= iG \cdot \delta r_j \langle \phi_{jlm}^k | - \nabla^2 + \hat{V}^{\text{nl}} | k + G \rangle + \delta \langle \phi_{jlm}^k | \hat{V}^{\text{loc}} | k + G \rangle \tag{27}$$

$$\delta H_{j'l'm',jlm}^k = \delta \langle \phi_{j'l'm'}^k | - \nabla^2 + \hat{V}^{\text{nl}} | \phi_{jlm}^k \rangle + \delta \langle \phi_{j'l'm'}^k | \hat{V}^{\text{loc}} | \phi_{jlm}^k \rangle$$

$$= \delta \langle \phi_{j'l'm'}^k | \hat{V}^{\text{loc}} | \phi_{jlm}^k \rangle. \tag{28}$$

The matrix elements of $\delta \hat{V}^{\text{loc}}$ are transformed in the following way:

$$\langle k + G' | \delta \hat{V}^{\text{loc}} | k + G \rangle = \delta \langle k + G' | \hat{V}^{\text{loc}} | k + G \rangle \tag{29}$$

$$\langle \phi_{jlm}^k | \delta \hat{V}^{\text{loc}} | k + G \rangle = \delta \langle \phi_{jlm}^k | \hat{V}^{\text{loc}} | k + G \rangle - \langle \delta \phi_{jlm}^k | \hat{V}^{\text{loc}} | k + G \rangle$$

$$= \delta \langle \phi_{jlm}^k | \hat{V}^{\text{loc}} | k + G \rangle - (iG \langle \phi_{jlm}^k | \hat{V}^{\text{loc}} | k + G \rangle$$

$$+ \langle \phi_{jlm}^k | \nabla_r \hat{V}^{\text{loc}} | k + G \rangle) \cdot \delta r_j \tag{30}$$

$$\langle \phi_{j'l'm'}^k | \delta \hat{V}^{\text{loc}} | \phi_{jlm}^k \rangle = \delta \langle \phi_{j'l'm'}^k | \hat{V}^{\text{loc}} | \phi_{jlm}^k \rangle - \langle \phi_{j'l'm'}^k | \nabla_r \hat{V}^{\text{loc}} | \phi_{jlm}^k \rangle \cdot \delta r_j. \tag{31}$$

In deriving these formulae, we used the information that the plane waves are independent of the atomic positions:

$$\delta \{ (1/\sqrt{\Omega}) \exp[i(k + G) \cdot r] \} = 0 \tag{32}$$

and the transition from $\delta\phi_{jlm}^k(r)$ to $\nabla_r \hat{V}^{\text{loc}}$ can be obtained by expanding the localized functions in plane waves (see equation (7) in Elsässer *et al* 1990).

Thus,

$$\delta H_{G',G}^k - \langle k + G' | \delta \hat{V}^{\text{loc}} | k + G \rangle = \langle k + G' | \delta \hat{V}^{\text{nl}} | k + G \rangle$$

$$= -\mathrm{i}(G' - G) \cdot \delta r_j \exp[\mathrm{i}(G' - G) \cdot r_j] \sum_{l=1}^{l_{\text{max}}} \bar{V}_{j,l}(k + G', k + G) \quad (33)$$

$$\delta H_{jlm,G}^k - \langle \phi_{jlm}^k | \delta \hat{V}^{\text{loc}} | k + G \rangle = \mathrm{i}G \cdot \delta r_j \langle \phi_{jlm}^k | -\nabla^2 + \hat{V}^{\text{loc}} + \hat{V}^{\text{nl}} | k + G \rangle$$

$$+ \langle \phi_{jlm}^k | \nabla_r \hat{V}^{\text{loc}} | k + G \rangle \cdot \delta r_j \quad (34)$$

$$\delta H_{j'l'm',jlm}^k - \langle \phi_{j'l'm'}^k | \delta \hat{V}^{\text{loc}} | \phi_{jlm}^k \rangle = \langle \phi_{j'l'm'}^k | \nabla_r \hat{V}^{\text{loc}} | \phi_{jlm}^k \rangle \cdot \delta r_j. \quad (35)$$

The gradient $\nabla_r \hat{V}^{\text{loc}}$ for real-space matrix elements around the atomic position r_j contains two terms (see appendix 3):

$$\nabla_r V_j^{\text{loc}}(r') = \nabla_r V_{j,L=0}^{\text{loc}}(r') + \nabla_r V_{j,L=1}^{\text{loc}}(r')$$

$$= \sum_G \mathrm{i}G \exp(\mathrm{i}G \cdot r_j) V^{\text{loc}}(G) j_0(Gr') + \hat{r}' \frac{\partial V_j^{\text{loc}}(r')}{\partial r'}. \quad (36)$$

The function $\partial V_j^{\text{loc}}(r)/\partial r$ (see equations (A3.4) and (A3.9)) is given by

$$\frac{\partial V_j^{\text{loc}}(r)}{\partial r} = -\sum_G V^{\text{loc}}(G) \exp(\mathrm{i}G \cdot r_j) G j_1(Gr). \quad (37)$$

The matrix elements of $\nabla_r \hat{V}_{j,L=0}^{\text{loc}}$ are given by ($q = |k + G|$)

$$\langle \phi_{jlm}^k | \nabla_r \hat{V}_{L=0}^{\text{loc}} | k + G \rangle = \frac{\int_0^{r_{jl}} \mathrm{d}r\, r^2 f_{jl}(r) \nabla_r V_{j,L=0}^{\text{loc}}(r) j_l(qr)}{\int_0^{r_{jl}} \mathrm{d}r\, r^2 f_{jl}(r) j_l(qr)} S_{jlm,G}^k \quad (38)$$

$$\langle \phi_{j'l'm'}^k | \nabla_r \hat{V}_{L=0}^{\text{loc}} | \phi_{jlm}^k \rangle = \int_0^{r_{jl}} \mathrm{d}r\, r^2 \left(f_{jl}(r)\right)^2 \nabla_r V_{j,L=0}^{\text{loc}}(r) \delta_{j',j} \delta_{l',l} \delta_{m',m}. \quad (39)$$

Here $f_{jl}(r)$ is the radial part in the localized basis function ϕ_{jlm} centred at an atomic site r_j, and r_{jl} is its cut-off radius (cf equation (6) in Elsässer *et al* 1990).

The Cartesian components ($\alpha = 1, 2, 3$) of the matrix elements of $\nabla_r \hat{V}_{j,L=1}^{\text{loc}}$ are given by ($q = k + G$)

$$(\langle \phi_{jlm}^k | \nabla_r V_{L=1}^{\text{loc}} | k + G \rangle)_\alpha = \mathrm{i} \exp(\mathrm{i}G \cdot r_j)$$

$$\times (\hat{q}_\alpha A_{l+1}(q) K_{lm}(\hat{q}) - \sum_{\substack{m' \\ l'=l-1}} C_{lm,l'm'}^\alpha K_{l'm'}(\hat{q})[A_{l-1}(q) + A_{l+1}(q)])$$

$$(40)$$

$$(\langle \phi_{j'l'm'}^k | \nabla_r V_{L=1}^{\text{loc}} | \phi_{jlm}^k \rangle)_\alpha = \int_0^{r_{jl}} \mathrm{d}r\, r^2 f_{jl'}^*(r) f_{jl}(r) \frac{\partial V_j^{\text{loc}}(r)}{\partial r}$$

$$\times \mathrm{i}^{l-l'} C_{lm,l'm'}^\alpha \delta_{j',j} \delta_{|l-l'|,1} \delta_{|m-m'|,1} \quad (41)$$

with the Clebsch–Gordan coefficients $C^{\alpha}_{lm,l'm'}$

$$\frac{x_{\alpha}}{r} K_{lm} = \sum_{\substack{l' \\ (l'=l\pm 1)}} \sum_{\substack{m' \\ (m'=m, m\pm 1)}} C^{\alpha}_{lm,l'm'} K_{l'm'} \tag{42}$$

and the radial integrals

$$A_{l'}(q) = \frac{4\pi}{\sqrt{\Omega_c}} \int_0^{r_{jl}} dr\, r^2 f_{jl}(r) \frac{\partial V_j^{loc}(r)}{\partial r} j_{l'}(qr). \tag{43}$$

In the case that localized functions of only one angular momentum for each atom are used, e.g. $l = l' = 2$ for transition metals and $l = l' = 0$ for hydrogen in our work, the matrix elements (41) vanish.

The fourth term of equation (17) is zero for semiconductors and insulators because of their energy gap. Also for metals the contributions to the forces due to redistributions of a few states around the Fermi energy are usually small (Ho *et al* 1983). This term can usually be neglected without degrading the accuracy of the calculated forces.

To summarize the mixed-basis force formalism, it has been outlined how the force contributions from changes in the localized basis functions and in the band occupations can be taken into account to get correct forces in transition-metal systems. An essential ingredient for this is the choice of localized basis functions, which are restricted to single atomic sites to avoid multi-centred expressions, additional to the plane waves, which are extended over the whole unit cell volume.

6. An example: restoring forces in PdH

As an example to demonstrate the capability of the force formalism described in the preceding section we choose a face-centred cubic PdH unit cell. This metal–hydrogen system will be discussed extensively in paper II, to which we refer the reader for more details. In this section we calculate the restoring forces that appear when the H atom is shifted away from the stable octahedral interstitial site at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ by a vector $\delta \hat{x}$, where δ is the distance to the octahedral site, and $\hat{x}$ is a unit vector pointing along the direction of the displacement. The Pd atom is located at $(0, 0, 0)$.

The forces calculated directly are denoted by $F\hat{x}$, where F is the magnitude of the force. In this simple example, the restoring forces are directed in the opposite direction to the displacements. These forces are compared with forces $(\Delta E_0^e / \Delta x)\hat{x}$, which are determined by total-energy changes ΔE_0^e connected with small finite shifts Δx around the displaced position δ.

The forces at the H atom and, according to Newton's law (*action = reaction*), on the Pd atom in the PdH unit cell calculated in the two ways are given in table 4. Newton's law is fulfilled for the forces $\Delta E_0^e / \Delta x$ *per definitionem*, and for the forces F up to a few per cent. This slight discrepancy is related to the spherical approximation made for the local part of the effective potential in the matrix elements containing localized functions (see appendix 3). But within this accuracy the directions and magnitudes of the forces calculated in the two ways coincide.

This simple example already demonstrates the high efficiency of the direct force calculation. For the calculation of F, on the one hand, for each displacement δ

Table 4. Restoring forces (Ryd/au) on H and on Pd due to displacements δ of H from the octahedral interstitial site in a PdH unit cell ($a = 7.70$ au $= 4.07$ Å). The unit vector $\hat{x}$ is given in Cartesian coordinates.

$\hat{x}$	δ/a	F_{Pd}	F_H	$\Delta x/a$	$(-\Delta E_0^e/\Delta x)_{Pd/H}$
$\frac{1}{\sqrt{3}}$ (111)	$-0.05\sqrt{3}$	-0.0092	$+0.0092$	$0.01\sqrt{3}$	$-/+0.0091$
	$-0.10\sqrt{3}$	-0.0212	$+0.0211$		$-/+0.0204$
	$-0.20\sqrt{3}$	$+0.0153$	-0.0146		$+/-0.0154$
$\frac{1}{\sqrt{2}}$ (110)	$-0.05\sqrt{2}$	-0.0078	$+0.0078$	$0.01\sqrt{2}$	$-/+0.0080$
	$-0.10\sqrt{2}$	-0.0346	$+0.0346$		$-/+0.0335$
(001)	-0.05	-0.0054	$+0.0055$	0.01	$-/+0.0060$
	-0.10	-0.0406	$+0.0404$		$-/+0.0417$

one self-consistent total-energy calculation is necessary, and additionally the force calculation, which takes a computer-time amount of about one iteration step. For $\Delta E_0^e/\Delta x$, on the other hand, at least three total energies need to be calculated self-consistently for the displacements δ and $\delta \pm \delta x/2$. With increasing complexity of the unit cell, the force calculations become an increasingly efficient tool for relaxation studies because of the many atomic degrees of freedom. Furthermore, in principle they open up the possibility for an application of first-principles molecular-dynamics schemes (Car and Parrinello 1985) to transition-metal systems.

7. Summary

In this contribution, which is the first of two papers about our first-principles study of hydrogen in transition metals, we outlined our computational techniques. The calculation of total energies in the frameworks of the Born–Oppenheimer and the local density-functional approximations was briefly reviewed. Non-local, norm-conserving ionic pseudopotentials for the interaction between valence electrons and ionic cores were applied, and a mixed basis of plane waves and atom-centred localized functions was used for the representation of the valence wavefunctions in crystals.

A detailed description of our mixed-basis formalism for the calculation of forces on atoms in a crystal is presented. The formalism had been successful in former applications but up to now it had been described only in a concise manner.

To obtain accurate results for the electronic forces calculated with the Hellmann–Feynman theorem, it is necessary to include contributions due to changes of the atom-centred basis functions with atomic displacements. The accuracy of the method was demonstrated for an example of restoring forces in PdH.

The second of our two papers deals with an application of our mixed-basis total-energy and force formalism to the study of local vibrations of interstitial H isotopes in Pd and Nb.

Acknowledgments

Appendix 1. Brillouin-zone summation

Because of the infinite periodicity of crystalline unit cells with periodic boundary conditions ($N \to \infty$) the N k vectors of Bloch functions are continuously distributed over the first Brillouin zone. Therefore sums over these k vectors can be replaced by integrals:

$$\sum_k \ldots \to \frac{\Omega}{(2\pi)^3} \int_\Omega d^3k \ldots \qquad (A1.1)$$

Technically these integrals are commonly approximated by the trapezoidal rule with a finite number N_s of sampling points K (Chadi and Cohen 1973, Monkhorst and Pack 1976) and the integrals reduce to sums again:

$$\frac{\Omega}{(2\pi)^3} \int_\Omega d^3k \ldots \to \sum_K \ldots \qquad (A1.2)$$

The occupation numbers f_{nk} of the single Bloch states with wavevector k are to be replaced by weights w_{nK} for the occupation of bands around the sampling points K. In the following we adopt the common use to denote the sampling points by small k as well.

For insulators and semiconductors the fully occupied valence bands have weights $w_{nk} = 2$, the empty conduction bands $w_{nk} = 0$. For metals the weights w_{nk} give the portion of bands in the volume represented by k which lies within the region limited by the Fermi energy ε_F. This energy is defined as the energy for which the $n_e = N_e/N$ electrons in the unit cell are just filling all states with $\varepsilon_{nk} \leqslant \varepsilon_F$:

$$\frac{1}{N_s} \sum_{nk} w_{nk} = n_e. \qquad (A1.3)$$

Several methods are available for the determination of the weights w_{nk} in metals, e.g. the linear tetrahedron method (Jepsen and Andersen 1971, Lehmann and Taut 1972) or the Gaussian smearing method (Fu and Ho 1983, Needs *et al* 1986). In this work the Gaussian smearing method was applied. Each of the discrete energy eigenvalues ε_{nk} at a sampling point k is smeared by a Gaussian:

$$\varepsilon_{nk} 2\delta(E - \varepsilon_{nk}) \to \varepsilon_{nk} \frac{2}{\Delta\sqrt{\pi}} \exp\left(-\frac{(E - \varepsilon_{nk})^2}{\Delta^2}\right). \qquad (A1.4)$$

The smearing constant Δ is chosen similar to the energy dispersion of the bands between neighbouring sampling points. The weights w_{nk} are given then by Gaussian error functions

$$w_{nk} = \frac{2}{\Delta\sqrt{\pi}} \int_{-\infty}^{\varepsilon_F} dE \exp\left(-\frac{(E - \varepsilon_{nk})^2}{\Delta^2}\right) = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{(\varepsilon_F - \varepsilon_{nk})/\Delta} dx \exp(-x^2)$$

$$\qquad (A1.5)$$

and the Fermi energy is calculated iteratively to fulfill equation (A1.3).

Besides the occupation numbers f_{nk} their changes δf_{nk} are needed for the calculation of forces. Like the f_{nk} by the weights w_{nk} the δf_{nk} are replaced by the changes δw_{nk} of the weights. These can be derived from equation (A1.5) as

$$\delta w_{nk} = \frac{2}{\sqrt{\pi}} \exp\left[-\frac{(\varepsilon_F - \varepsilon_{nk})^2}{\Delta^2}\right] \frac{\delta\varepsilon_F - \delta\varepsilon_{nk}}{\Delta}. \tag{A1.6}$$

With the conservation of the number n_e of electrons in the unit cell (see equation (A1.3))

$$\frac{1}{N_s} \sum_{nk} \delta w_{nk} = 0 \tag{A1.7}$$

and equation (A1.6), the change $\delta\varepsilon_F$ can be related to the $\delta\varepsilon_{nk}$:

$$\delta\varepsilon_F = \frac{\sum_{nk} \exp[-(\varepsilon_F - \varepsilon_{nk})^2/\Delta^2]\delta\varepsilon_{nk}}{\sum_{nk} \exp[-(\varepsilon_F - \varepsilon_{nk})^2/\Delta^2]}. \tag{A1.8}$$

Equations (A1.6) and (A1.8) together give the final relation between the δw_{nk} and the $\delta\varepsilon_{nk}$.

Appendix 2. Matrix representation

Schrödinger's equation (6) can be written formally as

$$\hat{H}|\psi_{nk}\rangle = \epsilon_{nk}|\psi_{nk}\rangle. \tag{A2.1}$$

The crystalline wavefunctions $|\psi_{nk}\rangle$ are expanded in a sufficiently complete, energy-independent basis set of Bloch functions $|j_k\rangle$:

$$|\psi_{nk}\rangle = \sum_j |j_k\rangle\langle j_k|\psi_{nk}\rangle = \sum_j |j_k\rangle\psi_j^{nk} \tag{A2.2}$$

where the $|j_k\rangle$ are e.g. the plane waves or localized functions of the mixed basis. Insertion of (A2.2) in (A2.1) leads to the generalized algebraic eigenvalue problem

$$\sum_j \langle i_k|\hat{H}|j_k\rangle\psi_j^{nk} = \sum_j \varepsilon_{nk}\langle i_k|j_k\rangle\psi_j^{nk} \tag{A2.3}$$

which is commonly solved by Cholesky transformation to a standard eigenvalue problem and diagonalization using numerical routines like the EISPACK library (see e.g. chapter 11 in Press *et al* 1986). A considerably more efficient way of solving eigenvalue problems for large matrices is possible by the use of iterative diagonalization techniques (Wood and Zunger 1985). In our calculations we used an algorithm originally given by Davidson (1975) which, in connection with Broyden's (1965) updating scheme (Vanderbilt and Louie 1984) for the effective potential in each iteration step, yielded a very fast convergence towards self-consistency.

For the calculation of forces, we write equation (A2.3) in matrix form as

$$\mathbf{H}\psi = \varepsilon \mathbf{S}\psi \qquad (A2.4)$$

and then

$$\delta\mathbf{H}\psi + \mathbf{H}\delta\psi = \delta\varepsilon\mathbf{S}\psi + \varepsilon\delta\mathbf{S}\psi + \varepsilon\mathbf{S}\delta\psi$$

$$\psi^{\dagger}(\delta\mathbf{H} - \varepsilon\delta\mathbf{S})\psi = \delta\varepsilon\psi^{\dagger}\mathbf{S}\psi - \psi^{\dagger}(\mathbf{H} - \varepsilon\mathbf{S})\delta\psi \qquad (A2.5)$$

The last term vanishes because $\mathbf{H}$ and $\mathbf{S}$ are both Hermitian matrices and ψ satisfies equation (A2.4), then

$$\delta\varepsilon = \psi^{\dagger}(\delta\mathbf{H} - \delta\mathbf{S})\psi. \qquad (A2.6)$$

Inserting back the indices, $\delta\varepsilon_{nk}$ is finally given by

$$\delta\varepsilon_{nk} = \sum_{i,j} \left(\psi_i^{nk}\right)^* \left(\delta\langle i_k|\hat{H}|j_k\rangle - \varepsilon_{nk}\delta\langle i_k|j_k\rangle\right)\psi_j^{nk}. \qquad (A2.7)$$

Appendix 3. Local part of the effective potential

The local part of the effective potential in Schrödinger's equation (6) for a crystal is given in Fourier space by (cf equation (A2) in Elsässer *et al* 1990)

$$V^{\text{loc}}(G) = V_{\text{HX}}(G) + V_{\text{ion}}^{\text{loc}}(G) = V_{\text{HX}}(G) + \sum_j \exp(-\mathrm{i}G \cdot r_j)V_{j,0}(G) \qquad (A3.1)$$

and in real space by the Fourier series (cf equation (A6) in Elsässer *et al* 1990):

$$V^{\text{loc}}(r) = \sum_G V^{\text{loc}}(G) \exp(\mathrm{i}G \cdot r_j) \exp[\mathrm{i}G \cdot (r - r_j)]. \qquad (A3.2)$$

For the calculation of matrix elements with localized functions $|\phi_{jlm}^k\rangle$ of the mixed basis, $V^{\text{loc}}(r)$ is expanded around a considered atomic site r_j $(r' = r - r_j)$ using an expansion theorem for plane waves (cf equation (12) in Elsässer *et al* 1990):

$$V_j^{\text{loc}}(r') = \sum_G V^{\text{loc}}(G) \exp(\mathrm{i}G \cdot r_j) \sum_{L=0}^{\infty} \sum_{M=-L}^{+L} 4\pi\mathrm{i}^L j_L(Gr')K_{LM}(\hat{G})K_{LM}(\hat{r}') \qquad (A3.3)$$

and then spherically approximated within a sphere around r_j with radius r_{jl} by restriction to the term with $L = 0$ only (cf equation (A7) in Elsässer *et al* 1990):

$$V_j^{\text{loc}}(r') = \sum_G V^{\text{loc}}(G) \exp(\mathrm{i}G \cdot r_j)j_0(Gr'). \qquad (A3.4)$$

For the force calculation we need the change $\delta V_{\text{ion}}^{\text{loc}}(G)$ due to virtual displacements δr_j as well as the gradient $\nabla_r V_j^{\text{loc}}(r')$. $\delta V_{\text{ion}}^{\text{loc}}(G)$ is obtained as

$$\delta V_{\text{ion}}^{\text{loc}}(G) = \sum_j -\mathrm{i}(G \cdot \delta r_j) \exp(-\mathrm{i}G \cdot r_j) V_{j,0}(G). \tag{A3.5}$$

The gradient $\nabla_r V_j^{\text{loc}}(r')$ measures the change in $V_j^{\text{loc}}(r')$ as $V^{\text{loc}}(r)$ is displaced. There are two contributions:

$$\nabla_r V_j^{\text{loc}}(r') = \nabla_{r_j} V_j^{\text{loc}}(r') + \nabla_{r'} V_j^{\text{loc}}(r'). \tag{A3.6}$$

The first term is the change due to the shift in the point of expansion r_j and the second term is the gradient of $V_j^{\text{loc}}(r')$ with the point of expansion fixed. From equation (A3.4), this is given in real space within a sphere around $r_j = r - r'$ by

$$\nabla_r V_j^{\text{loc}}(r') = \sum_G V^{\text{loc}}(G) \exp(\mathrm{i}G \cdot r_j)[\mathrm{i}G\, j_0(Gr') + \nabla_{r'} j_0(Gr')]. \tag{A3.7}$$

The gradient of the spherical Bessel function is

$$\nabla_{r'} j_0(Gr') = -G j_1(Gr')\, \hat{r}' \tag{A3.8}$$

and finally

$$\nabla_r V_j^{\text{loc}}(r') = \sum_G \mathrm{i}G \exp(\mathrm{i}G \cdot r_j) V^{\text{loc}}(G) j_0(Gr') - \hat{r}' \sum_G G$$
$$\times \exp(\mathrm{i}G \cdot r_j) V^{\text{loc}}(G) j_1(Gr') = \nabla_r V_{j,L=0}^{\text{loc}}(r') + \nabla_r V_{j,L=1}^{\text{loc}}(r'). \tag{A3.9}$$

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