

Theory of Periodic Systems Based on the All-Electron DFT FP-LAPW Method – Applications to Surfaces and Clusters

The purpose of these state-of-the-art calculations is to address key issues of interface and nano science: reactivity, stability, chemisorption bond strengths, band structure, magnetic properties, core-level chemical shifts for photoelectron spectroscopy, and adhesion of one nanophase to another.

Most of the calculations are carried out by the methods of Density Functional Theory because of the efficiency of this approach for the size of the systems to be investigated here. For periodic systems we have gathered an extensive experience with the all-electron full-potential linearized plane wave (FP-LAPW)-based code Wien [A1]. This code uses "forces" to optimize the structures. The periodic calculations take advantage of properties calculation in the \mathbf{k} -space through Fourier transform techniques employed in expansions of both the electronic wavefunctions and the potential generated by the nuclei. Long-range interactions are taken care of by expansions over the reciprocal lattice vectors \mathbf{G} . In outline, the schematic for Wien applied to adsorption, chemisorption and cluster growth is depicted above.

The Kohn-Sham equations of the Density Functional Theory [A2] are solved interactively to self-consistency as illustrated in the diagram Fig. 1A. The Wien code calculates core-level energy spectra owing to the full-potential contribution by the modified Desclaux's program LCORE. This is important for the interpretation and prediction of the core-level binding energy chemical shifts in photoelectron spectroscopy, the success of which is documented in our recent reports [A3]. The forces in Wien are calculated as spelled out in the section Geometry Optimization below. The SCF calculation outlined in Fig. 1A starts with superimposed electron density from all atoms in the unit cell (clmsum) which is updated after each cycle. LAPW0 then computes the "external potential" as a sum of the Coulomb and exchange-correlation potential using the total electron density as input, and returns the spherical (vsp) and non-spherical (vns) components as input into LAPW1, which solves the Kohn-Sham equations for eigenvalues of orbital energies and eigenfunctions. The latter are used for valence electron density calculation by LAPW2 (clmval), which is then added together with the core density calculated by LCORE (clmcor) and mixed with the "old" densities in MIXER which returns new charge density as input into LAPW0. Net spin is determined as the difference between spin-up and spin-down densities, and is refined by the second variational treatment of spin-orbit interactions in the valence band. The core level calculations at the fully relativistic level are particularly useful for the interpretation of both the chemical shifts and subtle effects of spin-orbit splittings that are observed with high-resolution XPS.

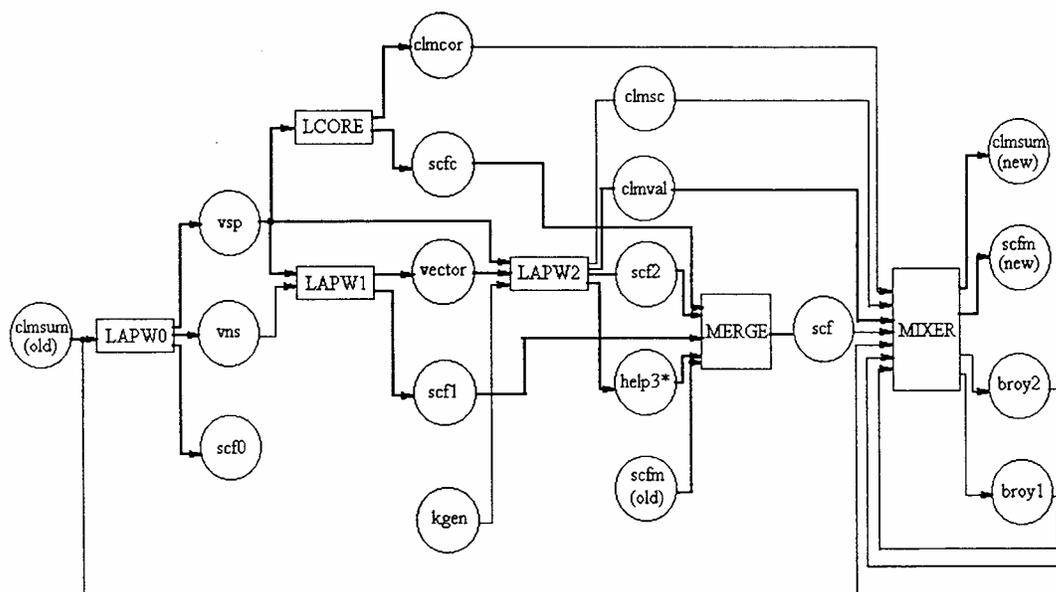


Fig. 1A Flow of programs in the DFT FP-LAPW code Wien.

The SCF cycle terminates upon convergence at a specified tolerance for energy and forces. Other details are described in the cited literature. The success of the subsequent optimization, described in some detail in the section *Geometry Optimization* below, depends on a judicious choice of the \mathbf{k} -vectors and good initial guesses, and is facilitated by parallel processing. Both of these items require experience with the method (with good initial guesses the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method is superior in performance to the damped Newton method) and, in the ongoing effort, a broad experience in catalytic chemistry for a good initial guess of the structure of surface intermediates. Some technical aspects of the LAPW calculations that handle rapid oscillations of the wavefunctions near nuclei, the long-range electrostatic effects, and convergence are outlined below

Geometry Optimization in the DFT FP-LAPW (WIEN) Calculations.

The methods for geometry optimization based on forces (or negative gradients of energy) on atoms within a unit cell of a periodic structure are outlined herein. Implemented in the Wien code are (a) the damped Newton and (b) the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithms, both of which utilize the driving forces calculated in a sequence outlined in (i) – (v) below.

(i) The Born-Oppenheimer Approximation (B.O.A.)

The Schrödinger Equation to be solved is

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}) \quad (1)$$

where:

$$\hat{\mathbf{H}} = \hat{\mathbf{T}}_N + \hat{\mathbf{T}}_e + \hat{\mathbf{V}}_{ee} + \hat{\mathbf{V}}_{eN} + \hat{\mathbf{V}}_{NN} \quad (2)$$

We can expand $\psi(r, R)$ as:

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{n=1}^{\infty} \varepsilon_n \chi_n(\mathbf{R}) \Phi_{n, \mathbf{R}}(\mathbf{r}) \quad (3)$$

where $\Phi_{n, \mathbf{R}}(\mathbf{r})$ is the electronic wave function, which satisfies the electronic equation:

$$\hat{\mathbf{H}}_e \Phi_{n, \mathbf{R}}(\mathbf{r}) = [\hat{\mathbf{T}}_e + \hat{\mathbf{V}}_{ee} + \hat{\mathbf{V}}_{eN}] \Phi_{n, \mathbf{R}}(\mathbf{r}) = E_n(\mathbf{R}) \Phi_{n, \mathbf{R}}(\mathbf{r}) \quad (4)$$

Substituting (3) into (1), and using the relation (4), we have:

$$\sum_{n=1}^{\infty} \varepsilon_n [\hat{\mathbf{T}}_N + E_n(\mathbf{R}) + \hat{\mathbf{V}}_{NN}] \chi_n(\mathbf{R}) \Phi_{n, \mathbf{R}}(\mathbf{r}) = \sum_{n=1}^{\infty} \varepsilon_n \chi_n(\mathbf{R}) \Phi_{n, \mathbf{R}}(\mathbf{r}) \quad (5)$$

where:

$$\hat{\mathbf{V}}_{NN} = \frac{1}{2} \sum_I \sum_{J \neq I} \frac{Z_I Z_J}{|R_I - R_J|} \quad (6)$$

is the nucleus-nucleus interaction, which is in principle a constant term for a given nuclear configuration. It can be simply absorbed into E_n after solving the electronic equation (4). Technically, this nuclei-nuclei interaction term diverges. Special treatment involving the cancellation theorem, and Ewald's summation technique to calculate the energy of a periodic array of point charges, have to be used.

$$\hat{\mathbf{T}}_N(\chi\Phi) = -\frac{1}{2} \sum_I [(\nabla_I^2 \chi)\Phi + \chi(\nabla_I^2 \Phi) + 2(\nabla_I \chi)(\nabla_I \Phi)] \quad (7)$$

The Born-Oppenheimer Approximation assumes

$$\nabla_I \Phi = 0 \quad \text{and} \quad \nabla_I^2 \Phi = 0 \quad (8)$$

Then we have the so-called nuclear equations:

$$-\frac{1}{2} \sum_I \nabla_I^2 \chi_n(\mathbf{R}) + E_n(\mathbf{R}) \chi_n(\mathbf{R}) = \varepsilon_n \chi_n(\mathbf{R}) \quad (9)$$

(ii) The Hellmann-Feynman Theorem (HF)

The HF Theorem: If $E_n(\lambda)$ is an eigenvalue of the Hamiltonian $\hat{\mathbf{H}}(\mathbf{r}, \lambda)$ with the eigenfunction $\Phi_n(\mathbf{r}, \lambda)$ and λ is a parameter,

$$\hat{\mathbf{H}}(\mathbf{r}, \lambda) |\Phi_n(\mathbf{r}, \lambda)\rangle = E_n(\lambda) |\Phi_n(\mathbf{r}, \lambda)\rangle \quad (10)$$

then we have:

$$\frac{\partial E_n}{\partial \lambda} = \left\langle \Phi_n(\mathbf{r}, \lambda) \left| \frac{\partial \hat{\mathbf{H}}(\mathbf{r}, \lambda)}{\partial \lambda} \right| \Phi_n(\mathbf{r}, \lambda) \right\rangle \quad (11)$$

Proof: Multiplying $\langle \Phi_n(\mathbf{r}, \lambda) |$ to both sides of Eq. (10), and integrating over all space of \mathbf{r} , we get:

$$E_n(\lambda) = \left\langle \Phi_n(\mathbf{r}, \lambda) \left| \hat{\mathbf{H}}(\mathbf{r}, \lambda) \right| \Phi_n(\mathbf{r}, \lambda) \right\rangle \quad (12)$$

So:

$$\begin{aligned} \frac{\partial E_n}{\partial \lambda} &= \left\langle \frac{\partial \Phi_n(\mathbf{r}, \lambda)}{\partial \lambda} \left| \hat{\mathbf{H}}(\mathbf{r}, \lambda) \right| \Phi_n(\mathbf{r}, \lambda) \right\rangle \\ &+ \left\langle \Phi_n(\mathbf{r}, \lambda) \left| \frac{\partial \hat{\mathbf{H}}(\mathbf{r}, \lambda)}{\partial \lambda} \right| \Phi_n(\mathbf{r}, \lambda) \right\rangle \end{aligned} \quad (13)$$

$$\begin{aligned} &+ \left\langle \Phi_n(\mathbf{r}, \lambda) \left| \hat{\mathbf{H}}(\mathbf{r}, \lambda) \right| \frac{\partial \Phi_n(\mathbf{r}, \lambda)}{\partial \lambda} \right\rangle \\ \frac{\partial E_n}{\partial \lambda} &= \left\langle \Phi_n(\mathbf{r}, \lambda) \left| \hat{\mathbf{H}}(\mathbf{r}, \lambda) \right| \Phi_n(\mathbf{r}, \lambda) \right\rangle \\ &+ E_n \frac{\partial}{\partial \lambda} \left[\left\langle \Phi_n(\mathbf{r}, \lambda) \left| \Phi_n(\mathbf{r}, \lambda) \right\rangle \right] \end{aligned} \quad (14)$$

Since $\Phi_n(\mathbf{r}, \lambda)$ are eigenfunctions of the Hamiltonian $\hat{\mathbf{H}}$, they form a complete basis set for infinite n , and:

$$\left\langle \Phi_n(\mathbf{r}, \lambda) \left| \Phi_n(\mathbf{r}, \lambda) \right\rangle = 1 \quad (15)$$

Then we have:

$$\frac{\partial E_n}{\partial \lambda} = \left\langle \Phi_n(\mathbf{r}, \lambda) \left| \frac{\partial \hat{\mathbf{H}}(\mathbf{r}, \lambda)}{\partial \lambda} \right| \Phi_n(\mathbf{r}, \lambda) \right\rangle$$

Notes:

(1) In the electronic equation, nuclear positions \mathbf{R} are taken as parameters, we should have:

$$\mathbf{F}_x^\alpha = -\frac{\partial E_n}{\partial X} = -\left\langle \Phi_n(\mathbf{r}, X) \left| \frac{\partial \hat{\mathbf{H}}(\mathbf{r}, X)}{\partial X} \right| \Phi_n(\mathbf{r}, X) \right\rangle \quad (16)$$

where \mathbf{F}_x^α is the Hellmann-Feynman (HF) force along the direction of the X-component of \mathbf{R} on the α^{th} atom.

(2) It can be shown that:

$$\frac{\partial^m E_n}{\partial \lambda^m} = \left\langle \Phi_n(\mathbf{r}, \lambda) \left| \frac{\partial^m \hat{\mathbf{H}}(\mathbf{r}, \lambda)}{\partial \lambda^m} \right| \Phi_n(\mathbf{r}, \lambda) \right\rangle \quad (17)$$

(iii) The Incomplete Basis Set Effect (IBS)

The HF theorem is in principle correct as long as the basis set $\Phi_n(\mathbf{r}, \lambda)$ is complete. But in any *ab initio* calculation $\Phi_n(\mathbf{r}, \lambda)$ are incomplete, which means that the HF force need to be corrected. That is, we will not have the exact relation Eq. (15). Instead, we will have:

$$\begin{aligned} \frac{\partial E_n}{\partial \lambda} &= \left\langle \Phi_n(\mathbf{r}, \lambda) \left| \hat{\mathbf{H}}(\mathbf{r}, \lambda) \right| \Phi_n(\mathbf{r}, \lambda) \right\rangle \\ &+ 2^* \left\langle \frac{\partial \Phi_n(\mathbf{r}, \lambda)}{\partial \lambda} \left| \hat{\mathbf{H}}(\mathbf{r}, \lambda) \right| \Phi_n(\mathbf{r}, \lambda) \right\rangle \end{aligned} \quad (18)$$

The first term on the right is the HF force, and the second term is a correction, which was first shown by Pulay [A4], and is regarded as the wavefunction force, or Pulay force.

The effect of the Pulay force is then generally regarded as the Incomplete Basis Set effect (IBS). In principle, the Pulay force $\mathbf{F}^{\text{IBS}} = 0$ only if the basis set $\Phi_n(\mathbf{r}, \lambda)$ is complete. However, a relatively weak condition has been shown that if the wavefunction $\Phi_n(\mathbf{r}, \lambda)$ were comprised of originless orbitals, for example the Plane-Wave (PW) basis set, we still have $\mathbf{F}^{\text{IBS}} = 0$ [A5].

- (1) For an LCAO approach, IBS is important. In fact, the CRYSTAL package does not calculate forces.
- (2) For a pure Plane-Wave (PW) approach, IBS is very small. Unfortunately, pure PW approach has its own problems, especially the convergence problem.
- (3) For a Plane-Wave Pseudo-Potential (PWPP) approach, IBS is not that important.
- (4) For the dual basis set approach such as the FP-LAPW method, IBS is serious. Fortunately, corrections to the IBS in the FP-LAPW method can be made in a known way.

(iv) The Force Calculation in the FP-LAPW Method

The explicit formation of the Pulay correction in the FP-LAPW approach are given by both YSK [A6] and SW [A7]. The two different approaches give similar results, and both have been implemented in the WIEN package.

$$\mathbf{F}^I = -\nabla_I \mathbf{E} = \mathbf{F}_{\text{HF}}^I - \left\{ \sum_{i=1}^n n_i \nabla \varepsilon_i - \int \rho(\mathbf{r}) \nabla_I V_{\text{eff}}(\mathbf{r}) d^3\mathbf{r} \right\} \quad (19)$$

where \mathbf{F}^I is the force acting on the I^{th} nucleus, \mathbf{F}_{HF}^I is the Hellmann-Feynman force, and $V_{\text{eff}}(\mathbf{r})$ is the effective potential.

(v) The Calculation of Optimized Structures Using Forces

The Pulay force is calculated by evaluating the following two terms:

- (1) \mathbf{F}^{core} : a correction due to the spherically treated core electrons.
- (2) $\mathbf{F}^{\text{valence}}$: a correction due to the discontinuous 2nd derivatives of wavefunctions across the boundaries of the Muffin-Tin spheres.

In summary, the total force is the combination of three terms:

$$\mathbf{F} = \mathbf{F}^{\text{HF}} + \mathbf{F}^{\text{Core}} + \mathbf{F}^{\text{Valence}} \quad (20)$$

where the Hellman-Feynman force \mathbf{F}^{HF} is calculated e.g. in the "LAPW0" step of the Wien code, and is in general easily done. \mathbf{F}^{Core} is calculated in the "LCORE" step, which is also easy. But calculations of $\mathbf{F}^{\text{Valence}}$ are more difficult.

In an SCF calculation, information from only two cycles is saved, the current cycle and the previous cycle for the convergence test and the mixing scheme. Evaluation of $\mathbf{F}^{\text{Valence}}$ needs information of at least three cycles. In the WIEN program, evaluation of $\mathbf{F}^{\text{Valence}}$ is done by adding an "-fc" flag in the "run_lapw" program, which is also interpreted as force convergence criterion. When the "-fc" flag is used, the SCF calculation first goes through the regular energy criterion convergence. After energy converges, it turns on the $\mathbf{F}^{\text{Valence}}$ calculation by changing the keyword "TOT" to "FOR" in the "case.in2" input file. At least 3 more cycles have to be calculated to find the

$\mathbf{F}^{Valence}$.

The correction by $\mathbf{F}^{Valence}$ is in general large. So the "-fc" flag should always be used for the "minimization", or geometry optimization.

After finding the forces on nuclei, we can now change positions of nuclei and perform a new SCF calculation. The movements of nuclei are guided by the forces using different schemes. In the WIEN program, two different schemes are used, the BFGS [48] and the damped Newton scheme [49],

$$\mathbf{R}_m^{\tau+1} = \mathbf{R}_m^\tau + \eta_m (\mathbf{R}_m^\tau - \mathbf{R}_m^{\tau-1}) + \delta_m \mathbf{F}_m^\tau \quad (21)$$

where \mathbf{R}_m^τ and \mathbf{F}_m^τ are the coordinates and the respective force at the time step τ . Damping and speed of motion are controlled by two parameters, the "friction" η_m and the "step size" δ_m , which are set in the input file by user. The "minimization" program in WIEN is for fixed lattice constants of the unit cell. That is, only internal coordinates of atoms within the unit cell are optimized. On the other hand, the lattice parameters of the unit cell are optimized by the "optimization" program, which is basically a job-controlling script file that minimizes the total energy with respect to the lattice parameters with fixed fractional internal nuclear positions. So the best geometry optimization process should include several steps: First, with fixed fractional internal coordinates of atoms, optimization of the lattice parameters. Second, with the "optimized" lattice parameters, the internal coordinates of nuclei are "minimized". These two steps could be repeated until a satisfactory geometry is reached.

Final Note: The basic task of geometry optimization is to find the minimum total energy of systems. The criterion of a good optimized geometry should be the "total energy minimum". Forces basically serve as a guide to effectively find the minimum geometry.

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