

## 5. Response properties in *ab initio* schemes

A number of important physical observables is expressed via derivatives of total energy (or free energy)  $E$ . Examples are:

$$\frac{\partial E}{\partial \mathbf{R}} \quad \text{forces on the nuclei; critical points on the potential energy surface (minima and saddle points)}$$

$$\frac{\partial^2 E}{\partial R_a \partial R_b} \quad \text{force constants; vibrational frequencies; infrared and Raman spectra}$$

$$\frac{\partial^3 E}{\partial R_a \partial R_b \partial R_c} \quad \text{anharmonic contributions to vibrational frequencies}$$

$$\frac{\partial E}{\partial \mathcal{E}} \quad (\mathcal{E} - \text{electric field}): \text{dipole moment}$$

$$\frac{\partial^2 E}{\partial R_a \partial \mathcal{E}_i} \quad \text{infrared intensities}$$

$$\frac{\partial^2 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j} \quad \text{polarizability; light scattering}$$

$$\frac{\partial^3 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \mathcal{E}_k} \quad \text{hyperpolarizability; second harmonic generation}$$

$$\frac{\partial^3 E}{\partial R_a \partial \mathcal{E}_i \partial \mathcal{E}_k} \quad \text{Raman intensity}$$

etc.

If total energy is available in a calculation with  $\{\mathbf{R}\}$  or  $\{\mathcal{E}\}$  as parameters, the above properties can be obtained by three methods:

1. A fit of sample points to an analytical form and subsequent differentiation. This approach is very often used, but the results are subject to numerical instability (much more data points are needed than there are parameters in the fitting function, for a numerically stable fit).
2. Finite differences. This method is good if calculation algorithm is accurate, so that numerical “noise” can be neglected. The following formulae are for the first derivative of

a numerical function  $f(x_1, \dots, x_N)$ , defined on a mesh with a step  $h$ ;

$$\left(\frac{\partial f}{\partial x}\right)_i = \frac{1}{2h} [f(\dots, x_i^0 + h, \dots) - f(\dots, x_i^0 - h, \dots)] + \frac{1}{6} \frac{d^3 f}{dx^3} h^2$$

...and for the second derivatives, with obvious notation of  $f(+)$   $\equiv f(\dots, x_i^0 + h, \dots)$  etc. :

$$\begin{aligned} \frac{\partial^2 f}{\partial x_i^2} &= \frac{1}{h^2} [f(+)+f(-)-2f(0)] + \frac{1}{12} \frac{\partial^4 f}{\partial x_i^4} h^2 \\ \frac{\partial^2 f}{\partial x_i \partial x_j} &= \frac{1}{2h_i h_j} [f(++)+f(--)+2f(00)-f(+0)- \\ &\quad -f(-0)-f(0+)-f(0-)] + O(f^{IV} h^2). \end{aligned}$$

3. Analytical differentiation, built in into the code. This typically means a considerable programming load and an additional amount of calculation. However, the differentiation is “exact”, and there exist a possibility to calculate many response properties (all components of force constants etc.) in a single run. Also this may be advantageous in reducing a number of different calculations to be done. For example, calculation of a second-order dynamical matrix of a system with  $N$  atoms demands at least  $9N(N-1)/2 + 1$  calculations for different displacement patterns if only the total energies are available, but  $[9N(N-1) + 2]/[2(3N-2)]$ , i.e. much less, if the forces are available as well.

## 5.1 General considerations

In the following, we consider the problem of differentiating an expression which is *variational* (like, e.g., energy) and depends implicitly and explicitly on some parameters. Examples of explicit parameters are, e.g., positions of nuclei (and possibly of basis functions pinned to them); the implicit dependence of the total energy is on variational parameters – those describing the decomposition of orbitals over basis functions. Moreover, we introduce a set of constraints that could be target pressure, or fixed spin moment. So we deal with constrained minimization, using Lagrange multipliers. The function to be minimized has a form

$$W = W'(\mathbf{C}, \lambda, \mathbf{R}) - \sum_m f_m(\mathbf{C}, \mathbf{R}) \lambda_m, \quad (5.1)$$

where  $W'$  is e.g. the total energy expression,  $\mathbf{C}$  – variational parameters,  $\lambda$  – Lagrange multipliers,  $\mathbf{R}$  – explicit parameters (e.g., positions of nuclei),  $f$  – constraints, formulated as

$$f_m(\mathbf{C}, \mathbf{R}) = 0 \quad (5.2)$$

(like orthonormality of orbitals, fixation of total magnetic moment etc.) In less general case, one can omit the constraints. Variational parameters will be determined from the equations

$$\begin{cases} \frac{\partial W}{\partial C_i} = 0, & \forall i \\ f_m(\mathbf{C}, \mathbf{R}) = 0, & \forall m \end{cases} \quad (5.3)$$

In the following, we use the notation:

$$\frac{\partial W}{\partial C_i} \equiv W_i; \quad \frac{\partial W}{\partial R_a} \equiv W^a \quad (5.4)$$

The *optimized* energy will be

$$E = W(\mathbf{C}(\mathbf{R}), \lambda(\mathbf{R}), \mathbf{R}),$$

and its gradient

$$E^a = W^a + \sum_i W_i C_i^a - \sum_m f_m \lambda_m^a = W^a, \quad (5.5)$$

where  $W^a$  can be obtained by direct differentiating in  $R_a$ , and  $W_i=0, f_m=0$  at equilibrium. Similarly, the second derivative yields:

$$E^{ab} = W^{ab} + \sum_i W_i^a C_i^b - \sum_m f_m^a \lambda_m^b, \quad (5.6)$$

and other terms,  $W_i C_i^{ab}$  and  $f_m \lambda_m^{ab}$ , disappear for the same reason. Since  $W$  is variational, it must be stationary with respect to variations of  $\mathbf{C}$ :

$$W_i + \sum_j W_{ij} C_j - \sum_m f_{mi} \lambda_m = 0. \quad (5.7)$$

This is something like Hartree-Fock, or Kohn–Sham equation equation, written down for fixed positions of nuclei. Differentiating in  $R_a$  yields:

$$\frac{dW_i}{dR_a} = W_i^a + \sum_j W_{ij} C_j^a - \sum_m f_{mi} \lambda_m^a = 0, \quad (5.8)$$

and since  $f_m = 0$  in a stationary state,

$$\frac{df_m}{dR_a} = f_m^a + \sum_j f_{mj} C_j^a = 0. \quad (5.9)$$

So we arrive at a system of response equations

$$\begin{cases} \sum_j W_{ij} C_j^a - \sum_m f_{mi} \lambda_m^a = -W_i^a, \\ \sum_j f_{mj} C_j^a = -f_m^a, \end{cases} \quad (5.10)$$

which has to be solved in addition to “zero-order” equation (5.7). Once this is done,  $W_i^a$  and  $f_m^a$  can be inserted in Eq. (5.6) for  $E_{ab}$ .

A similar analysis, but including more coupled terms, can be done for third derivatives. This approach is described by Pulay.<sup>35</sup>

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<sup>35</sup>Peter Pulay, *Analytical Derivative Techniques and the Calculation of Vibrational Spectra*, in: *Modern Electronic Structure Theory, Part II*, ed. by David R. Yarkony, World Scientific, Singapore (1995), pp. 1191–1240.

## 5.2 Forces

Let us discuss in more detail the evaluation of force, that must be, according to Eq. (5.5),  $E^a = W^a$ . In practical calculations, evaluation of this derivative may be considerably complicated by the necessity to take into account derivatives of the basis functions. This is necessary if e.g. basis functions are centered on atoms and are displaced with them. This is not necessary if a position-independent basis set (e.g., planewaves) is used. The reason is the following. For the *exact* wavefunction,

$$E^a = \langle \psi | \mathcal{H}^a | \psi \rangle$$

by the power of the Hellmann–Feynman theorem, as was shown in Eq. (3.19). We reproduce here this argumentation for completeness:

$$\begin{aligned} E^a &\equiv \frac{d}{dR^a} \langle \psi | \mathcal{H} | \psi \rangle = \underbrace{\langle \psi^a | \mathcal{H} | \psi \rangle}_{E|\psi} + \langle \psi | \mathcal{H}^a | \psi \rangle + \underbrace{\langle \psi | \mathcal{H} | \psi^a \rangle}_{E\langle\psi|} = \\ &= \langle \psi | \mathcal{H}^a | \psi \rangle + E [\langle \psi^a | \psi \rangle + \langle \psi | \psi^a \rangle] = \\ &= \langle \psi | \mathcal{H}^a | \psi \rangle + E \underbrace{[\langle \psi | \psi \rangle]}_{=\text{const}} = \langle \psi | \mathcal{H}^a | \psi \rangle. \end{aligned} \quad (5.11)$$

However, if the wavefunction contains parameters  $p_t$  dependent on perturbation (i.e., displacement of ions) either implicitly or explicitly, then (5.11) is not generally valid, because

$$\langle \psi^a | \mathcal{H} | \psi \rangle + \langle \psi | \mathcal{H} | \psi^a \rangle = 2 \operatorname{Re} \langle \psi^a | \mathcal{H} | \psi \rangle = \sum_t \frac{\partial \langle \psi | \mathcal{H} | \psi \rangle}{\partial p_t} p_t^a \neq 0. \quad (5.12)$$

The validity of the Hellmann–Feynman theorem can be restored if either

$$\forall p_t^a = 0,$$

i.e. the basis is independent on positions of nuclei, as is for instance the case for plane waves, or

$$\frac{\partial \langle \psi | \mathcal{H} | \psi \rangle}{\partial p_t} = 0,$$

i.e. all parameters are fully optimized, that is normally the case if the basis is *complete*. Or, at least, for each basis function its derivative with respect to perturbation must also be present in the basis. In practical terms, Hellmann–Feynman forces are seldom useful, because even basis sets extended to include their gradients are not complete enough.

The total energy in the density functional theory is given by Eq. (3.17):

$$E_{\text{tot}}^{\text{el.}} = \sum_{(i \text{ occupied})} \varepsilon_i - \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \int V_{\text{XC}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E_{\text{XC}}[\rho].$$

When considering a dynamical problem, one must add here a contribution from atomic cores that is not a constant anymore:

$$E_{\text{tot}}[\rho] = E_{\text{tot}}^{\text{el.}} + \frac{e^2}{2} \sum_{\alpha\beta} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}. \quad (5.13)$$

Given a fixed configuration of atoms  $\{\mathbf{R}_\alpha\}$ , the displacement of one atom  $\mathbf{R}_\alpha \rightarrow \mathbf{R}_\alpha + \Delta_\alpha$  changes the total energy by

$$\delta E = \sum_{(i \text{ occupied})} \delta \varepsilon_i + \sum_{\beta(\text{core})} \delta \epsilon_\beta^{(\text{core})} - \int d\mathbf{r} \rho(\mathbf{r}) \delta V_{\text{KS}}(\mathbf{r}) - \mathbf{F}_\alpha^{\text{HF}} \cdot \Delta_\alpha. \quad (5.14)$$

The Hellmann–Feynman force is purely electrostatic, due to the displacement of density:

$$\mathbf{F}_\alpha^{\text{HF}} = Z_\alpha \frac{d}{d\Delta_\alpha} \left[ - \sum_{\beta \neq \alpha} \sum_{\tau} \frac{eZ_\beta}{|\mathbf{R}_\alpha + \Delta_\alpha - \mathbf{R}_\beta + \tau|} + e \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_\alpha - \Delta_\alpha|} d\mathbf{r} \right], \quad (5.15)$$

$\tau$  are lattice translation vectors. Other contributions adding up to the total force are:<sup>36</sup>

$$\mathbf{F}_\alpha \equiv - \frac{d E_{\text{tot}}}{d \Delta_\alpha} = \mathbf{F}_\alpha^{\text{HF}} + \mathbf{F}_\alpha^{\text{IBS}} + \mathbf{F}_\alpha^{\text{core}}. \quad (5.16)$$

$\mathbf{F}^{\text{IBS}}$  is “incomplete basis set”, or “Pulay” force, due to the use of finite number of position-dependent basis functions:

$$\mathbf{F}_\alpha^{\text{IBS}} = -2 \sum_{(i \text{ occupied})} \text{Re} \left[ \left\langle \frac{\delta \varphi_i}{\delta \Delta_\alpha} \left| \hat{T} + V_{\text{eff}} - \varepsilon_i \right| \varphi_i \right\rangle \right] - \frac{1}{\delta \Delta_\alpha} \sum_{(i \text{ occupied})} \langle \varphi_i | \delta \hat{T} | \varphi_i \rangle. \quad (5.17)$$

$\mathbf{F}^{\text{core}}$  is a “core correction”, due to the fact that for core electrons (at least in the FLAPW method) only spherical part of the potential is taken into account.

$$\mathbf{F}_\alpha^{\text{core}} = - \int \rho_\alpha(\mathbf{r}) \nabla V_{\text{KS}}(\mathbf{r}). \quad (5.18)$$

To give an idea of relative importance of different contributions to the force, the values (in mRy/a.u., for  $\Delta_\alpha=0.089$  a.u.) as calculated by the FLAPW method for Si are shown on the right. (after C. Ambrosch-Draxl, lecture at the Workshop *The Physics of the Electronic Behaviour in the Core Region: All-Electron LAPW Electronic Structure Calculations*, 22.06–04.07.1998, Trieste. )

$F^{\text{numerical diff.}}$	=	-41.45
$F$ by Eq. (5.16)	=	-41.38
$F^{\text{HF}}$	=	-64.90
$F^{\text{IBS}}$	=	3.06
$F^{\text{core}}$	=	20.46

### 5.3 Dynamical matrix

We discuss now the calculation of second derivatives of energy in ion displacements, according to Eq. (5.6). For this, we need to know  $C_i^b$ , i.e., Kohn–Sham orbitals *to 1st order* in displacements. The Hellmann–Feynman theorem holds up to 3d order in perturbations:

$$\frac{\partial^2 E}{\partial R_a \partial R_b} = \int \left[ \frac{\partial \rho_R}{\partial R_a} \frac{\partial V_R}{\partial R_b} + \rho \frac{\partial^2 V_R}{\partial R_a \partial R_b} \right] d\mathbf{r}. \quad (5.19)$$

<sup>36</sup>B. Kohler, S. Wilke, M. Scheffler, R. Kouba and C. Ambrosch-Draxl, *Force calculation and atomic-structure optimization for the full-potential augmented plane-wave code WIEN*, Comp. Phys. Commun. **94**, 31 (1996).

The set of Kohn–Sham equations (3.16)

$$\begin{aligned}
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{SCF}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) &= \varepsilon_i \varphi_i(\mathbf{r}); \\
V_{\text{SCF}}(\mathbf{r}) &= e^2 \sum_{\alpha} \frac{-Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{XC}}}{\delta \rho(\mathbf{r})}; \\
\rho(\mathbf{r}) &= \sum_{\substack{i \\ \text{(occupied)}}} |\varphi_i(\mathbf{r})|^2.
\end{aligned} \tag{5.20}$$

can be “linearized”, introducing small parameter  $\lambda$ :

$$\begin{aligned}
\varphi_i(\mathbf{r}) &= \varphi_i^{(0)}(\mathbf{r}) + \lambda \varphi_i^{(1)}(\mathbf{r}); \\
V_{\text{SCF}}(\mathbf{r}) &= V_{\text{SCF}}^{(0)}(\mathbf{r}) + \lambda V_{\text{SCF}}^{(1)}(\mathbf{r}); \\
\rho(\mathbf{r}) &= \rho^{(0)}(\mathbf{r}) + \lambda \rho^{(1)}(\mathbf{r}).
\end{aligned} \tag{5.21}$$

The “zero-order” system for  $\varphi^{(0)}$ ,  $V_{\text{SCF}}^{(0)}$  and  $\rho^{(0)}$  is (5.20), and the “first-order” system (where terms linear in  $\lambda$  are retained) can be easily written once the nature of perturbation (that must be proportional to  $\lambda$ ) is specified. As we are interested at present in displacements of ions  $\lambda \mathbf{w}_{\alpha}$  as an example of such perturbations, the “first-order” equations acquire the form:

$$\begin{aligned}
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{SCF}}^{(0)}(\mathbf{r}) - \varepsilon_i \right] \varphi_i^{(1)}(\mathbf{r}) &= -V_{\text{SCF}}^{(1)}(\mathbf{r}) \varphi_i^{(0)}(\mathbf{r}); \\
V_{\text{SCF}}^{(1)}(\mathbf{r}) &= e^2 \sum_{\alpha} \frac{Z_{\alpha} \mathbf{w}_{\alpha} (\mathbf{r} - \mathbf{R}_{\alpha})}{|\mathbf{r} - \mathbf{R}_{\alpha}|^3} + e^2 \int \frac{\rho^{(1)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \rho^{(1)}(\mathbf{r}) \left[ \frac{dV_{\text{XC}}(\mathbf{r})}{d\rho} \right]_{\rho^{(0)}}; \\
\rho^{(1)}(\mathbf{r}) &= 2 \text{Re} \sum_{\substack{i \\ \text{(occupied)}}} \varphi_i^{(0)*}(\mathbf{r}) \varphi_i^{(1)}(\mathbf{r}).
\end{aligned} \tag{5.22}$$

The first of this equations is Sternheimer equation, i.e. the Schrödinger equation to the first order. The “perturbation”  $\lambda \mathbf{w}_{\alpha}$  could be constrained to just one atom, or it could be a phonon with given wavevector  $\mathbf{q}$  and polarization  $\mathbf{A}$ ,

$$\mathbf{w}_{\alpha} = \mathbf{A} e^{i\mathbf{q}\mathbf{R}_{\alpha}} + \mathbf{A}^* e^{-i\mathbf{q}\mathbf{R}_{\alpha}}.$$

The system of equations (5.22) has to be solved self-consistently together with (5.20).  $\rho^{(1)}$  and  $V_{\text{SCF}}^{(1)}$  can be directly used in Eq. (5.19), and the second term on the right side of Eq. (5.19) can be obtained from analytical differentiation of the second equation in (5.22), similarly to how the forces were obtained from zero-order Kohn–Sham results.