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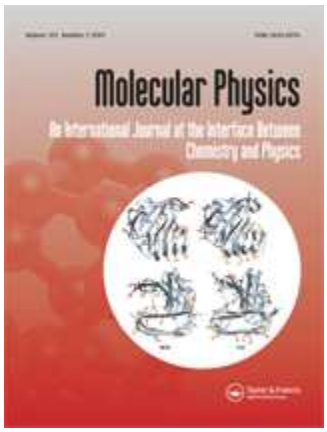

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Article in honor of Prof. H.-J. Werner's 60^{th} birthday

Analytical stress tensor and pressure calculations with the CRYSTAL code

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The calculation of the stress tensor and related properties and its implementation in the CRYSTAL code are described. The stress tensor is obtained from the earlier implemented analytical gradients with respect to the cell parameters. Subsequently, the pressure and enthalpy is computed, and a test concerning the pressure driven phase transition in KI is used as an illustration. Finally, the possibility of applying external pressure is implemented. The constant pressure optimization offers an alternative optimization method, in addition to the already implemented optimization at constant volume.

Keywords: analytical gradient; stress tensor; pressure; enthalpy

Contents

1. Introduction

The calculation of the total energy has become an important part of electronic structure theory, and a set of methods and codes are available. Nowadays, density functional calculations are feasible for large systems; and in many cases such calculations have become routine work. After the total energy is computed, then, from the minimum of the total energy, the optimal geometry is obtained. This is usually facilitated with the availability of analytical gradients, see e.g. [1–3].

After the equilibrium structure of a solid is determined, there are further properties of interest which are closely related to the total energy, such as the bulk modulus or elastic constants. Even more important is the situation when the energy as a function of the volume is known, and the pressure has to be determined. When the pressure has been computed, the enthalpy can be obtained, and the

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search for possible phase transitions can be performed. If the derivative of the energy with respect to the unit cell parameters is known, then from these derivatives, the aforementioned properties (pressure, enthalpy) can be computed.

The stress tensor [4, 5] is closely related to the derivatives of the total energy with respect to the cell parameters. The ab initio calculation of the stress tensor was pioneered some time ago [6]. In this article, the implementation of the stress tensor in the electronic structure code CRYSTAL [7, 8] is reported. The article is organized as follows: in section 2, the variables are defined. The definition of the stress tensor, tests concerning the accuracy of the implementation, the calculation of pressure and enthalpy, and some examples are given in section 3. In section 4, the possibility of applying external pressure is demonstrated; and the optimization at constant volume is compared with the optimization at constant pressure. Finally, the paper is summarized.

2. Variables

An elastic deformation is given by the expression:

$$\vec{r}\,' = (\mathbb{1} + \epsilon)\vec{r} \tag{1}$$

or

$$r'_j = \sum_{k=1}^{3} (\delta_{jk} + \epsilon_{jk}) r_k \tag{2}$$

where δ_{jk} is the Kronecker delta. Here, the case of pure strain is assumed, and then ϵ_{jk} is the symmetric strain tensor[4]:

$$\begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{12} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{13} & \epsilon_{23} & \epsilon_{33} \end{pmatrix} = \begin{pmatrix} \epsilon_1 & \frac{1}{2}\epsilon_6 & \frac{1}{2}\epsilon_5 \\ \frac{1}{2}\epsilon_6 & \epsilon_2 & \frac{1}{2}\epsilon_4 \\ \frac{1}{2}\epsilon_5 & \frac{1}{2}\epsilon_4 & \epsilon_3 \end{pmatrix} \tag{3}$$

The primitive cell is given by three vectors: $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$. a_{ij} are defined in such a way that $a_{11} = a_{1x}$ is the x-component of $\vec{a}_1$, $a_{12} = a_{1y}$ the y-component of $\vec{a}_1$, and $a_{13} = a_{1z}$ the z-component of $\vec{a}_1$, i.e.:

$$\begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix} = \begin{pmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{4}$$

When a distortion is applied, then the cell parameters transform as:

$$a'_{ij} = \sum_{k=1}^{3} (\delta_{jk} + \epsilon_{jk}) a_{ik} \tag{5}$$

The derivatives (see also [9, 10])

$$\left.\frac{\partial a'_{ij}}{\partial \epsilon_{lm}}\right|_{\epsilon_{lm}=0} = \lim_{\epsilon_{lm}\to 0} \frac{a'_{ij}(\epsilon_{lm}) - a'_{ij}(\epsilon_{lm}=0)}{\epsilon_{lm}} = \sum_{k=1}^{3} \delta_{jl}\delta_{km}a_{ik} = \delta_{jl}a_{im} \tag{6}$$

and

$$\left.\frac{\partial E}{\partial \epsilon_{lm}}\right|_{\epsilon_{lm}=0} = \tag{7}$$
$$\lim_{\epsilon_{lm}\to 0} \frac{E(\vec{a}_1\,'(\epsilon_{lm}), \vec{a}_2\,'(\epsilon_{lm}), \vec{a}_3\,'(\epsilon_{lm})) - E(\vec{a}_1\,'(\epsilon_{lm}=0), \vec{a}_2\,'(\epsilon_{lm}=0), \vec{a}_3\,'(\epsilon_{lm}=0))}{\epsilon_{lm}} =$$
$$\sum_{i,j=1}^{3} \frac{\partial E}{\partial a'_{ij}} \left.\frac{\partial a'_{ij}}{\partial \epsilon_{lm}}\right|_{\epsilon_{lm}=0} = \sum_{i,j=1}^{3} \frac{\partial E}{\partial a_{ij}}\delta_{jl}a_{im} = \sum_{i=1}^{3} \frac{\partial E}{\partial a_{il}}a_{im}$$

are required for the calculation of the stress tensor.

3. The stress tensor and related properties

The stress tensor is a symmetric tensor, and following the notation of [4] it is given as:

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{pmatrix} = \begin{pmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{pmatrix} \tag{8}$$

It can be computed from the total energy as

$$\sigma_{ij} = \frac{1}{V}\frac{\partial E}{\partial \epsilon_{ij}} \tag{9}$$

or equivalently, using equation 3:

$$\sigma_i = \frac{1}{V}\frac{\partial E}{\partial \epsilon_i} \tag{10}$$

where $V = \vec{a}_1(\vec{a}_2 \times \vec{a}_3)$ is the volume of the unit cell. Here, the sign is according to the convention used in [4, 5].

In the case of hydrostatic pressure, the stress tensor becomes diagonal, and the pressure is obtained as

$$\sigma_{ij} = -p\delta_{ij} \tag{11}$$

The calculation of the stress tensor thus makes the pressure p and the enthalpy $H = E + pV$ accessible. The implementation is straightforward: The derivatives $\frac{\partial E}{\partial a_{ij}}$ constitute the difficult part and were implemented in the past for the case of

Table 1. Stress tensor σ_{ij}, in hartree/bohr^3, computed for oxalic acid dihydrate.

component	numerical	analytical
σ_1	-0.00093087	-0.00093087
σ_2	-0.00064440	-0.00064415
σ_3	-0.00092248	-0.00092197
σ_4	0	0
σ_5	-0.00000555	-0.00000564
σ_6	0	0

3 dimensional periodicity [11] and for the case of 1 and 2 dimensional periodicity [12].

In addition, this offers the possibility to apply external pressure: by adding a term $-p\delta_{ij}$ to the stress tensor, an optimization at constant pressure p is implemented.

3.1. *Test 1: Oxalic acid dihydrate*

A first test was done with oxalic acid dihydrate, which has a monoclinic lattice, and the stress tensor is non-diagonal and thus not too trivial. The experimental geometry as determined in [13] was used, and basis sets as in [14] were employed. The stress tensor was determined numerically, by applying two elastic distortions with $\epsilon_i = 0.001$ and $\epsilon_i = -0.001$, and then performing a numerical differentiation:

$$\sigma_i^{numerical} = \frac{1}{V}\frac{\Delta E}{\Delta \epsilon_i} \tag{12}$$

The energy was evaluated at the Hartree-Fock level, and this test therefore serves essentially to verify that the transformation in equation 7 is implemented properly, and to check the accuracy. The results are compared in table 1, and it is apparent, that a good accuracy is obtained.

3.2. *Test 2: The NaCl → CsCl phase transition in KI*

As a practical example, the phase transition from the NaCl to the CsCl structure in KI is studied. The earlier suggested procedure [15] is to compute the energy as a function of the volume ($E(V)$ curve), then perform a fit for the function $E(V)$, obtain the pressure p as the derivative of the fitting function $p = -\frac{\partial E}{\partial V}$ and then the enthalpy $H = E + pV$. With the present implementation, the pressure is readily available via the stress tensor. Thus this procedure can be simplified, and the pressure and enthalpy can be computed analytically. This requires that the stress tensor is of the form $-p\delta_{ij}$. In the present implementation, this was assumed to be fulfilled, if all non-diagonal components of the stress tensor are below a threshold value, and the diagonal elements do not differ by more than a threshold value.

The total energies of KI in the NaCl and CsCl structure were computed, at the level of the local density approximation, with basis sets as were used for KI in [16]. The $E(V)$ curves were obtained by fitting the computed energy values with a polynomial of degree four. This is displayed in figure 1 (top). Subsequently, the pressure as a function of the volume was computed analytically and numerically (figure 1, middle). When the analytical differentiation with respect to the volume (crosses and circles in figure 1) is compared with the numerical differentiation of the polynomials which fit $E(V)$ (full and dashed lines in figure 1), then the results

are virtually identical. This confirms that the implementation is reasonable. Also, the minimum of the energy and the zero of the pressure agree well.

By adding pV to the energy, the enthalpy is obtained (figure 1, bottom). The analytically computed enthalpies (crosses and circles) were obtained using the analytical derivative for the pressure and subsequently computing the enthalpy, the numerically computed enthalpies (full and dashed lines) were obtained with the numerically computed pressure. Again, when comparing the results employing analytical or numerical differentiation of the $E(V)$ curve, then the enthalpy curves are virtually identical.

As a by product of this test of the implementation and accuracy, the critical pressure at the NaCl $\rightarrow$ CsCl phase transition is obtained from the intersection of the two enthalpies for the NaCl and the CsCl structure. This pressure is 1.0 GPa (present work), and in reasonable agreement with the experiment (1.9 GPa [17]) or earlier calculations (2.75 GPa [18]).

The fact that the stress tensor and the pressure is now available as an analytical derivative simplifies the calculation of further elastic properties such as the elastic constants. For example, the bulk modulus can now be obtained by one numerical differentiation of the pressure with respect to the volume (first part of equation 13), instead of two numerical differentiations (second part of equation 13) which was necessary earlier; a similar argument holds for the elastic constants.

$$B = -V\frac{\partial p}{\partial V} = V\frac{\partial^2 E}{\partial V^2} \tag{13}$$

4. Applying external pressure

Once the stress tensor has been computed, it is subsequently one possible option to add external pressure.

For this purpose, an external part $\sigma_{ij}^{external}$ is added to the stress tensor as defined in equation 9:

$$\sigma_{ij}^{total} = \sigma_{ij} + \sigma_{ij}^{external} \tag{14}$$

and thus the total stress σ_{ij}^{total} is obtained. When this is zero, then this means that a system is described, where an external stress is applied. As the optimizer works with the gradient with respect to the cell parameter, the stress tensor σ_{ij}^{total} has to be back transformed to obtain the modified gradients with respect to the cell parameter. Thus, the matrix a_{ij} of the cell vectors has to be inverted, with $(a^{-1})_{jk}$ being the inverse:

$$\sum_{j=1}^{3} a_{ij}(a^{-1})_{jk} = \delta_{ik} \tag{15}$$

Then, using this in equation 7, the back transformation is obtained:

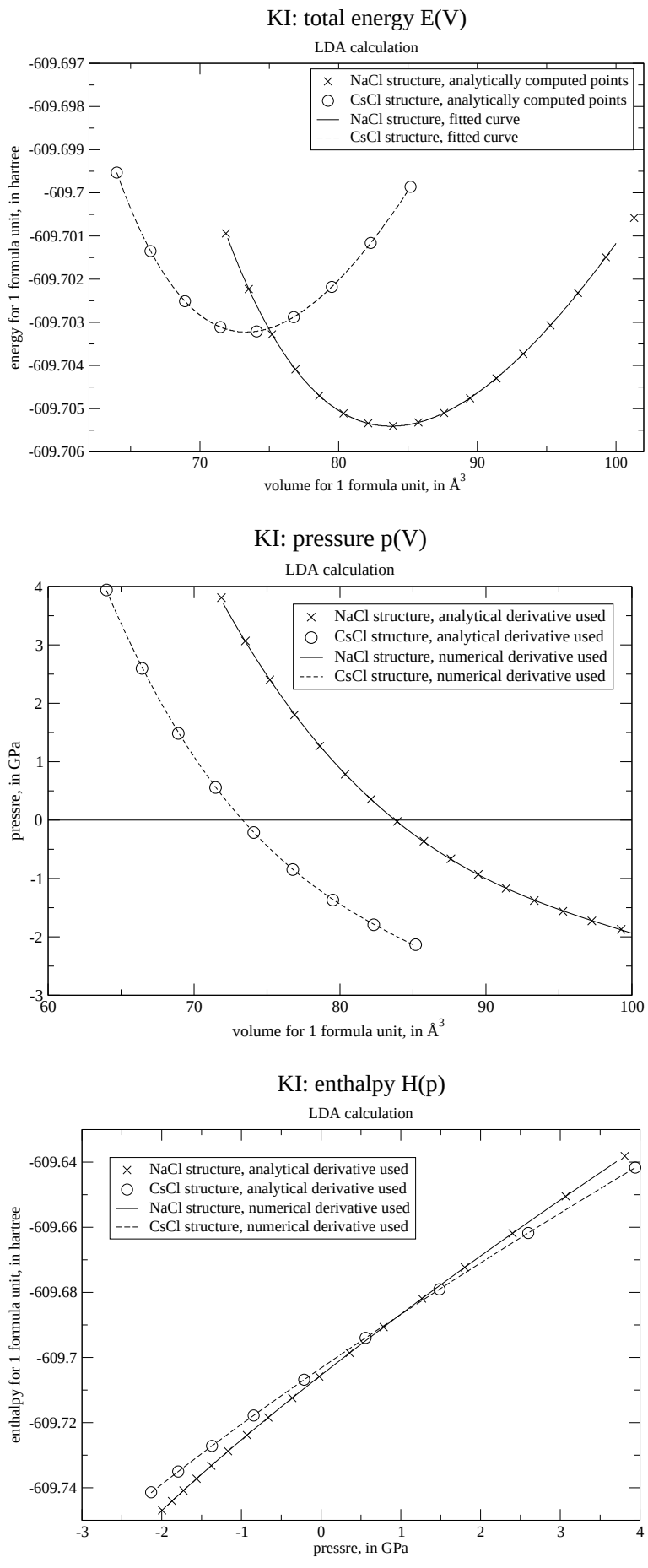

Figure 1. The total energy as a function of the volume (top figure), the pressure as a function of the volume (middle figure), and the enthalpy as a function of the pressure (bottom). The crosses and circles refer to the points where the total energy was calculated and subsequently the pressure and enthalpy derived analytically. The full and dashed lines are obtained by fitting the energies as a function of the volume with a polynomial, and subsequently computing the derivative of this polynomial.

$$\sum_{m=1}^{3}\sum_{i=1}^{3}\frac{\partial E}{\partial a_{il}}a_{im}(a^{-1})_{mn} = \sum_{i=1}^{3}\frac{\partial E}{\partial a_{il}}\delta_{in} =$$

$$\frac{\partial E}{\partial a_{nl}} = \sum_{m=1}^{3}\frac{\partial E}{\partial \epsilon_{lm}}\bigg|_{\epsilon_{lm}=0}\cdot a_{mn} = V\sum_{m=1}^{3}a_{mn}\sigma_{lm} \tag{16}$$

Exploiting equation 16, we thus obtain for the total gradient with respect to the cell parameter, after having added the external stress:

$$\left(\frac{\partial E}{\partial a_{ij}}\right)^{total} = \frac{\partial E}{\partial a_{ij}} + V\sum_{m=1}^{3}a_{mi}\sigma_{jm}^{external} \tag{17}$$

$\frac{\partial E}{\partial a_{ij}}$ is thus the gradient with respect to the cell parameter without external stress, and $\left(\frac{\partial E}{\partial a_{ij}}\right)^{total}$ the gradient with respect to the cell parameter in the presence of an external stress.

In the present implementation, the option of a general external stress tensor is possible. As the stress tensor must be symmetric, this means six input parameters. In principle any form is possible, with special cases such as hydrostatic or uniaxial pressure. The most important case is that of hydrostatic pressure, where the tensor is diagonal (see equation 11).

As a test, in figure 2, the $E(V)$ curve for Al_2O_3 is displayed. The pluses are data points obtained with the present implementation where the energy is optimized in the presence of external (hydrostatic) pressure. The squares are data points computed with the energy optimization under the constraint of a fixed volume, as implemented in the CRYSTAL06 release [8]. As can be seen, the data from both methods agrees very well, and the data points lie well on the $E(V)$ curve, which was obtained with a polynomial fit of degree four.

Similarly, in figure 3, the $E(V)$ curve for oxalic acid dihydrate is displayed. This system is monoclinic and the stress tensor more general (in the case of non-hydrostatic pressure, the stress tensor is not diagonal). Again, the data from fixed volume optimization (squares) and the data from the constant pressure optimization (pluses) agree well and lie on a smooth curve. This confirms that the present implementation is reliable.

When comparing the number of steps required for the geometry optimization, it turned out that both schemes (constant pressure versus constant volume) require a similar number of steps. The most important parameter is to have a good initial guess.

5. Conclusion

In this article, the calculation of the stress tensor and the implementation in the electronic structure code CRYSTAL is described. The stress tensor is obtained from the analytical gradient with respect to the cell parameters, and subsequently pressure and enthalpy can be computed, all based on analytical expressions without the need to compute any numerical derivatives. An additional feature is to add terms to the stress tensor, which allows to apply external pressure. This implementation

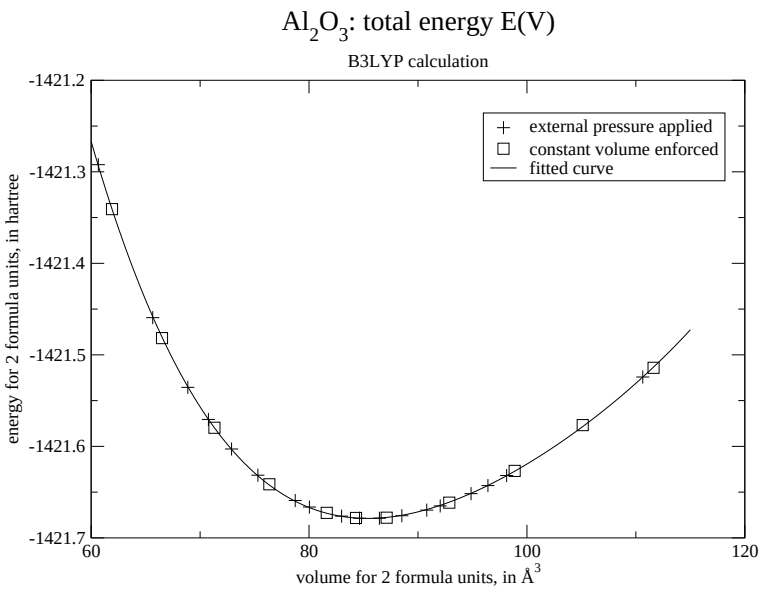

Figure 2. The total energy, on the B3LYP level, as a function of the volume for Al_2O_3. The pluses are data points computed with the present implementation of applying external pressure. The squares are data points obtained from an optimization at constant volume. The full line is a fit through the data points.

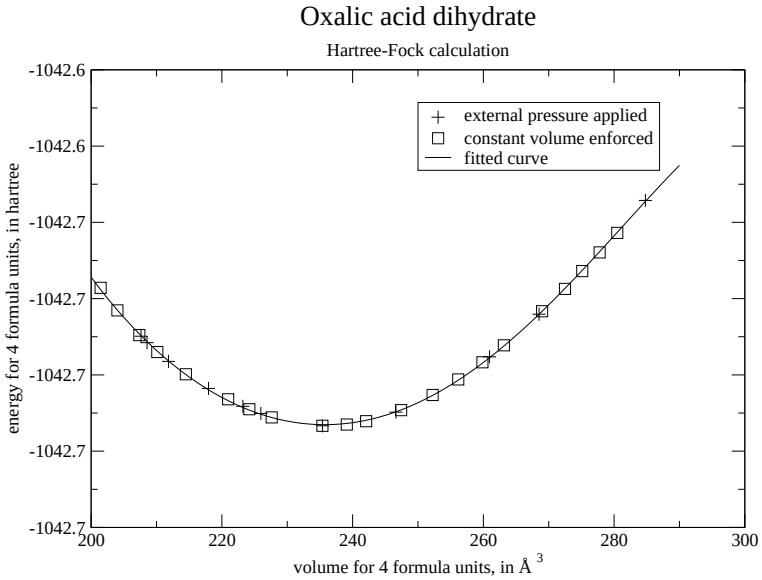

Figure 3. The total energy, on the Hartree-Fock level, as a function of the volume for oxalic acid dihydrate. The pluses are data points computed with the present implementation of applying external pressure. The squares are data points obtained from an optimization at constant volume. The full line is a fit through the data points.

also facilitates the calculation of properties such as the bulk modulus or elastic constants, as only one more numerical derivative is required.

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