How strong is it? The interpretation of force and compliance constants as bond strength descriptors†

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Knowledge about individual covalent or non-covalent bond strengths is the Holy Grail of many modern molecular sciences. Recent developments of new descriptors for such interaction strengths based on potential constants are summarised in this *tutorial review*. Several publications for and against the use of compliance matrices (inverse force constants matrix) have appeared in the literature in the last few years. However the mathematical basis for understanding, and therefore interpreting, compliance constants is still not well developed. We therefore summarise the theoretical foundations and point to the advantages and disadvantages of the use of force constants *versus* compliance constants for the description of both non-covalent and covalent interactions.

Introduction

Like other chemical concepts, for example aromaticity or hybridization, the notion of bond orders and bond strengths leads to occasionally heated discussions in the literature.[1–3] Although many of these concepts often lack a solid physical grounding, without a characterisation or classification of different bonding situations, there would be no systematic classification of the boundless chemical diversity. Furthermore, knowledge of individual covalent or non-covalent bond strengths is crucial in drug design, molecular recognition[4] or the construction of new catalyst systems.[5] Yet the evaluation of bond strength or bond orders is not at all trivial. For covalent bonds *e.g.* the frequently used bond dissociation enthalpies (BDE) and other indirect methods can be far from adequate in their description of the intrinsic strength of a particular bond. The BDE of the carbon–carbon double bond in substituted olefins varies over 400 kJ mol^{-1} due to different stabilities and differences concerning the singlet–triplet gap of the fragments, though the actual character or strength of the C=C bond is the same.[6]

On the other hand, the unique experimental determination of non-covalent bond strengths is often impossible and only approximate values are proposed. Though non-covalent bonds are the key to many phenomena in biochemistry, the understanding of hydrogen bonds in biological macromolecules is still hampered by the fact that their strengths are usually inferred indirectly. In the case of C–H···O hydrogen bonds, this indirect assessment leads to interaction strengths that range from "repulsive" through "negligible" in the adenine–thymine base pair to "large" in supramolecular complexes.[7]

To separate real differences from deceptive ones suggested by different indirect proxy methods, alternative ways to directly determine covalent or non-covalent bond strengths

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without reference to arbitrary or ill-defined states are therefore needed. The calculation of compliance constants (elements of the inverted Hessian matrix) offers such an alternative.

In order to clarify the sometimes vague interpretation[2,8] of compliance constants and force constants this *tutorial review* will summarise the main features of, and differences between, these two intrinsic bond strength descriptors.

Before we go into detail, we would like to point out the difference between the terms ''bond strength'' and ''bond stiffness''. Both terms characterise two different portions of the potential energy surface. Bond strength as it is commonly understood is equivalent to the energy needed for the complete separation of individual molecular fragments (BDE, see above). Bond stiffness, on the other hand, usually expressed as force constants, describes the change in energy for small displacements from the equilibrium structure, that is the intrinsic bond strength. In what follows we use the expression ''bond strength'' in terms of this intrinsic bond property.

Force constants

The potential energy V of any molecule can be expanded exactly in an infinite Taylor series as

$$V = V_0 + \boldsymbol{G}^{\mathrm{T}}\boldsymbol{Z} + \tfrac{1}{2}\boldsymbol{Z}^{\mathrm{T}}\boldsymbol{H}\boldsymbol{Z} + \ldots \qquad (1)$$

where $\boldsymbol{Z}$ is the column vector of a fully determined but otherwise arbitrary set of displacement coordinates, and $\boldsymbol{G}$ and $\boldsymbol{H}$ are the corresponding gradient (vector of first derivatives $\partial V/\partial Z_i$) and Hessian (matrix of second derivatives $\partial V/\partial Z_i\partial Z_j$), respectively.

Chemists are mainly interested in the stationary points on the potential energy surface (PES), which are either local minima or transition states. Since the gradient $\boldsymbol{G}$ at these points is always zero with respect to all displacement coordinates, the second term in eqn (1) disappears. This assumption will be made throughout this *tutorial review*.

In order to describe the relative energy ($V_0 = 0$) of a molecule the geometry of which is slightly distorted compared to that for which the Taylor series was expanded, it is usually sufficient to assume a harmonic potential around the equilibrium. This justifies the termination of the Taylor series after the third term, resulting in

$$V = \tfrac{1}{2}\boldsymbol{Z}^{\mathrm{T}}\boldsymbol{H}\boldsymbol{Z} \qquad (2)$$

usually known as the quadratic form or harmonic approximation. The elements of the Hessian $\boldsymbol{H}$ are referred to as force constants, or *rigid* force constants to distinguish them from the *relaxed* force constants.[9] Up to now the formalism is valid for any set of coordinates. In the following we discuss the properties of the Hessian in terms of an internal coordinate system.

Internal coordinates

Internal coordinates like interatomic distances, valence and dihedral angles are commonly used for the description of molecular geometries, since they are much more intuitive to chemists than their Cartesian counterparts. Among them we have to distinguish between non-redundant and redundant sets. Redundant internal coordinates are widely used in geometry optimization processes. They are more straightforward to define than non-redundant sets,[10–12] because there is no need to take into account linear dependences. There are a few problems arising with force constants in redundant coordinates that we will address later. However, we will begin the discussion in terms of a non-redundant set first.

Eqn (2) is therefore written explicitly in terms of a non-redundant set of internal displacement coordinates $\boldsymbol{Q}$

$$V = \tfrac{1}{2}\boldsymbol{Q}^{\mathrm{T}}\boldsymbol{H}_q\boldsymbol{Q} \qquad (3)$$

where $\boldsymbol{H}_q$ is the corresponding Hessian in internal coordinates. As Decius[13] pointed out, $\boldsymbol{H}_q$ is in principle determined by the frequencies of a sufficient set of isotopic molecules, and can be constructed on that basis for any set of internal coordinates. Thus it is—at least indirectly—observable. Due to their definition as second derivatives of energy, *rigid* force constants provide a measure of the steepness of the potential well for a molecule in its equilibrium configuration. Since the second derivative of the energy with respect to displacements is equivalent to the first derivative of the force, it describes the force required to distort a coordinate by a unit amount *while holding all other coordinates fixed in their equilibrium configurations.*[14]

$$\boldsymbol{H} = \left(\frac{\partial^2 V}{\partial Q_i \partial Q_j}\right)_0 \qquad (4)$$

Due to this property force constants are frequently used as bond strength descriptors in the literature. However, there are several problems associated with their interpretation that we will now discuss in detail.

A simple example

A simple example should illustrate the meaning of force constants for the 2-dimensional function $f(x,y) = x^2 + y^2$, which has its global minimum at $f(0,0) = 0$ (*cf.* Fig. 1, P_1). To displace the x-coordinate by some amount away from this minimum a force has to be applied against this very coordinate. As can be seen from Fig. 1, this displacement does not introduce a force in the y-coordinate, since the distortion takes place along the minimum path with respect to y. This

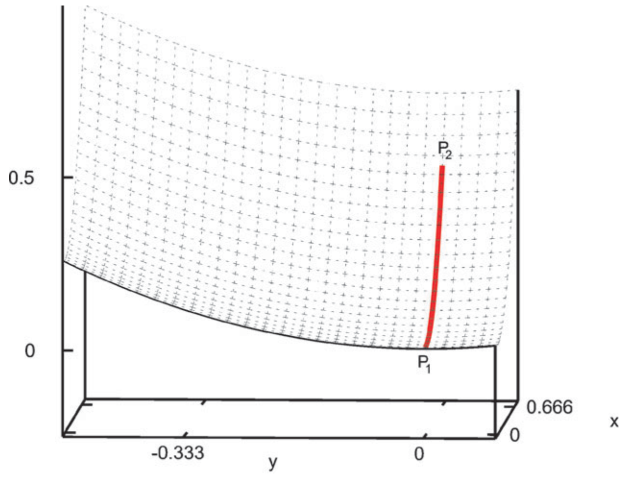

Fig. 1 Plot of the two-dimensional function $f(x,y) = x^2 + y^2$ (uncoupled). Point 1 (P_1) reflects the global minimum, point 2 (P_2) a small displacement of the x-coordinate.

behaviour is due to the fact that this function does not contain coupling terms between x and y. Thus $\partial^2 f/\partial x \partial y = 0$, resulting in a Hessian of diagonal form. In such cases f can be regarded as an energy function of two uncoupled harmonic springs that can be varied independently of each other. This is an important aspect to which we will return.

However, potential functions for molecules *contain* coupling terms between various internal coordinates since all atoms "feel each other". Thus, for energy functions f that describe molecules, in general $\partial^2 f/\partial x \partial y \neq 0$ holds. That means that the Hessian is a non-diagonal one. A simple function of that type is $f(x,y) = x^2 + y^2 + xy$, which is plotted in Fig. 2. If the coordinate x is deflected under the restriction that y must not be altered, there will necessarily be a force induced along y in addition to the force on x (see Fig. 2, P_2). For both functions, the coupled and the uncoupled, the diagonal force constants corresponding to the x-coordinate $\partial^2 f/\partial x^2 = 2$ are equal. From this one could erroneously infer that the force required to distort this coordinate would be the same for both. That this is not the case can be seen from the gradients which are $\partial f/\partial x = 2x$ and $\partial f/\partial y = 2y$ for the uncoupled function and $\partial f/\partial x = 2x + y$ and $\partial f/\partial y = 2y + x$ for the coupled function. If one distorts the x-coordinate in the coupled function by some amount x, while $y = 0$ is held at the equilibrium value, the gradient at the point $P_2(x,0)$ along x will be $\partial f/\partial x = 2x$ which is identical to that of the uncoupled function. But, due to the coupling term, an additional force $\partial f/\partial x = x$ will be induced along y, which is obviously *not* the case for the uncoupled function. Therefore in coupled functions the force needed to distort x under the condition that y must not be altered will be greater than in uncoupled cases. Note that, as mentioned above, the diagonal force constants are the same. This clarifies that diagonal force constants cannot be taken as bond strength descriptors for molecules since they do not reflect couplings between coordinates. These couplings are given by the off-diagonal elements. They have to be taken into account for a reasonable description of the force needed to distort one particular coordinate.

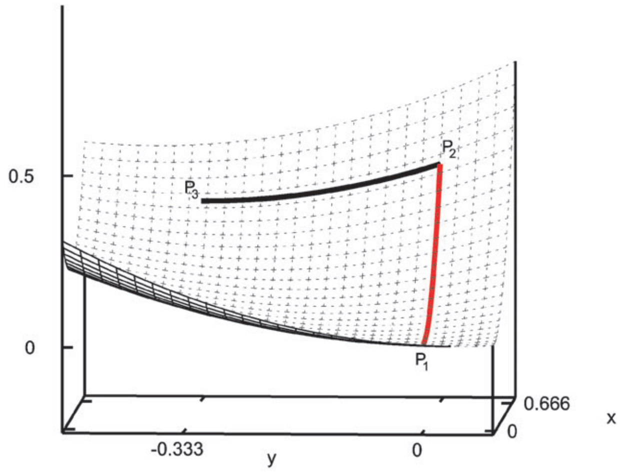

Fig. 2 Plot of the two-dimensional function $f(x,y) = x^2 + y^2 + xy$ (with a coupling term). Point 1 (P_1) reflects the global minimum, point 2 (P_2) a small displacement of the x-coordinate while y is held fixed. Point 3 (P_3) depicts the situation after relaxation with respect to y.

Interpretation as Hookean springs

Force constants are often interpreted as the spring constants of Hookean springs that connect the atoms in a molecule. Hence the question of why the distortion of one particular bond can induce a force into another one arises. If no more springs are used to construct the molecule than are required by the number of degrees of freedom, and no redundancies are present, any spring should be distortable without affecting the others. Since this is obviously not the case for molecules, such coupled systems cannot be explained by a model of *independent* harmonic springs with fixed Hookean constants. It would be more appropriate to explain the bonds in such systems with springs whose constants and equilibrium positions depend on the geometry of the whole molecule and thus on the other spring constants, too. The traditional picture of describing molecules as atoms connected *via* harmonic springs with fixed force constants thus has to be rejected in general, despite the fact that this assumption is frequently made in classical force field calculations.

Dependence on coordinate selection

The most telling criticism of the use of force constants, however, is that the magnitude of a force constant depends on the nature of the internal coordinates used to describe the molecule. We illustrate this problem for the water molecule, which can be described in terms of the two O–H bonds and the H–O–H angle, or the two O–H bonds and the non-bonded H···H distance (*cf.* Fig. 3), respectively, without referring to explicit values.[3] The stretching of the same coordinate (the O–H bond r_{OH^1} in our example) by a unit amount in two different non-redundant sets with the restriction that all other coordinates must not be altered would lead to two different geometries. Both geometries reflect two different points on the same PES. Thus the force constants and the force needed to distort this very coordinate are different for both sets of coordinates. In other words, it makes a difference if one

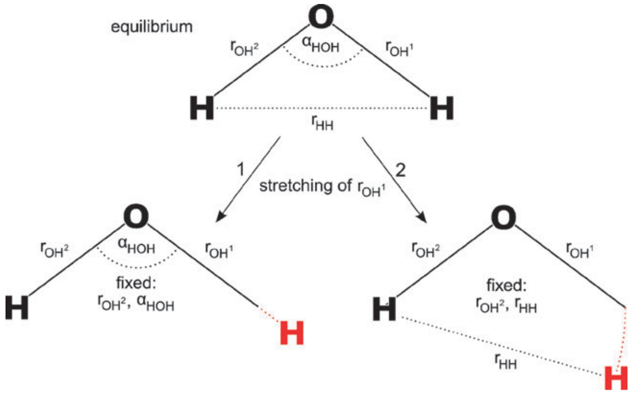

Fig. 3 Stretching of one O–H bond (r_{OH^1}) in water by the same amount under the restriction that the other internal coordinates remain unaltered. The coordinate system 1 (left side) is comprised of the two O–H distances r_{OH^1}, r_{OH^2} and the H–O–H angle α. The coordinate system 2 consists of the three distances r_{OH^1}, r_{OH^2} and r_{HH}. Both distortions lead to two different geometries, which means two different points (energies) on the potential energy surface.

(1) distorts the O–H bond r_{OH^1}, while leaving the other O–H bond r_{OH^2} and the H–O–H angle α_{HOH} fixed (*cf.* Fig. 3, left), or if one

(2) distorts the O–H bond r_{OH^1}, while leaving the other O–H bond r_{OH^2} and the H···H distance r_{HH} fixed (*cf.* Fig. 3, right).

This dependence on coordinate selection is troublesome, as the putative measure of the O–H bond strength varies dramatically. Of course, if one intends to use force constants as bond strength descriptors, they must have a distinct value. The energy of a molecule and the strength of a specific bond in it must not depend on the coordinate system.

Mathematically speaking, the Hessians $\boldsymbol{H}_1$ and $\boldsymbol{H}_2$ for two different sets of non-redundant coordinates that have n coordinates in common are related by[15]

$$\boldsymbol{H}_1 = \begin{pmatrix} \boldsymbol{E} & \boldsymbol{I} \\ 0 & \boldsymbol{J} \end{pmatrix} \boldsymbol{H}_2 \begin{pmatrix} \boldsymbol{E} & 0 \\ \boldsymbol{I} & \boldsymbol{J} \end{pmatrix} \tag{5}$$

where $\boldsymbol{E}$ is a $n \times n$ unit matrix, $\boldsymbol{I}$ and $\boldsymbol{J}$ are non-zero blocks, and $\mathbf{0}$ is a zero block. From eqn (5) it can be seen that the upper left-hand corners of $\boldsymbol{H}_1$ and $\boldsymbol{H}_2$ are different, and thus the force constants even for the unaltered coordinates are not the same. This is the strict proof for the *general* dependence of force constants on coordinate systems. Note the positions of the zero blocks $\mathbf{0}$. We will need this fact in our later discussion about compliance matrices.

This dependence would obviously not occur if the coordinates were uncoupled, that is if $\boldsymbol{H}$ is diagonal. The vibrational modes are independent of each other only for such normal coordinates. Thus, the motion could be explained by a classical spring model, where the diagonal elements of the Hessian are the spring constants. However, normal coordinates are linear combinations of internal coordinates. Thus, it is hard to imagine what kind of harmonic spring would describe a normal mode, even if the modes are observable in principle. Nevertheless, one thing is certain: by the definition of normal modes these springs do not correspond to particular primitive internal coordinates.

Since the distortion of a bond in general affects the whole molecule, forces are induced into all other bonds that would normally lead to stretching, bending, *etc.* of those coordinates. Nevertheless, in the case of *rigid* force constants these relaxations are forbidden by definition. The resulting force required to stretch one particular bond is the sum over all forces, including the induced ones in the other coordinates.

Thus *rigid* force constants do not provide an unambiguous measure of the strength of a specific bond. Their indiscriminate use as bond strength descriptors (*e.g.* in empirical force fields where most of the coupling terms are ignored) may lead to arbitrary results.

We have mentioned that redundant internal coordinates are frequently used in geometry optimization processes. In such coordinate systems, the number of internal coordinates used to describe the system exceeds the degree of internal freedom. As we will now show, the interpretation of force constants in such systems is equally worrisome.

Redundant internal coordinates

As stated above, eqn (2) is valid for any set of coordinates, therefore the expansion in terms of redundant internal coordinates must also hold true.[16] In what follows, all matrices $\mathbb{M}$ that correspond to the redundant set will be printed blackboard bold, while the matrices $\boldsymbol{M}$ that correspond to a non-redundant subset of the coordinates are printed bold. So let us consider a redundant set of internal coordinates $\mathbb{Q}$ (for example, but not limited to, a set containing all possible atom–atom distances), then eqn (2) becomes

$$V = \tfrac{1}{2}\mathbb{Q}^{\mathrm{T}}\mathbb{H}_q\mathbb{Q} \tag{6}$$

Since $\mathbb{Q}$ denotes a set of redundant internal coordinates, there necessarily exists a corresponding set of internal coordinates $\boldsymbol{Q}$ from which the redundancies have been removed. The remaining coordinates are linear combinations of the non-redundant subset. Thus, a uniquely defined matrix $\boldsymbol{A}$ exists, which expresses the transformation between both sets[13,17]

$$\mathbb{Q} = \boldsymbol{AQ} \tag{7}$$

If we choose the ordering of the coordinates $\mathbb{Q}$ such that those of the subset $\boldsymbol{Q}$ are the first ones, it is clear that $\boldsymbol{A}$ consists of a unit matrix $\boldsymbol{E}$ plus a matrix $\boldsymbol{R}$ of proper dimension that expresses the redundancies

$$\boldsymbol{A} = \begin{pmatrix} \boldsymbol{E} \\ \boldsymbol{R} \end{pmatrix} \tag{8}$$

Substitution of eqn (7) into eqn (6) results in

$$V = \tfrac{1}{2}\boldsymbol{Q}^{\mathrm{T}}\boldsymbol{A}^{\mathrm{T}}\mathbb{H}_q\boldsymbol{AQ} \tag{9}$$

and from this, by comparison with eqn (3), it can be seen that the non-redundant Hessian $\boldsymbol{H}_q$ can be expressed as

$$\boldsymbol{H}_q = \boldsymbol{A}^{\mathrm{T}}\mathbb{H}_q\boldsymbol{A} \tag{10}$$

Counterintuitively, in this case the non-redundant Hessian $\boldsymbol{H}_q$ consists of linear combinations of the redundant one $\mathbb{H}_q$, and not *vice versa*. Therefore an infinite number of Hessian matrices $\mathbb{H}_q$ in redundant internal coordinates $\mathbb{Q}$ that solve eqn (10) exists. Nevertheless, an expression for the redundant Hessian $\mathbb{H}_q$ starting from the non-redundant Hessian $\boldsymbol{H}_q$ can be obtained by

$$\mathbb{H}_q = \boldsymbol{A}^{-\mathrm{T}}\boldsymbol{H}_q\boldsymbol{A}^{-} \tag{11}$$

where $\boldsymbol{A}^{-} = (\boldsymbol{A}^{\mathrm{T}}\boldsymbol{uA})^{-1}\boldsymbol{A}^{\mathrm{T}}\boldsymbol{u}$ and $\boldsymbol{u}$ is an arbitrary positive definite matrix of appropriate size.[18]

Due to the fact that the matrix $\boldsymbol{u}$ is involved in the transformation, it becomes clear that force constants are more or less arbitrary in the redundant case. This has been pointed out earlier by the groups of Overend[16,19] and Günthard.[20] Therefore force constants evaluated in redundant coordinates have no physical meaning at all and have to be rejected for the description of bond strengths. Note, however, that redundant force constants are frequently used *e.g.* in force field calculations.[21]

Still, it is common practice to choose $\boldsymbol{u} = \boldsymbol{E}$ as the unit matrix. Assuming this, $\mathbb{H}_q$ is indeed well but not uniquely defined according to

$$\mathbb{H}_q = \boldsymbol{A}^{\mathrm{T}+}\boldsymbol{H}_q\boldsymbol{A}^{+} \tag{12}$$

with $\boldsymbol{A}^{+} = (\boldsymbol{A}^{\mathrm{T}}\boldsymbol{A})^{-1}\boldsymbol{A}^{\mathrm{T}}$ being the Moore–Penrose inverse[22] of $\boldsymbol{A}$. In general $\boldsymbol{H}_q$ is *not* a submatrix of $\mathbb{H}_q$, and therefore the corresponding elements in both matrices are different. This has been pointed out by several authors.[16,20,23] However the redundant Hessian $\mathbb{H}_q$ always satisfies eqn (6) and can be constructed in a unique and straightforward manner. This is a kind of universal solution, although it has no physical meaning. This means that, even in the case of a well-defined redundant Hessian, the force constants cannot be regarded as reliable and unique bond strength descriptors.

This applies to geometry optimizations as well, which are usually based on an initial Hessian guess, comprised of empirical force constants.[11,24] This method can lead to inappropriate starting values, in particular for weak chemical interactions. A diagonal hydrogen-bond stretch force constant *e.g.* may differ by more than one order of magnitude from a regular chemical bond stretch constant.[10]

It is likely that such initial guesses are often ill-defined, and thus prevent fast convergence. Still, this method is usually faster than the explicit calculation of the initial Hessian.

Cyclobutane

In order to reveal the dependence of force constants on coordinate systems, we would like to present these findings in a more common chemical context, namely cyclobutane. Every chemist is familiar with the concept of ring strain, and there is no controversy about the fact that the C–C bond in cyclobutane is weaker (and longer) than in butane itself.[25] So let us see how force constants describe this chemical phenomenon.

Fig. 4 shows the submatrix of force constants corresponding to the four C–C bonds in cyclobutane (left) and the three C–C bonds in n-butane (right), respectively, computed at the MP2/aug-cc-pvtz level of theory[26,27] for two different choices of non-redundant coordinates. Looking at the matrix expressed in Fogarasi *et al.*'s natural internal coordinates[28] (left, upper matrix)—which means a non-redundant set of primitive stretchings and symmetry adapted linear combinations for the bendings and torsions (see ESI†)—everything is in line with our intuitions. The four bonds in cyclobutane are equivalent in terms of their strength and, what is important as well, the C–C bonds in cyclobutane (4.173 N cm^{-1}) are described as being weaker than the C–C bonds in n-butane (4.708 N cm^{-1} and 4.679 N cm^{-1}; see Fig. 4, right).

Turning to *z*-matrix-type internal coordinates, where *both* the stretchings *and* the bendings and torsions are expressed as primitive internals, the following findings are obvious: (1) in the case of cyclobutane the coupling is pronounced; (2) the four C–C bonds in cyclobutane are described as being different; (3) due to the pronounced coupling the C–C bonds in cyclobutane have a higher force constant and are therefore erroneously described as being *stronger* than the C–C bonds in butane.§ Nevertheless, as stated above, the C–C bond in cyclobutane is in fact *weaker* than in butane, which of course should be mirrored by any appropriate bond strength descriptor. As noted several times in this *tutorial review*, in spite of these ambiguities, force constants are often used as bond strength descriptors throughout the literature.

We would therefore like to revive the quite useful and very straightforward concept of using *compliance constants* to assign individual bond strength in arbitrary molecules. It does not suffer from these shortcomings, but has—apart from a few exceptions[9,29,30]—not become generally accepted.

Compliance constants

Decius[31] pointed out that the potential energy of a molecule cannot just be written as a quadratic form in internal displacement coordinates as shown in eqn (3), but also as a quadratic form in terms of generalized displacement forces (negative gradient) $\boldsymbol{G}_q$

$$V = \tfrac{1}{2}\boldsymbol{G}_q{}^{\mathrm{T}}\boldsymbol{C}\boldsymbol{G}_q \tag{13}$$

The gradient $\boldsymbol{G}_q$ is the vector of first derivatives of the potential energy with respect to the displacement coordinates $\boldsymbol{Q}$ and can be obtained by differentiation of eqn (3)

$$\boldsymbol{G}_q = \boldsymbol{H}_q\boldsymbol{Q} \tag{14}$$

Substitution of this expression into eqn (13) results in

$$V = \tfrac{1}{2}\boldsymbol{Q}^{\mathrm{T}}\boldsymbol{H}_q{}^{\mathrm{T}}\boldsymbol{C}\boldsymbol{H}_q\boldsymbol{Q} \tag{15}$$

Since the Hessian $\boldsymbol{H}_q$ is positive definite, there is only one solution for $\boldsymbol{C}$ that fulfils eqn (3)

$$\boldsymbol{C} = \boldsymbol{H}_q{}^{-1} \tag{16}$$

Eqn (15) is an alternative formulation of the potential energy, although matrix inversion in general is a computationally demanding problem and one makes every effort to avoid this task. However, in this section we wish to point out some significant advantages of this expression compared to the conventional expansion into displacement coordinates.

Independence of coordinate selection

As mentioned above, the main problem associated with the interpretation of force constants is their strong dependence on the definition of the coordinates. Cyvin and Slater first noted, however,[32] that the elements of $\boldsymbol{H}_q{}^{-1}$ are invariant with respect to changes in the coordinate system. This invariance was later proven by Decius[13] and it was he who coined the phrase "compliance matrix" for $\boldsymbol{H}_q{}^{-1}$ to emphasize this special property.

For two sets of coordinates that have *n* coordinates in common, the transformation law for two compliance matrices is[15]

$$\boldsymbol{C}_1 = \begin{pmatrix} \boldsymbol{E} & 0 \\ \boldsymbol{K} & \boldsymbol{L} \end{pmatrix} \boldsymbol{C}_2 \begin{pmatrix} \boldsymbol{E} & \boldsymbol{K} \\ 0 & \boldsymbol{L} \end{pmatrix} \tag{17}$$

where $\boldsymbol{E}$ is a $n \times n$ unit matrix, $\boldsymbol{K}$ and $\boldsymbol{L}$ are non-zero blocks and $\boldsymbol{0}$ is a zero block. Note that due to the positions of the zero blocks $\boldsymbol{0}$ in eqn (17), and in contrast to the transformation of the Hessians (*cf.* eqn (5)), the upper left-hand blocks of $\boldsymbol{C}_1$ and $\boldsymbol{C}_2$ are identical. Thus the elements $C_{i,i}$, termed compliance constants (diagonal elements), and compliance coupling constants $C_{i,j}$ (off-diagonal elements), for corresponding

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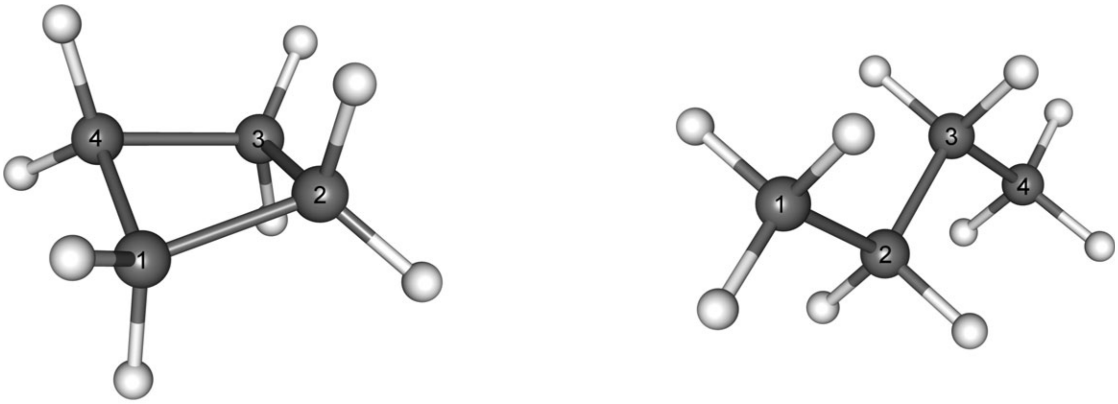
§ Using a simple ball and stick model, this higher rigidity is nevertheless exactly what most chemists would expect from a rigid ring system like cyclobutane, since the distortion of any bond in cyclobutane has a greater impact on the other bonds compared to butane.



Natural Internal Coordinates

	1-2	2-3	3-4	4-1
1-2	4.173			
2-3	0.051	4.173		
3-4	0.155	0.051	4.173	
4-1	0.051	0.155	0.051	4.173

Z-Matrix Coordinates

	1-2	2-3	3-4	4-1
1-2	4.914			
2-3	-0.459	4.906		
3-4	-0.864	0.813	5.504	
4-1	0.786	-0.771	-0.976	5.340

Natural Internal Coordinates

	1-2	2-3	3-4
1-2	4.708		
2-3	0.124	4.679	
3-4	0.016	0.124	4.708

Z-Matrix Coordinates

	1-2	2-3	3-4
1-2	4.708		
2-3	0.124	4.679	
3-4	0.016	0.124	4.708

Fig. 4 Force constants for the carbon–carbon bonds in cyclobutane and n-butane for two different sets of non-redundant internal coordinates. All values are given in N cm^{-1}.‡

coordinates, are both true constants with respect to changes in the remaining coordinate system. They have a physical meaning that will be worked out now.

For reasons of simplicity we first assume a set of non-redundant, linearly independent, internal coordinates. Since we expand the energy into forces, we are interested in finding a point $\boldsymbol{Q}$ on the PES that corresponds to a specific gradient $\boldsymbol{G}_q$. Bearing in mind that there are no redundancies present, the linear set of eqn (14) can easily be solved by multiplying from the left by the inverse Hessian $\boldsymbol{H}_q^{-1}$

$$\boldsymbol{Q} = \boldsymbol{H}_q^{-1}\boldsymbol{G}_q \tag{18}$$

Since every possible gradient $\boldsymbol{G}_q$ can be regarded as a linear combination of canonical unit gradients

$$\boldsymbol{G}_q = \begin{pmatrix} G_1 \\ G_2 \\ \vdots \end{pmatrix} \tag{19}$$

$$= G_1\begin{pmatrix} 1 \\ 0 \\ \vdots \end{pmatrix} + G_2\begin{pmatrix} 0 \\ 1 \\ \vdots \end{pmatrix} + \cdots \tag{20}$$

it can easily be seen from eqn (18) that the first column of $\boldsymbol{H}_q^{-1}$ contains the displacements in $\boldsymbol{Q}$ due to a unit force applied on the first coordinate. That means that a unit force $G_1 = 1$ is applied on the first coordinate while all other forces $G_{i\neq 1}$ thereby induced are allowed to relax. For this specific gradient the displacement $\boldsymbol{Q}$ is simply the first column of $\boldsymbol{C}$, but the same interpretation holds true for all other columns of $\boldsymbol{H}_q^{-1}$, respectively. That means the diagonal elements of the compliance matrix $\boldsymbol{C} = \boldsymbol{H}_q^{-1}$ contain the information about the displacement of the corresponding coordinate, if a unit force is applied to it, while—and this is the important point—*all other forces are allowed to relax*. The displacements of all other coordinates are not zero, but they are uniquely defined in the first row of $\boldsymbol{C}$, which are the compliance coupling constants.

If more than one force is applied, it becomes clear from simple matrix algebra that the overall displacement $\boldsymbol{Q}$ is given by adding the columns of $\boldsymbol{C}$ multiplied with the corresponding forces G_i.

A simple example

To further illustrate that point, let us again consider the function $f(x,y) = x^2 + y^2 + xy$ which is plotted in Fig. 5.

If we are looking for the point at which the gradient is 1 with respect to x and 0 with respect to y, we have to solve eqn (18) for this function

$$\begin{pmatrix} x \\ y \end{pmatrix} = \boldsymbol{H}^{-1}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{21}$$

$$\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} \frac{2}{3} & -\frac{1}{3} \\ -\frac{1}{3} & \frac{2}{3} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{2}{3} \\ -\frac{1}{3} \end{pmatrix} \tag{22}$$

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‡ Traditionally force constants are given in the non-SI unit mdyne Å^{-1} which is equivalent to N cm^{-1}. Therefore the commonly used unit for compliance constants is Å mdyne^{-1}, which is equivalent to cm N^{-1}.

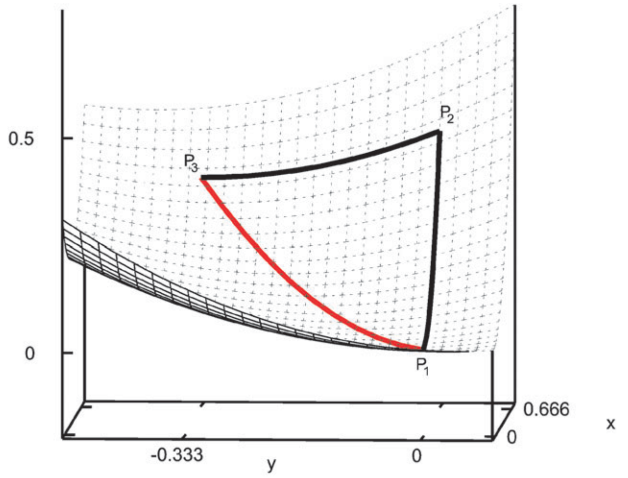


Fig. 5 Plot of the two-dimensional function $f(x,y) = x^2 + y^2 + xy$ (with a coupling term). Point 1 (P_1) reflects the global minimum, point 2 (P_2) a small displacement of the x-coordinate while y is held fixed. Point 3 (P_3) depicts the situation after relaxation with respect to y. The red line represents the minimum energy path (MEP).

The displacement in x and y is given by the first column of $\boldsymbol{H}^{-1}$, where the diagonal element refers to the distortion in x and the off-diagonal term corresponds to the displacement in y. Compliance constants thus represent a relaxed distortion of a molecule and are therefore closely related to the minimum energy path (MEP).[33] The red line in Fig. 5 depicts this. The black line, by contrast, represents the pathway if a force is introduced on x while y remains unchanged, as required by *rigid* force constants.

Redundant internal coordinates

Now one might ask whether eqn (14) can be solved in redundant coordinates, too. Obviously the potential energy of a molecule can be expressed in non-redundant as well as in redundant internal coordinates, and the energy has to be independent of it. Thus one can express the potential energy in terms of compliance matrices $\boldsymbol{C}$ and $\mathbb{C}$, respectively, with $\mathbb{C} = \mathbb{H}_q{}^{+}$ being the Moore–Penrose inverse,[22] because $\mathbb{H}_q$ is singular:

$$\tfrac{1}{2}\boldsymbol{Q}^{\mathrm{T}}\boldsymbol{H}_q\boldsymbol{Q} = \tfrac{1}{2}\mathbb{Q}^{\mathrm{T}}\mathbb{H}_q\mathbb{Q} \tag{23}$$

$$\boldsymbol{Q}^{\mathrm{T}}\boldsymbol{H}_q\boldsymbol{C}\boldsymbol{H}_q\boldsymbol{Q} = \mathbb{Q}^{\mathrm{T}}\mathbb{H}_q\mathbb{C}\mathbb{H}_q\mathbb{Q} \tag{24}$$

Using eqns (10) and (7) it follows that

$$\mathbb{Q}^{\mathrm{T}}\mathbb{H}_q\boldsymbol{A}\boldsymbol{C}\boldsymbol{A}^{\mathrm{T}}\mathbb{H}_q\mathbb{Q} = \mathbb{Q}^{\mathrm{T}}\mathbb{H}_q\mathbb{C}\mathbb{H}_q\mathbb{Q} \tag{25}$$

From this one can infer that

$$\mathbb{C} = \boldsymbol{A}\boldsymbol{C}\boldsymbol{A}^{\mathrm{T}} \tag{26}$$

Unlike the relation between non-redundant and redundant Hessian matrices (*cf.* eqn (10)), the redundant compliance matrix $\mathbb{C}$ is now a linear combination of the non-redundant one. Decius stated[13] that in contrast to the Hessian this matrix $\mathbb{C}$ is uniquely defined. This statement needs to be handled with care. In general it is not true, since $\mathbb{H}_q$ is not uniquely defined (*cf.* eqn (11)). Briefly, Decius however is right if $\boldsymbol{u} = \boldsymbol{E}$ (*cf.* eqn (12)). Bearing this assumption in mind, we can now solve eqn (14) for the redundant set

$$\mathbb{Q} = \mathbb{C}\mathbb{G}_q \tag{27}$$

This solution is not unique, but it is the best solution in a least-squares sense.[34]

Eqn (27) states that the displacement of redundant coordinates due to forces applied is given in a similar manner as in the non-redundant case in eqn (18). That this interpretation holds true in the redundant case is somewhat astounding, but can clearly be seen from the shape of the redundant compliance matrix

$$\mathbb{C} = \boldsymbol{A}\boldsymbol{C}\boldsymbol{A}^{\mathrm{T}} \tag{26}$$

$$= \begin{pmatrix} \boldsymbol{E} \\ \boldsymbol{R} \end{pmatrix} \boldsymbol{C} \begin{pmatrix} \boldsymbol{E} & \boldsymbol{R}^{\mathrm{T}} \end{pmatrix} \tag{28}$$

$$= \begin{pmatrix} \boldsymbol{C} & \boldsymbol{C}\boldsymbol{R}^{\mathrm{T}} \\ \boldsymbol{R}\boldsymbol{C} & \boldsymbol{R}\boldsymbol{C}\boldsymbol{R}^{\mathrm{T}} \end{pmatrix} \tag{29}$$

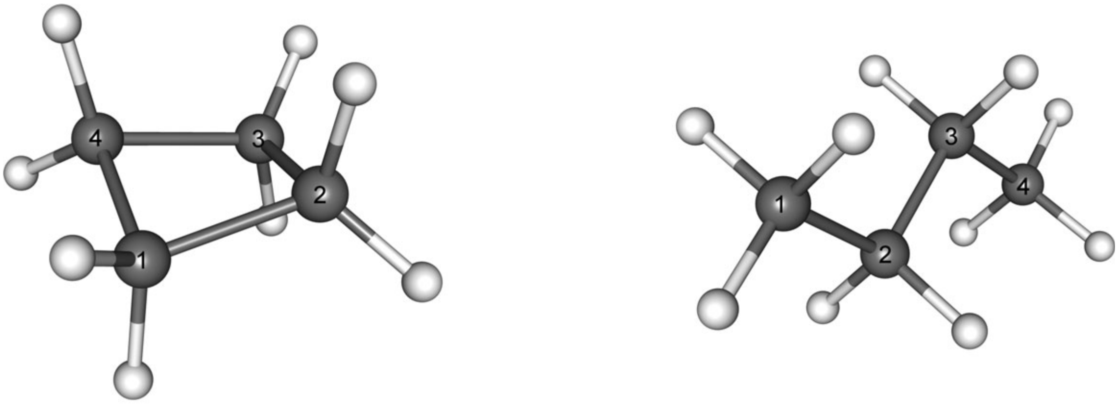
As Jones and Ryan[17] have shown, in contrast to the Hessian, $\boldsymbol{C}$ is a submatrix of $\mathbb{C}$ if the transformation matrix $\boldsymbol{A}$ is defined according to eqn (8). Nevertheless, they made the same assumption as Decius concerning the uniqueness of this matrix.

It is immediately clear that a force applied to a coordinate of the non-redundant subset causes a displacement in the non-redundant coordinates as given by eqn (18). Furthermore the coordinates of the redundant subset are distorted according to eqn (7). Thus the corresponding column of the redundant compliance matrix is given by the same transformation (*cf.* eqn (29)) and additionally expresses the distortion of the redundant coordinates. The interpretation of compliance constants in redundant sets is therefore exactly the same as in the non-redundant case.

During the whole derivation we have been assuming that we know the matrix $\boldsymbol{A}$, that means we have a redundant set of coordinates and a corresponding subset of non-redundant coordinates. This is of course often difficult to accomplish, since the generation of non-redundant sets is a cumbersome task and prone to error. However, the interpretation of redundant compliance constants is straightforward, and there is no need to generate a non-redundant subset, since eqn (27) holds true for any compliance matrix $\mathbb{C}$ that has been transformed from a non-redundant set *via* the matrix $\boldsymbol{A}$ with $\boldsymbol{u} = \boldsymbol{E}$. Because Hessian matrices are usually computed in terms of Cartesian coordinates and have to be transformed to a set of internal coordinates, this condition is automatically satisfied if the well-known Wilson B-Matrix method[35] is used. The proof of this statement, an effective algorithm for the computation of redundant compliance matrices from cartesian Hessians, and a corresponding computer program will be presented in a forthcoming paper.

Discussion

In this last section we would like to show the performance of compliance constants as bond strength descriptors. Please note that in this case a lower value corresponds to a stronger bond.



Natural Internal Coordinates

	1-2	2-3	3-4	4-1
1-2	0.255			
2-3	-0.006	0.255		
3-4	-0.010	-0.006	0.255	
4-1	-0.006	-0.010	-0.006	0.255

Z-Matrix Coordinates

	1-2	2-3	3-4	4-1
1-2	0.255			
2-3	-0.006	0.255		
3-4	-0.010	-0.006	0.255	
4-1	-0.006	-0.010	-0.006	0.255

Natural Internal Coordinates

	1-2	2-3	3-4
1-2	0.230		
2-3	-0.010	0.233	
3-4	0.002	-0.010	0.230

Z-Matrix Coordinates

	1-2	2-3	3-4
1-2	0.230		
2-3	-0.010	0.233	
3-4	0.002	-0.010	0.230

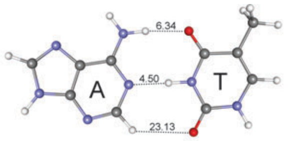
Fig. 6 Compliance constants for the carbon–carbon bonds in cyclobutane and n-butane for two different sets of non-redundant internal coordinates. All values are given in cm N^{-1}.‡

First we return to our cyclobutane/n-butane example. Looking at Fig. 6, the following features of compliance constants as bond strength descriptors are striking. (1) All four C–C bonds in cyclobutane are described as being equal. This holds true for both coordinate systems. (2) The strength of corresponding bonds does not depend on the coordinate system in either molecule. (3) The coupling between coordinates is lower by two orders of magnitude than the diagonal terms throughout. (4) Most importantly, in accordance with the bonding situation in strained ring systems (*vide supra*), by using compliance constants the C–C bond strength in cyclobutane (0.255 cm N^{-1}) is described as being *weaker* than the C–C bonds in n-butane (0.230 cm N^{-1}, 0.233 cm N^{-1}).

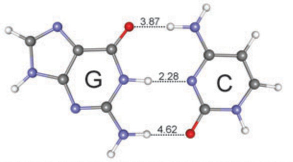
All advantages of compliance constants also apply, of course, to non-covalent interactions. Nevertheless, the concept of using compliance constants as descriptors for weak chemical interactions has been criticized by Pulay and Baker.[2,8] In the final section of one of their papers[2] they state: "…*we conclude that compliance constants (or relaxed force constants) measure the total interaction between fragments, but not individual bonding interactions, and are therefore not useful diagnostics of the strength of weak interatomic interactions*." This statement is primarily based on the fact that there are often non-zero diagonal compliance constants for pairs of atoms that are many Ångstroms apart. As we have shown in this tutorial review, because compliance constants describe the elasticity, a force between any two atoms A and B in a polyatomic system can, of course, lead to a relatively small displacement (high relaxed force constant) even if these two atoms are many Ångstroms apart. However, this is a true physical phenomenon, since the compliance constants reflect that the work has to be done against the sum of many through-bond and through-space interactions. Simply put, the work has to be done against the potential of all other atoms around A and B, which is also true if A and B are not bonded in a Lewis sense. One should of course not regard a low compliance constant between atoms that are several Ångstroms apart as a chemical bond. Nevertheless, a high value of a compliance constant can sufficiently justify that a chemical bond (covalent, hydrogen bond, *etc.*) is weak, and therefore compliance constants are indeed useful for the description of the bonding situation between weakly bound fragments.

Fig. 7 summarizes our recent results on differences in individual hydrogen bond strengths in AT and GC base pairs (left column). Using compliance constants we have shown *e.g.* that the central interresidue N–H···N hydrogen bond between guanine and cytosine is by far the strongest hydrogen bond in both Watson–Crick base pairs.[7] Returning to the critique by Pulay and Baker concerning the utility of compliance constants as non-covalent bond strength descriptors: how should one construe the large C–H···O compliance value (23.13 cm N^{-1}) for AT in comparison with the considerably lower N–H···N or N–H···O values? This large compliance constant of course reflects the weaker C–H···O hydrogen bond, that means a strictly local property and not a somehow delocalised "*total interaction between fragments*."

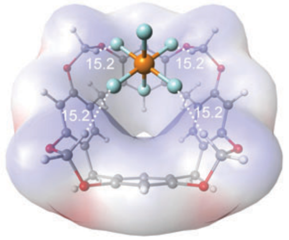
Furthermore we were able for example to clearly discriminate between C–H···F hydrogen bonds and anion···π



(a) Adenine-thymine base pair with compliance constants for the hydrogen bonds



(b) Guanine-cytosine base pair with compliance constants for the hydrogen bonds



(c) PF_6-anion recognition by a resorcinarene receptor. The electrostatic potential is plotted on the van der Waals surface (translucent)

Fig. 7 Some recent applications of compliance constants used as bond strength descriptors for non-covalent interactions.[7,36] All numerical values are given in cm N^{-1}.‡

interactions at work during the recognition of anions by resorcinarene receptors (right column).[36] To the best of our knowledge this is the first direct quantification of this type of weak, non-covalent C–H···anion interaction.

Summary

Rigid force constants answer the question of which force has to be applied against a specific internal coordinate in order to achieve a given displacement (unit N cm^{-1}), with the restriction that all other coordinates remain unchanged. Compliance constants, on the other hand, address the question of which displacement is caused by a given force on a single coordinate (unit cm N^{-1}), while all other forces thereby introduced are allowed to relax. The displacements of all other coordinates caused by these forces are given by the compliance coupling constants, which are the off-diagonal terms of the compliance matrix. If—as it is frequently done in force field studies—*rigid* force constants are employed for the description of individual bond strength, the bonding situation is always described as being too strong since the values of rigid force constants are necessarily higher than the values of the corresponding relaxed force constants. Relaxed force constants (the reciprocal of individual compliance constants) measure the force required to distort a coordinate by a unit amount while allowing all other coordinates to relax. The use of individual inverted compliance constants as relaxed force constants in cases where stretching terms of empirical force fields are missing might therefore lead to more reliable results in *e.g.* molecular dynamics simulations.

In sum, due to their properties, the diagonal terms of the compliance matrix describe a more local property of a chemical bond than rigid force constants do. It is likely that compliance constants are therefore much more transferable than rigid force constants, since they do not depend on the choice of the coordinates. Their *transferability* as *e.g.* force field parameters is however limited to similar chemical environments and should of course not be overstrained. Nevertheless, the values of compliance constants are *unique* for any molecule, which means that their *comparability* is indeed unlimited. This property makes them useful for answering questions related to the stiffness or compliance of covalent and non-covalent chemical bonds. Since the concept is independent of the method used for the description of a molecule provided the matrix of energy second derivatives is available, it is thus generally applicable to any quantum chemical or empirical description of any chemical system.

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