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How Strong Is the Gallium≡Gallium Triple Bond? Theoretical Compliance Matrices as a Probe for Intrinsic Bond Strengths

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Abstract: The inverted matrix of force constants (B3LYP/6-311++G(3df,3pd) level of theory) has been used to estimate the intrinsic gallium−gallium bond strengths of several model compounds with different formal gallium−gallium bond orders. The gallium−gallium bond strength (0.87 aJ/Å^2) in a "gallyne" model compound [H−Ga−Ga−H]Na$_2$ (C_{2h}-symmetry) has been calculated to be weaker than the gallium−gallium double bond (1.20 aJ/Å^2) in [H$_2$Ga=GaH$_2$]Na$_2$.

Although quantum mechanical calculations of molecular structures and properties have become an essential part of chemistry, the study of specific bond strengths in a polyatomic molecule still represents an interesting challenge. For example, modern quantum chemical methods, which use the MO approximation, have achieved a high degree of accuracy in calculating the energy and its derivatives for molecular systems involving up to thousand basis functions.[1,2] However, the higher the quality of the molecular orbital wave function, the less their clarity. An interpretation in terms of chemical concepts sometimes even becomes more difficult. There are a number of procedures, which analyze the calculated wave function or the charge density to give evidence on local molecular properties.[3−7] Nevertheless, it is well-known that the molecular orbital wave function is invariant under orbital transformation, which means there is no unique set of localized molecular orbitals aside from the set of the canonical delocalized molecular orbitals.[8] Furthermore, different analysis or localization methods may possibly lead to different chemical interpretations.

Therefore, we would like to point out that there exists a completely different approach to localized diatomic data, namely the calculation of the complete and inverted Hessian matrix.[9]

What is the force needed to distort a specific bond in a molecule, while all other bonds stay at their equilibrium distance?[10] The force constants F_{ij} in a polyatomic system are defined as the partial second derivatives of the molecular energy E in terms of the nuclear coordinates q.[11] Thus, the force constants represent the answer to this specific question. In other words, they give a qualitative description of the sum of all interactions between any two atoms (bonded or not) in a molecule.

$$F_{ij} = \left(\frac{\partial^2 E}{\partial q_i \partial q_j}\right)_0 \qquad (1)$$

In contrast to some of the population analysis of the wave function, which rely on the explicit assignment of the basis functions to atoms, the complete matrix of force constants avoids any arbitrary partitioning of the Hilbert space spanned by the basis set. Additionally, unlike bond dissociation energies, the elements of the complete Hessian matrix do not depend on the stability of the fragments, which emerge from the bond fission. The force constants measure the intrinsic bond strength. Nevertheless, the Cartesian force constants have to be transformed to a complete and nonredundant set of internal coordinates in order to gain any chemical implication. This transformation can be settled by routines that were developed in Peter Pulay's group.[12] As Pulay and Cioslowski pointed out, even force constants expressed in a set of internal coordinates, are not invariant to the choice of the individual coordinates.[13,14] Thus, different choices of internal coordinates lead to different values of a specific bond strength. This numerical ambiguity of the internal force constants has always hampered their application.[15−18]

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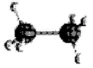
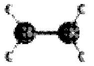
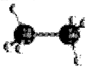
Table 1: Calculated (B3LYP/6-311++G(3df,3pd)) Diagonal Elements of the Inverted Hessian Matrix Corresponding to the C−C Bond

Molecule			
Formula	H_3CCH_3	H_2CCH_2	HCCH
Symmetry	D_{3d}	D_{2h}	$D_{\infty h}$
Nimag [a]	0	0	0
X-X-Distance [Å]	1.527	1.324	1.196
F_{ij}[aJ/Å^2] [b]	4.025	9.606	17.331

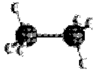
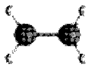
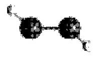
[a] The number of imaginary frequencies. [b] The diagonal elements of the inverted force constant matrix are given as the reciprocal values for comparability reasons.

Table 2: Calculated (B3LYP/6-311++G(3df,3pd)) Diagonal Elements of the Inverted Hessian Matrix Corresponding to the Si−Si Bond

Molecule			
Formula	H_3SiSiH_3	H_2SiSiH_2	HsiSiH
Symmetry	D_{3d}	C_{2h}	C_{2h}
Nimag [a]	0	0	0
X-X-Distance [Å]	2.348	2.160	2.010
F_{ij}[aJ/Å^2] [b]	1.619	2.174	2.711

[a] The number of imaginary frequencies. [b] The diagonal elements of the inverted force constant matrix are given as the reciprocal values for comparability reasons.

Table 3: Calculated (B3LYP/6-311++G(3df,3pd)) Diagonal Elements of the Inverted Hessian Matrix Corresponding to the Ga−Ga Bond

Molecule				
Formula	$[H_3GaGaH_3]^{2-}$	$[H_2GaGaH_2]^{2-}$	$[HGaGaH]^{2-}$	$[HGaGaH]^{2-}$
Symmetry	D_{3d}	D_{2h}	$D_{\infty h}$	C_{2h}
Nimag [a]	0	0	2	0
X-X-Distance [Å]	2.648	2.415	2.213	2.472
F_{ij}[aJ/Å^2] [b]	0.460	1.306	2.450	0.748

[a] The number of imaginary frequencies. [b] The diagonal elements of the inverted force constant matrix are given as the reciprocal values for comparability reasons.

To eliminate this ambiguity, we suggest the use of the inverted matrix of force constants, which was introduced as early as 1947 by Taylor and Pitzer.[19] Decius proved in 1962, that the inverse matrix of force constants (compliance matrix) is indeed invariant to the internal coordinates using the complete set of experimentally determined force constants in NO_2 and $GeCl_4$.[20]

Together with the possibility of modern computer systems and programs to efficiently calculate the complete matrix of energy second derivatives for large molecular systems using correlated wave functions, the use of the inverted Hessian matrix could make the unequivocal calculation of bond strengths in polyatomic molecules a straightforward task.[21,22]

In the following example, we have applied the procedure of the inverted theoretical Hessian matrix to a question, which recently led to a discussion in the literature.[23−25] The point was, whether the gallium−gallium bond in $Na_2[Mes^*{}_2C_6H_3{-}GaGa{-}C_6H_3Mes^*{}_2]$ (Mes* = 2,4,6-*i*-$Pr_3C_6H_2$) is the first experimentally proven Ga≡Ga triple bond (Gallyne) or not.[26] Whereas the original paper of Su et al. uses essentially the experimental bond length of the gallium−gallium bond as a criterion for their interpretation as a triple bond, following papers additionally made use of different population analysis and localization procedures to corroborate this view.[27−29] Nevertheless, the calculated bond order of the gallium−gallium bond assumes values between 2.36 (WBI) and 3.02 (NPA) for the C_{2h}-symmetric minimum of the $[H{-}Ga{-}Ga{-}H]^{2-}$ dianion[27] and values between 2.02 (WBI) and 2.79 (NPA) in a recent study of a more realistic model compound.[29]

On the other hand, the groups of Cotton and Power put forward that, among other things, the reason for the short gallium−gallium bond in $Na_2[Mes^*{}_2C_6H_3{-}GaGa{-}C_6H_3Mes^*{}_2]$ is due to the interaction of the phenyl substituents with the sodium ions. They suggest a bond order lower than 3.[30−32]

To calculate the bond strength via the compliance matrix we initially computed the full matrix of energy second derivatives (B3LYP/6-311++G3df,3pd) for the optimized geometries for each element of the homologous series $[Ga_2H_2]^{2-}$, $[Ga_2H_4]^{2-}$, and $[Ga_2H_6]^{2-}$ on behalf of model systems for Ga≡Ga triple, Ga=Ga double, and Ga−Ga-single bonds.[33] We transformed the original Cartesian force constants into a nonredundant set of internal coordinates using an algorithm developed in Pulay's group.[12]

$$\mathbf{F_2} = \mathbf{U^T F_1 U} \tag{2}$$

In eq 2, **U** is the transformation matrix which yields the force constants $\mathbf{F_1}$ (expressed in coordinate system 1) from $\mathbf{F_2}$ (expressed in coordinate system 2). **U** is given by eq 3, where $\mathbf{B_1}$ and $\mathbf{B_2}$ are the **B** matrices[11] corresponding to the two coordinate systems.

$$\mathbf{U} = \mathbf{B_2B_1T}\,(\mathbf{B_1B_1T})^{-1} \tag{3}$$

In a further step, we used a Gauss−Jordan elimination technique

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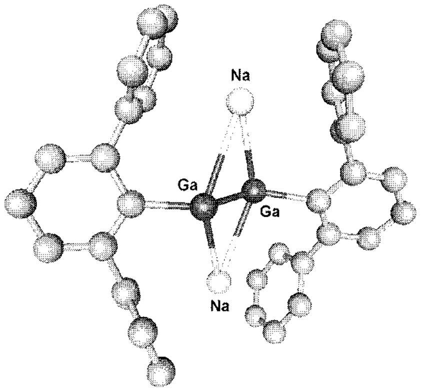

Figure 1. Part of the recently synthesized compound $Na_2[Mes^*{}_2C_6H_3-GaGa-C_6H_3Mes^*{}_2]$ ($Mes^* = 2,4,6\text{-}i\text{-}Pr_3C_6H_2$). The local symmetry of the R−Ga−Ga−R fragment is C_{2h}.

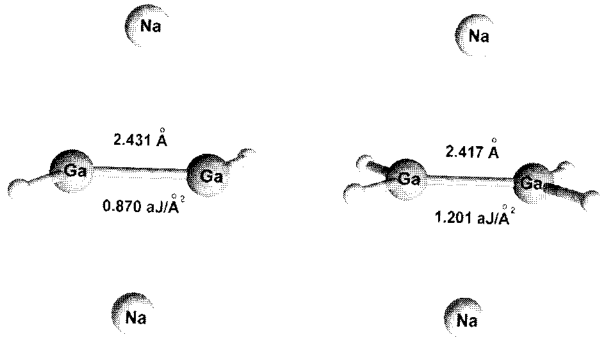

Figure 2. Ga−Ga distances and the accompanying reciprocal values of the elements of the inverted Hessian matrix (B3LYP/6-311++G-(3df,3pd) in $(HGa-GaH)(Na)_2$ and $(H_2Ga-GaH_2)(Na)_2$.

to produce the inverse of the Hessian matrix expressed in internal coordinates.[34]

In the following, the diagonal elements of this inverted Hessian matrix in [Å^2/aJ] are quoted as their reciprocal values in [aJ/Å^2] for the sake of clarity and comparability.

The results for the gallium compounds are compiled in Table 3 in addition to the values of the analogous carbon and silicon series in Tables 1 and 2. While there is roughly a doubling of the value for the C−C bond (see Table 1) in the carbon series (ethane: 4.02 aJ/Å^2, ethene: 9.61 aJ/Å^2, ethyne: 17.33 aJ/Å^2) going from each bond order to the next higher one, this increasing tendency is definitely weakened in the silicon series (see Table 2) Si_2H_6 (1.62 aJ/Å^2), Si_2H_4 (2.17 aJ/Å^2), and Si_2H_2 (2.71 aJ/Å^2). These data reflect the well-known trend of Si−Si multiple bonds being considerably weaker when compared with the analogous carbon bonds.[35,36]

Now, we focus on the gallium compounds. Our computed geometries confirm the results of earlier studies on the whole.[27−32] However, for the trans-bent $[H-Ga-Ga-H\ ]^{2-}$ structure, the analysis of the inverted matrix of force constants is not in line with an interpretation as a triple bond. Our calculated reciprocal diagonal elements (0.46 aJ/Å^2, 1.31 aJ/Å^2, 2.45 aJ/Å^2) for gallium compounds (see Table 3) with prototypes of formal Ga−Ga single, Ga═Ga double, and Ga≡Ga triple bonds (meaning the linear $[H-Ga-Ga-H\ ]^{2-}$ structure) indeed correlate with the formal number of bonds. The linear arrangement of the $[H-Ga-Ga-H]^{2-}$ dianion certainly represents a stationary point on the hyper surface. However, a further analysis of the Hessian matrix shows that it is a second-order saddle point. On the other hand, in the case of the C_{2h}-symmetric minimum, an arrangement, which is to be found in the X-ray structure of the real compound (see Figure 1), the value is 0.75 aJ/Å^2. This is just between the strength of the prototypes of a Ga−Ga single (0.46 aJ/Å^2) and a Ga═Ga double bond (1.30 aJ/Å^2). The interpretation as a triple bond is therefore at least questionable and the definition of what constitutes a multiple bond may be stretched too far in this case.[37] Of course, all dianions studied so far represent only one part of the real compound. The computed wave functions of those charged systems tend to be metastable with respect to electron elimination or internal constraints.[38,39] To mimic the complete systems we have additionally computed the inverted Hessian matrix of the neutral compounds $(HGa-GaH)(Na)_2$ and $(H_2Ga{=}GaH_2)(Na)_2$ (see Figure 2). For this type of coordination the choice of the internal coordinates is not trivial and the numerical value of the "real space" force constant of the Ga−Ga bond is not invariant to the coordinate system.[40] The inclusion of the two sodium ions led to an increase of the corresponding reciprocal value of the diagonal element in the inverted Hessian matrix from 0.748 aJ/Å^2 to 0.870 aJ/Å^2 in $(HGa{=}GaH)(Na)_2$. Nevertheless, this value is still below the computed 1.201 aJ/Å^2 of the Ga═Ga double bond in the D_{2h}-symmetric $(H_2Ga{=}GaH_2)(Na)_2$ system (see Figure 2).

Our calculations of the inverse Hessian Matrix for the model systems $(HGa-GaH)(Na])_2$ and $(H_2Ga{=}GaH_2)(Na)_2$ reveal a weak interaction of the two gallium atoms and seem to be in agreement with a gallium−gallium bond order between one and two in $(HGa-GaH)(Na])_2$. The short gallium−gallium distance in $Na_2[Mes^*{}_2C_6H_3-GaGa-C_6H_3Mes^*{}_2]$ is an effect of the small Ga−Ga force constant.

We believe the procedure of the inversion of the Hessian matrix offers direct access to localized diatomic data in poyatomic molecules. Contrary to "real space" force constants, which are not invariant to the choice of the used coordinate system, the elements of the inverted Hessian matrix are able to provide an unambiguous measurement of the interaction strength between any pair of atoms in a polyatomic molecule.

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