# A Theorem for Mean Square Amplitudes, Compliants, and Force Constants

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In this note some deductions from Schwarz' inequality [1] are pointed out. The inequality is used to prove a theorem about mean-square amplitudes and compliants in the theory of molecular vibrations. Some remarks are also made about a similar theorem for force constants.

Let $r_i$ and $r_j$ be arbitrary displacement coordinates. According to Schwarz' inequality

$$\frac{|\langle r_i r_j\rangle|}{\sqrt{\langle r_i^2\rangle\langle r_j^2\rangle}} \leq 1 \tag{1}$$

or

$$\frac{|\sigma_{ij}|}{\sqrt{\sigma_{ii}\ \sigma_{jj}}} \leq 1 \tag{2}$$

where $\sigma_{ii}=\langle r_i^2\rangle$, $\sigma_{jj}=\langle r_j^2\rangle$ and $\sigma_{ij}=\langle r_i r_j\rangle$ are the appropriate mean-square amplitude quantities.[2]

The inequality must also hold in the classical limit of $T\rightarrow\infty$.[3,2] Since $\sigma_{ij}\rightarrow kTn_{ij}$, one obtains for the appropriate compliants:[4,2]

$$\frac{|n_{ij}|}{\sqrt{n_{ii}\ n_{jj}}} \leq 1 \tag{3}$$

Similar relations may be deduced for force constants. Take for instance a two-dimensional F-matrix block in terms of independent coordinates. The above inequality (3) necessarily holds for the compliants $n_{ii}=N_{11}=F_{22}/\varDelta$, $n_{jj}=N_{22}=F_{11}/\varDelta$ and $n_{ij}=N_{12}=-F_{12}/\varDelta$, where $\varDelta=F_{11}\times F_{22}-F_{12}^2$. Hence one obtains immediately

$$\frac{|F_{12}|}{\sqrt{F_{11}\ F_{22}}} \leq 1 \tag{4}$$

for the corresponding force constants. This is a special case of a theorem of force constants, which is deducible from the mathematical properties of the F matrix, studied in details by Fadini.[5,6] For instance, from the nonsingularity theorem of F as the matrix of potential energy[6] (*Satz* 4), *i.e.* $\varDelta>0$, it is found at once for a two-dimensional block

$$\frac{|F_{12}|}{\sqrt{F_{11}F_{22}}} < 1 \tag{5}$$

This is even an improvement of eqn. (4) because of the lack of the equality sign. It follows from eqn. (5)

$$\frac{|N_{12}|}{\sqrt{N_{11}N_{22}}} < 1 \tag{6}$$

without sign of equality. It is likely possible to deduce more general theorems of the type (3) and (2) about compliants and mean-square amplitude quantities with the aid of the developed properties of the F matrix.[6] But the interesting feature of the present proof of eqns. (1)–(3) is its simplicity and direct utilization of the property that $\sigma_{ij}$ are mean values.

Finally it may be mentioned that the here treated theorems all reflect familiar features known from experience of analyzing molecular vibrations.

1. Margenau, H. and Murphy, G. M. *The Mathematics of Physics and Chemistry*, D. van Nostrand, 2nd Ed., New York 1956, p. 134.
2. Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo, and Elsevier, Amsterdam 1968.
3. Decius, J. C. *J. Chem. Phys.* **21** (1953) 1121.
4. Decius, J. C. *J. Chem. Phys.* **38** (1963) 241.
5. Fadini, A. *9th European Congress on Molecular Spectroscopy, Madrid, Spain, September 10–15*, Abstract of Papers (1967), p. 24.
6. Fadini, A. *Arbeitsbericht des Instituts für theoretische physikalische Chemie der Universität Stuttgart* **13** (1969) 41.

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