

# Ab initio study of the Pugh criterion for FCC lattices

Klaas Luyckx and William Wenborn

*Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium*

Seán Mooney

*School of Physics, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland*

(Dated: December 7, 2024)

The ability for materials to deform, eg. ductility is critical in engineering and material science. A straightforward way to determine if a material is ductile or not is the Pugh criterion where the bulk-, shear- and Young-modulus are brought into relation. To determine these properties, an *ab initio* study using density functional theory (DFT) is employed using the Quantum Espresso software. Both the stress-tensor formalism, and the Birch Murnaghan equation of state to determine the bulk modulus is used. Our study includes elements such as Ac, Ca, Al, Ce, La, Mg, Ni, Pt, Po, Se, Si, and Th. These calculations allowed us to study ductility, even for hypothetical phases that cannot be studied experimentally.

## I. INTRODUCTION

When subjected to a tensile test, materials will generally exhibit two types of behaviors. Some materials elongate and become narrower in the middle before eventually breaking at their thinnest point; these materials are classified as ductile. Other materials break with almost no elongation, these are referred to as non-ductile materials. The extent of the deformation before breaking can be taken as a measure of ductility.

In his 1954 paper, S.F.Pugh proposed that the ductility of a material can be inferred from the much simpler elastic moduli, allowing the ductility of a material to be determined without resorting to elaborate tensile tests[1]. The Pugh criterion states that a metal is expected to be ductile if  $B/G > 1.75$  or  $\nu > 0.26$ , where  $\nu$  is Poisson's ratio,  $B$  the bulk modulus and  $G$  the shear modulus.

This research utilises DFT to explore the Pugh criterion for an array of unary face-centered cubic (FCC) crystals. Experimental results are limited to elements that occur naturally in fcc phase, but DFT enables us to explore elements across the periodic table and investigate the physical mechanisms underlying ductility.

## II. METHODOLOGY

All calculations were performed using the Quantum-Espresso (QE) package [2–4], versions 7.3. For all materials, an ultrasoft pseudopotential (USPP) was used. For this pseudopotential, a Generalized Gradient Approximation + Spin-Orbit coupling (GGA+SO) for the exchange correlation energy was used. For the exchange-correlation (XC) functional, the modified Perdew–Burke–Ernzerhof (PBESOL), which has been optimized for solids, had been used for Ca, Al, Pt, Se, Si, Ni, Mg and Po [5]. Due to this modified PBESOL not being available for all elements, a PBE functional was used from the QE pseudopotential database [6] for Th, Ac, Ca and La.

The motivation behind the use of spin-orbit coupling in the pseudopotential is due to the high number of lanthanides and actinides in the elemental table. For consistency, this was then also applied to all other elements.

The choice of the elements used in this work may seem arbitrary, but these elements were picked specifically such that at least two elements are within a certain property. These properties are: Orbital type, elemental class (semi-metal, poor metal, etc), proton count and valence electrons (Except for Nickel and Platinum which have respectively 10 and 1 valence electron(s)). Two are chosen such that correlation coefficients between these properties (+some more) and the elastic properties can be calculated. This is then used to predict the elastic properties for other elements in the table.

As is common in density functional theory (DFT) calculations, the first task was to carry out convergence testing for all systems of interest to determine appropriate computational parameters. Specifically, the parameters were converged with respect to the hydrostatic pressure to ensure the accuracy of subsequent calculations. First, the size of the k-mesh was increased incrementally until the variation of the hydrostatic pressure became minimal. Similarly, the kinetic energy cutoffs of the wavefunction ( $ecutwfc$ ) and charge density ( $ecutrho$ ) were converged. Based on the convergence testing results, a standard set of parameters was decided which works for all different elements and is used in all future calculations. The k-mesh size is set to  $9 \times 9 \times 9$ , while the kinetic energy cutoff values are defined as  $ecutwfc = 100\text{Ry}$  and  $ecutrho = 400\text{Ry}$ .

Following this parameter optimization, a relaxation calculation was performed on all systems to find the ground state geometry. As all crystals of interest are simple cubic FCC structures, the only degree of freedom of the undeformed geometry is the lattice parameter. Next, a Birch-Murnaghan (BM) equation of state fit was applied to all systems. The purpose of this was two-fold. Firstly, a Birch-Murnaghan fit returns the bulk modulus

of the crystal in question. And secondly, it serves as a means of geometry optimization which gives an extra way to check the validity of the lattice parameter.

The final set of DFT calculations conducted was to determine the elastic constants of the crystals. The shear as well as the bulk modulus were computed from the elastic constants. Bulk moduli calculated via the Birch-Murnaghan fit and through the stress tensor method were compared to check for internal consistency of the calculations. The elastic constants were determined using the stress tensor method, where a set of deformations were applied to each crystal and the elastic constants determined by the matrix equation,

$$C = \Sigma E^{-1},$$

where  $\Sigma$  and  $E$  are the stress and strain tensors, respectively, expressed in Voigt notation.

The applied stress tensors were of the following form

$$F_1 = \begin{pmatrix} 1+\delta_1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, F_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1+\delta_1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, F_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \delta_2 \\ 0 & 0 & 1+\delta_1 \end{pmatrix},$$

$$F_4 = \begin{pmatrix} 1 & \delta_2 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, F_5 = \begin{pmatrix} 1 & 0 & \delta_2 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, F_6 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \delta_2 \\ 0 & 0 & 1 \end{pmatrix}$$

For the values of  $\delta_1$  and  $\delta_2$ , following combinations were used  $(\delta_1, \delta_2) = \{(0.01, 0.01), (0.03, 0.01), (0.01, 0.03), (0.03, 0.03)\}$ .

In every case, this result was averaged with the negative  $\delta$  values to decrease computational errors. After this, the resulting elastic constants were averaged.

The elastic constants are expressed in this 6x6  $C$ -matrix, which in theory has only three independent contributions for a cubic crystal. The theoretical matrix has following form

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix}$$

From these elastic constants, the bulk modulus and shear modulus were calculated as  $B = \frac{C_{11}+2C_{12}}{3}$  and  $G = \frac{C_{11}-C_{12}+3C_{44}}{5}$ . From these moduli, the Poisson's ratio was calculated as  $\nu = \frac{3B-2G}{2(3B+G)}$ .

When the bulk modulus, shear modulus and Poisson's ratio were calculated, the Pugh criterion could be evaluated.

### III. RESULTS AND DISCUSSION

The equilibrium volume is calculated by conducting a vc-relax calculation, an automatic optimisation procedure available in QE. The results are shown in table I and

compared with different computational and experimental sources. The first source employs Quantum-Espresso 7.0 using the PBE-GGA methods and Projector Augmented Wave method (*PAW*) for the electron-ion interactions [7]. The second source uses VASP 5.2.2 with PBE-GGA-*PAW* pseudopotentials [8]. The difference between the calculated result and the result found in literature is expressed as  $\Delta = \frac{V_1-V_2}{(V_1+V_2)/2} \cdot 100\%$ . For most elements, the calculated  $V_0$  is in good agreement with the values in literature. A notable difference between the computed results and the reference papers is found for Cerium. This can be explained by how the electrons are treated in the pseudopotential, where in this paper the  $4f$ -electrons are in the 'core' state. Those from the sources, [7, 8], use a *PAW* pseudopotential where the  $4f$ -electrons are considered as valance electrons. This is also in agreement with other sources[9]. Furthermore, a somewhat larger difference is found for the Lanthanides (La, Ce), possibly because of the same reasoning as before.

el.	$V_0$	[7] $V_0$	[7] $\Delta$	[8] $V_0$	[8] $\Delta$	Exp. $V_0$	$\Delta$
Mg	22.76	23.13	-1.63	23.03	1.17		
Al	16.25	16.49	-1.49	16.47	-1.41	16.50 <sup>a</sup>	-1.59
Si	14.31	14.49	-1.22			13.96 <sup>b</sup>	2.34
Ca	40.69	42.19	-3.62	42.17	-3.57	43.34 <sup>c</sup>	-6.31
Ni	10.32	10.84	-5.04	10.85	4.88	10.87 <sup>a</sup>	-0.28
Se	19.08	20.38	-6.58				
La	33.10	36.95	10.98	37.10	11.40	35.20 <sup>e</sup>	-6.15
Ce	37.69	26.52	34.78	26.1	36.34	34.39 <sup>e</sup>	9.17
Pt	15.04	15.66	-4.02	15.67	-4.10	15.09 <sup>c</sup>	-0.33
Po	33.51	32.56	2.89				
Ac	45.46	45.55	-0.19	45.37	0.20	37.45 <sup>c</sup>	19.32
Th	32.63	32.18	1.39	32.07	1.73	32.86 <sup>c</sup>	-0.7

<sup>a</sup> [10] <sup>b</sup> [11, 12] <sup>c</sup> [13] <sup>d</sup> [14] <sup>e</sup> [15]

Table I. Equilibrium volumes  $V_0$  in  $\text{\AA}^3$  and differences  $\Delta$  in % between two other computational methods and experimental results.

Next, the Birch-Murnaghan equation of state is fit for 40 different volumes around the equilibrium volume of the crystal in steps of 1%. From this, the bulk modulus is calculated. The results are shown in table II, where they are compared with different computational and experimental sources. Again, the difference between the calculated result and the result found in literature is expressed as  $\Delta = \frac{B_1-B_2}{(B_1+B_2)/2} \cdot 100\%$ . For this, there is a larger difference for materials in group 4 (Ni, Ce) and group 6 (Ce, Pt, Po). Possibly, the BM-fit with this pseudopotential isn't the best choice for these elements. For the other elements, the results are in agreement with literature. Furthermore, the elastic constants were calculated using the stress tensor method with different deformations. Table III shows the results for the elastic constants, as well as the calculated bulk and shear modulus. The bulk modulus is compared with the result from the BM fit. Here we see the results are overall in agreement, which

means the calculations are internally consistent.

el.	$B_0$	[7] $B_0$	[7] $\Delta$	[8] $B_0$	[8] $\Delta$	Exp. $B_0$	$\Delta$
Mg	36.1	35.12	2.7	36.05	0.14	45 <sup>a</sup>	-21.9
Al	81.9	77.51	5.5	76.90	6.3	76 <sup>a</sup>	7.5
Si	89.9	82.85	8.2			100 <sup>a</sup>	-10.6
Ca	17.1	17.37	-1.6	16.82	1.7	17 <sup>a</sup>	0.6
Ni	232.6	202.29	13.0	197.87	14.93	180 <sup>a</sup>	25.5
Se	84.9	69.42	20.1			83 <sup>a</sup>	2.3
La	26.0	24.55	5.7	24.83	4.6	27 <sup>b</sup>	-3.7
Ce	29.9	38.12	-24.2	37.65	-22.9	22 <sup>b</sup>	30.4
Pt	284.1	247.47	13.8	246.74	14.1	230 <sup>a</sup>	21.0
Po	36.4	49.64	-30.8				
Ac	25.6	23.89	6.9	21.63	16.8		
Th	56.5	55.03	2.6	55.28	2.2	54 <sup>a</sup>	4.5

<sup>a</sup> [16–18] <sup>b</sup> [17]

Table II. Bulk moduli  $B$  in  $GPa$  determined with a BM fit of the FCC structures, compared between two computational methods and experimental results with differences  $\Delta$  in %.

el.	$C_{11}$	$C_{12}$	$C_{44}$	$\epsilon$ $B$	BM $B$	$\Delta$	$G$
Mg	42.7	30.0	29.2	34.2	36.1	-5.41	20.0
Al	59.4	93.1	-59.7	81.8	81.9	-0.12	-42.5
Si	298.2	-20.0	157.0	86.1	89.9	-4.32	157.8
Ca	18.7	16.3	8.1	17.1	17.1	0.00	5.3
Ni	276.6	172.3	135.3	207.1	232.6	-11.60	102.0
Se	132.9	60.3	60.3	84.5	84.9	-0.47	50.7
La	39.2	22.2	10.6	27.9	26.0	7.05	9.8
Ce	43.3	24.6	23.0	30.9	29.9	3.29	17.6
Pt	363.3	248.1	68.4	286.5	284.1	0.84	64.1
Po	6.6	55.7	-18.6	39.2	36.4	7.41	-21.0
Ac	40.4	17.6	22.4	25.2	25.6	-1.57	18.0
Th	90.3	44.1	54.1	59.5	56.5	5.17	41.7

Table III. Elastic constants determined by the stress tensor method  $\epsilon$  in  $GPa$  and the difference  $\Delta$ , in %, between the bulk modulus of the stress tensor method and the BM fit.

Finally, the Pugh criterion is evaluated. To do this, the values for the bulk modulus and shear modulus, calculated from the elastic constants, are used to calculate  $B/G$  and Poisson's ratio  $\nu$ , this is displayed in table IV. As discussed before, the Pugh criterion states that a material is expected to be ductile if  $B/G > 1.75$  or  $\nu > 0.26$ . By this criterion, the ductility of the different materials is determined. For Aluminum and Polonium the value of  $B/G$  is negative since these materials have a negative shear modulus in the fcc structure. Materials with a negative shear modulus are not mechanically stable unless some specific constraints are met. In this case the Pugh criterion can't be evaluated.

To answer the question if there is the possibility to predict the elastic properties of materials across the table, a

element	$B$ ( $GPa$ )	$G$ ( $GPa$ )	$B/G$	$\nu$	Ductile
Mg	34.2	20.0	1.71	0.255	No
Al	81.8	-42.5	-1.92	0.814	/
Si	86.1	157.8	0.55	-0.069	No
Ca	17.1	5.3	3.20	0.358	Yes
Ni	207.1	102.0	2.03	0.288	No
Se	84.5	50.7	1.67	0.250	No
La	27.9	9.8	2.85	0.343	Yes
Ce	30.9	17.6	1.76	0.261	Yes
Pt	286.5	64.1	4.47	0.396	Yes
Po	39.2	-21.0	-1.87	0.825	/
Ac	25.2	18.0	1.40	0.212	No
Th	59.5	41.7	1.43	0.216	No

Table IV. Evaluation of the Pugh criterion

careful analysis of the correlation between different properties and their obtained values has to be made. In this work, the choice was made to use both categorical and continuous properties to evaluate the correlation coefficients. For the categorical properties, the orbitals ( $l$ ), type (semi-metal, Actinides, etc) and period was used. Due to it being categorical, and the elastic properties being continuous, a correlation ratio (or  $\eta^2$ -coefficient [19]) is calculated for these.  $\eta^2$  itself has values between 0 and 1, if equal to 1, there is association with the values and their categories, if 0 then there is no association.

For the (semi-)continuous variables the number of protons ( $P$ ), valence electrons, unit cell volume ( $V_0$ ), molar mass ( $M$ ) and electro-negativity ( $\chi$ ) are taken. In an ideal case, one wants to have a linear correlation between these values. Therefore, the Pearson correlation coefficient ( $r$ ) is used [19]. However, it is important to note that Pearson's  $r$  assumes the data to be linear and quite sensitive to outliers. Therefore, also the Kendall rank coefficient [20] ( $\tau$ ) is evaluated, since this does not assume linear data and is not sensitive to outliers.

Table V shows that categorizing the element by its type is a good first start to determine in what kind of range these moduli will lie in. Especially the bulk modulus and Poisson ratio have high correlations. The same cannot be said for the orbital type. Apart from the bulk modulus and  $B/G$  ratio, it is not easy to determine the right properties with the orbital type alone. Of course, since the coefficient for  $G$  is so low, it is natural to assume that the coefficient for the  $B/G$  ratio will therefore also be low. For the period, it is clear that the amount of occupied shells an element, has no big impact on the elastic properties. This becomes clear when realizing that elasticity is determined by the bonding between atoms, since occupied shells do not directly contribute to bonding between atoms (in ideal circumstances), there is little correlation. Finally, it is important to stress here that the population used in this work is small, this naturally skews the results to more extreme values.

As can be seen by Pearson's  $r$  in figure 1 and Kendall's  $\tau$  in figure 2, there is generally no clear pattern for de-

	$l$	Type	Period
$\eta_B^2$	0.9257	0.9361	0.07849
$\eta_G^2$	0.1964	0.7792	0.0777
$\eta_{B/G}^2$	0.6006	0.8598	0.2119
$\eta_\nu^2$	0.1190	0.9046	0.1321

Table V. Correlation coefficients for different types of categorical properties with the bulk modulus  $B$ , the shear modulus  $G$ , the  $B/G$  ratio and the Poisson ratio  $\nu$ .

terminating the parameters. However, some of them stand out, the volume seems to be an okay parameter for determining the bulk modulus and somewhat for the shear modulus. This should come as no surprise as the volume is used to determine a BM fit, but is also directly connected with the stress tensor method.

The electro-negativity ( $\chi$ ) also stands out. These coefficients are not very high but still high enough that a rough estimate *could* be made. This property is linked to how many electrons an atom can attract, which in turn is linked to the bond strength, and thus the elasticity. From the fact that Kendall's  $\tau$  shows a higher value for  $\chi$ , shows that there is not necessarily a linear relationship (since Kendall's  $\tau$  does not assume linearity). And as such, trying to predict values requires determining what kind of relationship the two have to have a quantitative way of predicting the values.

It is quite clear that for both methods, the Poisson modulus has no correlation at all, which is due to the ratio being quite monotonous in its range, especially for FCC lattices. However, it is not useless to calculate this, since there is an indication that that there is some kind of anti-linear relationship between the two, as Pearson  $r$  is quite high and Kendall  $\tau$  is low in absolute value. This ratio is calculated using  $B$ , but if one doesn't know  $G$  and would like an estimate this could be a way.

Lastly, the proton count  $P$  and the molar mass  $M$  don't show promising results at all, the proton count doesn't immediately contribute to the bonding strength, but it does determine the size of the nucleus, which could have effects on stability. However, it is clear that this is not the case.

#### IV. CONCLUSION

In this study, we have successfully used density functional theory to calculate the ductility of various FCC materials using the Pugh criterion. By calculating the bulk modulus via the Birch-Murnaghan equation of state and stress tensor methods, we could validate our approach through internal consistency checks. While some were still off by a lot like Polonium (7.5%), Nickel (-11.6%) and Lanthanum (7.1%), further improvement like taking into account non linear stress methods or us-

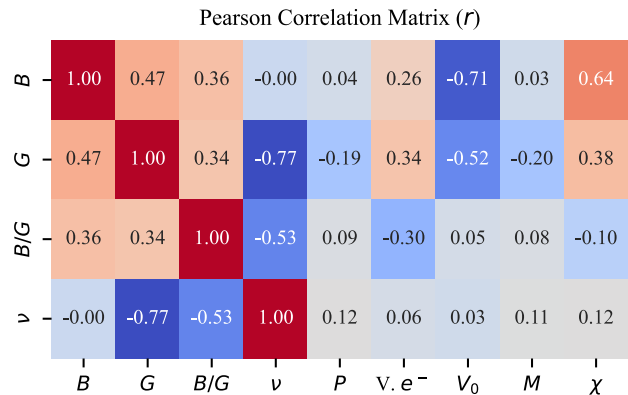


Figure 1. Pearson  $r$  for various properties against the elastic constants.

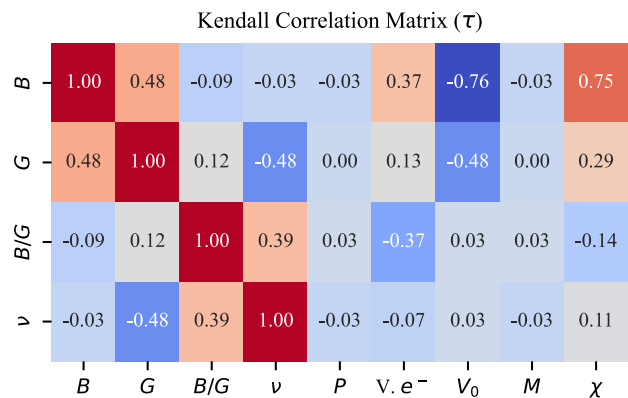


Figure 2. Kendall  $\tau$  for various properties against the elastic constants.

ing stronger convergence criteria could improve these results for better internal consistency. Furthermore, the stress tensor method provided the shear modulus  $G$  which could be used to determine the  $B/G$  ratio and the Poisson modulus  $\nu$ . Using the fact that a material is ductile if  $B/G > 1.75$  or  $\nu > 0.26$ , we found that only Pt, La and Ca were ductile, while Ce, Se and Mg were on the edge of being (non)-ductile. On the other hand, Ac, Th, Ni and Si were non-ductile. Lastly, Al and Po were found to have a negative  $B/G$  ratio indicating structural instability of the material at 0K and 0 pressure.

The applicability of DFT to predict elastic properties, even for hypothetical phases, was evaluated by calculating the correlation coefficients between various properties and the elastic constants. The correlation analysis highlights promising results for the orbital  $l$  of the element and the atom type to estimate an upper and lower bound for the elastic constants. Also the equilibrium volume and electronegativity could be used to determine these bounds. However, the population size was small and many of these properties were not calculated using DFT. Doing this could greatly increase statistical accuracy and precision.

- 
- [1] S. Pugh, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **45**, 823 (1954).
- [2] P. Giannozzi *et al.*, *The Journal of Chemical Physics* **152**, 154105 (2020), <https://doi.org/10.1063/5.0005082>.
- [3] P. Giannozzi *et al.*, *Journal of Physics: Condensed Matter* **21**, 395502 (19pp) (2009).
- [4] P. Giannozzi *et al.*, *Journal of Physics: Condensed Matter* **29**, 465901 (2017).
- [5] D. R. Hamann, *Physical Review B* **88**, 10.1103/physrevb.88.085117 (2013).
- [6] A. D. Corso, *Computational Materials Science* **95**, 337 (2014).
- [7] Bosoni *et al.*, *Nature Reviews Physics* **6**, 45 (2023).
- [8] T. Angsten, T. Mayeshiba, H. Wu, and D. Morgan, *New Journal of Physics* **16**, 015018 (2014).
- [9] L. Huang and H. Lu, *Physical review. B./Physical review. B* **99**, 10.1103/physrevb.99.045122 (2019).
- [10] E. R. Jette and F. Foote, *The Journal of Chemical Physics* **3**, 605 (1935).
- [11] S. J. Duclos, Y. K. Vohra, and A. L. Ruoff, *Physical Review Letters* **58**, 775 (1987).
- [12] S. J. Duclos, Y. K. Vohra, and A. L. Ruoff, *Physical review. B, Condensed matter* **41**, 12021 (1990).
- [13] R. W. G. Wyckoff, *Crystal Structures* **1** (1963).
- [14] W. Chen, D. V. Semenok, I. A. Troyan, A. G. Ivanova, X. Huang, A. R. Oganov, and T. Cui, *Phys. Rev. B* **102**, 134510 (2020).
- [15] J. Olsen, L. Gerward, U. Benedict, and J.-p. Itié, *Physica B+C* **133**, 129 (1985).
- [16] G. W. C. Kaye and T. H. Laby, *Tables of physical and chemical constants and some mathematical functions*, 15th ed. (Longman, London, 1986).
- [17] O. Chemical Rubber Company (Cleveland and D. R. Lide, *CRC handbook of chemistry and physics : 1998-1999 ; a ready-reference book of chemical and physical data*, 79th ed. (CRC Press, Boca Raton, 1998).
- [18] A. M. James and M. P. Lord, *Macmillan's chemical and physical data* (Macmillan, London, 1992).
- [19] D. R. A. Fisher, *Nature* **131**, 383 (1933).
- [20] R. N. Forthofer and R. G. Lehnen, Rank correlation methods, in *Public Program Analysis: A New Categorical Data Approach* (Springer US, Boston, MA, 1981) pp. 146–163.