

Estimating stretching force constants for geometry optimization¹

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Abstract

The rate of convergence of geometry optimizations depends upon the accuracy of the initial estimate of the Hessian. A set of parameters dependent on the rows of the periodic table are developed for use in Badger's rule to approximate bond stretching force constants. © 1997 Elsevier Science B.V.

Keywords: Geometry optimization; Badger's rule; Force constants

1. Introduction

The efficiency of a gradient based geometry optimization depends upon several factors [1], some of which relate to the method of optimization, such as the coordinate system and the type of quasi-Newton optimization algorithm, and others which relate to the structure of the molecule, specifically the initial geometry and the initial Hessian (second derivative or force constant matrix). The closer the initial geometry and Hessian are to the final values, the faster the optimization. The most accurate estimate of the Hessian is obtained by a direct calculation. However, for an N variable system, direct numerical calculation of the Hessian requires up to N times the work of a gradient calculation and thus is often made impractical by the size of the system. Furthermore, during optimization, the initial guess approaches the correct Hessian through the use of updating schemes. Thus, the accuracy of an explicit calculation of the Hessian is often not necessary; an estimate that is within 10–20% of

the actual value is sufficient to ensure rapid convergence of the optimization. Force constants for bends and torsions fall in reasonably narrow ranges, but bond stretch force constants vary more widely. In a previous paper, we provided simple estimates of force constants for angle bends and torsions and for bond stretches through the second full row of the periodic table (up to Cl) [2]. In the intervening dozen years computational chemistry has grown rapidly and calculations involving heavier elements are carried out more frequently. In this short note, we extend the initial estimate of the Hessian to bond stretches involving atoms through period 6 (up to At).

Simple estimates of stretching force constants, F , can be made using Badger's rule [3] (or variations thereof):

$$F = A / (r - B)^3, \quad (1)$$

where r is the bond length, A is a constant that is the same for all bonds and B is a constant that depends upon the period of the bonded atoms. In previous work that fitted Badger's rule to calculated force constants for selected molecules containing elements from the first three periods, a value of 1.734 hartree bohr was obtained for A [2].

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Table 1

Bond lengths, force constants and *B* parameters at HF, MP2 and B3LYP levels of theory (see text for basis sets)

Period	Molecule	Bond length/bohr			Force constant/hartree/bohr ²			<i>B</i> /bohr		
		HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
1–1	H ₂	1.3886		1.4033	.413598		.378666	– .2239		– .2573
2–1	H ₂ O			1.8306			.515464			.3323
	NH ₃			1.9264			.443873			.3515
	HF	1.7713		1.7650	.597936		.572072	.3452		.3178
	LiH	3.0990	3.0990	3.0635	.067719	.064928	.065395	.1516	.1099	.0815
	CH ₄	2.0464	2.0597	2.0665	.376835	.366527	.348328	.3831	.3809	.3590
2–2	LiF	2.8732	2.9671	2.9323	.226903	.194244	.197427	.9035	.8927	.8691
	CH ₃ F			2.6134			.381980			.9576
	CF ₄	2.5039			.557939			1.0446		
	F ₂	2.6504	2.6852	2.6519	.603655	.364727	.407673	1.2289	1.0037	1.0317
	C ₂ H ₆		2.8836	2.8927		.315306	.290873		1.1185	1.0794
	LiCH ₃	3.7816	3.7996	3.7397	.084976	.069589	.074792	1.0489	.8788	.8882
3–1	H ₂ S			2.5502			.269895			.6912
	PH ₃			2.6920			.214663			.6855
	HCL	2.4444		2.4367	.301169		.321068	.6521		.6822
	NaH	3.6412	3.6251	3.5609	.050029	.050991	.051394	.3808	.3853	.3296
	SiH ₄	2.8095	2.8027	2.8082	.193249	.200884	.189309	.7315	.7514	.7159
3–2	LiCl	3.9904	3.9084	3.8837	.085690	.089898	.088470	1.2654	1.2266	1.1875
	CH ₃ Cl			3.4072			.214871			1.4014
	CCl ₄	3.4628			.204803			1.4246		
	FCI	3.1926		3.1436	.346891		.287252	1.4827		1.3228
	NaF	3.5208	3.6278	3.5728	.145209	.133118	.125888	1.2351	1.2749	1.1757
	SiF ₄	2.9930			.507450			1.4868		
	CH ₃ SiH ₃	3.6229	3.5590	3.5684	.197149	.197633	.182641	1.5587	1.4965	1.4510
	NaCH ₃	4.3856	4.4217	4.3482	.059791	.053351	.053894	1.3132	1.2304	1.1676
3–3	NaCl	4.5749	4.5226	4.4893	.063181	.072177	.068110	1.5585	1.6371	1.5475
	SiH ₃ Cl			3.9286			.180029			1.8010
	SiCl ₄	4.0125			.176930			1.8725		
	Cl ₂	4.1442	3.8084	3.8595	.172243	.198181	.179344	1.9850	1.7478	1.7291
4–1	HBr	2.7063		2.7203	.230984		.251428	.7483		.8168
	KH	4.4614			.034720			.7787		
	TiH ₄	3.1383			.130223		.119714	.7681		.7538
	FeH ₃	3.1523		3.0505	.105479		.117549	.6096		.5979
	ZnH ₂	2.9688		2.8592	.105098		.151336	.4231		.6048
	GeH ₄	2.9066		2.8993	.173518		.174914	.7527		.7511
	H ₂ Se			2.8088			.223289			.8285
4–2	LiBr	4.2348		4.0980	.080076		.084797	1.4475		1.3634
	CH ₃ Br			3.7141			.177173			1.5751
	CBr ₄	3.7423			.188908			1.6485		
	FBr	3.3547		3.3736	.316060		.274014	1.5910		1.5239
	KF	4.1924			.078208			1.3831		
	TiH ₃ F			3.2702			.320489			1.5147
	TiF ₄	3.2494			.440176			1.6701		

Table 1 Continued

Period	Molecule	Bond length/bohr			Force constant/hartree/bohr ²			B/bohr		
		HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
	FeH ₂ F			3.3233			.269788			1.4641
	FeF ₃	3.2742			.352489			1.5735		
	ZnHF			3.3016			.255808			1.4091
	ZnF ₂	3.1986			.352738			1.4983		
	GeH ₃ F			3.3300			.263999			1.4572
	GeF ₄	3.1370			.496718			1.6200		
	CH ₃ GeH ₃	3.7119			.201621			1.6630		
	Ti(CH ₃) ₄	3.9326			.181200			1.8095		
	Zn(CH ₃) ₂	3.6737			.149043			1.4078		
	KCH ₃	5.2452			.036780			1.6327		
	Ni(CO) ₄	3.4602		3.4297	.130106		.156242	1.0892		1.1992
4–3	NaBr	4.8588		4.6985	.056976		.064550	1.7366		1.7036
	SiBr ₄	4.3383			.135599			1.9999		
	ClBr	4.3778		4.1271	.162286		.178511	2.1753		1.9934
	KCl	5.3465			.044358			1.9527		
	TiH ₃ Cl			4.1119			.166858			1.9297
	TiCl ₄	4.1305			.169478			1.9595		
	FeH ₂ Cl			4.0944			.136098			1.7588
	FeCl ₃	4.2654			.132059			1.9062		
	ZnHCl			4.0311			.134499			1.6862
	ZnCl ₂	4.1450			.138523			1.8231		
	GeH ₃ Cl			4.1412			.148268			1.8714
	GeCl ₄	4.1288			.184936			2.0201		
	SiH ₃ GeH ₃	4.5831			.097561			1.9733		
4–4	KBr	5.6648			.038782			2.1155		
	TiH ₃ Br			4.3967			.144170			2.1055
	TiBr ₄	4.4181			.137262			2.0891		
	FeH ₂ Br			4.3457			.121215			1.9182
	FeBr ₃	4.5494			.119251			2.1086		
	ZnHBr			4.2695			.123140			1.8547
	ZnBr ₂	4.3799			.126662			1.9877		
	GeH ₃ Br			4.4285			.127138			2.0392
	GeBr ₄	4.4271			.146652			2.1490		
	Br ₂	4.6167		4.3861	.152994		.162329	2.3704		2.1838
	Ge ₂ H ₆	4.6586			.094013			2.0165		
5–1	RbH	4.7779		4.6762	.030334		.031208	.9257		.8604
	ZrH ₄	3.5112		3.5112	.106270		.105569	.9748		.9692
	RuH ₃	3.3562		3.2888	.103814		.088721	.8000		.5951
	SnH ₄	3.2829		3.2351	.150563		.137869	1.0246		.9095
5–2	RbF	4.4440		4.6277	.064144		.068580	1.4427		1.6926
	AgF	3.8139		3.8411	.174882		.142205	1.6656		1.5395
	RuF ₃	3.6316			.294656			1.8261		
	ZrF ₄	3.5460		3.6461	.357042		.273708	1.8525		1.7958
	SnF ₄	3.5106		3.5155	.395929		.243507	1.8745		1.5916
5–3	RbCl	5.6402		5.6105	.039089		.041915	2.1002		2.1520
	AgCl	4.6927		4.5267	.080908		.104589	1.9150		1.9768

Table 1 Continued

Period	Molecule	Bond length/bohr			Force constant/hartree/bohr ²			B/bohr		
		HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
5–4	ZrCl ₄	4.5088		4.5088	.154144		.148684	2.2681		2.2410
	RuCl ₃	4.5073			.132915			2.1532		
	SnCl ₄	4.4731		4.4731	.166865		.129067	2.2909		2.0958
	RbBr	5.9785		5.9654	.033564		.035295	2.2540		2.3029
	AgBr	4.8635		4.7535	.076073		.087246	2.0281		2.0448
	SnBr ₄	4.7556		4.8231	.137293		.100431	2.4268		2.2384
	RuBr ₃	4.7259		4.7442	.114929		.097821	2.2549		2.1369
5–5	ZrBr ₄	4.7654		4.7720	.139325		.121378	2.4480		2.3456
	RbI	6.5129		6.4097	.026682		.028360	2.4924		2.4701
	AgI	5.2354		5.0222	.060327		.077598	2.1722		2.2056
	RuI	5.1358		5.0426	.082755		.083236	2.3789		2.2911
6–1	I ₂	5.4142		5.4085	.097343		.071983	2.8025		2.5204
	CsH	5.1925		5.0995	.026594		.027275	1.1676		1.1084
	H ₃ Bi			3.3623			.126872			.9714
6–2	OsH ₃			3.2640			.111437			.7675
	CsF	4.9508		4.9345	.065720		.061294	1.9738		1.8875
	TlF	4.0241		4.1014	.151376		.132833	1.7698		1.7468
6–3	HgO			3.8659			.134765			1.5226
	CsCl	6.0361		5.9945	.036442		.035428	2.4124		2.3366
	TlCl	4.9217		4.9969	.079776		.079504	2.1309		2.2029
	BiCl ₃	4.6596		4.7244	.128640		.109118	2.2797		2.2103
6–4	BaS			5.5888			.060233			2.5240
	CsBr	6.4422		6.3691	.029789		.030469	2.5666		2.5226
	BiBr ₃	5.0062		5.0666	.099988		.085782	2.4178		2.3426
6–5	BaBr ₂			6.0174			.047345			2.6965
	CsI	6.9316		6.8332	.023505		.024141	2.7376		2.6764
	TlI	5.6247		5.7007	.050992		.049838	2.3849		2.4361
	HgI ₂			5.1916			.081492			2.4205

The following variation of Badger's rule has been used by Rappé et al. in their development of a universal force field [4].

$$F = GZ_i^* Z_j^* / r_{ij}^3, \quad (2)$$

where G is a constant, Z_k^* is effective atomic charge

and r_{ij} is the bond length estimated from atomic radii, bond order and electronegativity. The disadvantage of this method is that several parameters are required for each atom. In this work, the simpler Eq. (1) is used to generate a table of parameters suitable for estimating stretching force constants for geometry optimizations,

Table 2
Parameter B for Badger's rule computed at the B3LYP level of theory

Period	1 H	2 Li–F	3 Na–Cl	4 K–Br	5 Rb–I	6 Cs–At
1	– 0.2573	0.3401	0.6937	0.7126	0.8335	0.9491
2		0.9652	1.2843	1.4725	1.6549	1.7190
3			1.6925	1.8238	2.1164	2.3185
4				2.0203	2.2137	2.5206
5					2.3718	2.5110

where errors of 10–20% are acceptable. It should be noted that these estimates are not intended for use in molecular mechanics or vibrational frequency calculations, where significantly better accuracy is required.

2. Procedure

Over 80 simple molecules were chosen to represent bonds involving the first 6 periods. Atoms chosen include alkali metals, halogens, group IV atoms and transition metals. Geometries were fully optimized and frequency calculations performed using GAUSSIAN 94 [5] at the following levels of theory.

Level of calculation.	Molecules involving:
HF/3-21G	Periods 1–5 with periods 1–5
HF/LanL2DZ	Period 6 with 1–5
MP2/6-31G*	Periods 1–3 with 1–3
B3LYP/6-31G*	Periods 1–3 and Br with 1–3 and Br
B3LYP/6-311G*	Period 4 with 1–4 (except Br)
B3LYP/LanL2DZ	Periods 5 and 6 with 1–6

For compatibility with our earlier work [2], the previously determined value of 1.734 hartree bohr

was used for A . The B parameters were calculated from,

$$B = r - (1.734/F_{\text{str}})^{1/3}. \quad (3)$$

Analytic force constants, bond lengths and B parameters are given in atomic units in Table 1. The averaged B parameters of the B3LYP calculations, excluding some unusual results, appear in Table 2. Estimated force constants were calculated from the computed bond lengths and the averaged parameters using Eq. (1). Fig. 1 compares the estimated force constants to those computed at the B3LYP levels of theory.

3. Discussion

Several molecules, LiH, NaH and Ni(CO)₄, with unusually low B parameters were not included in the averaging. Ni(CO)₄ was rejected because it had the largest error, 40%, for its estimated force constant. The hydrides were rejected by the Q-test. For Ni(CO)₄, the small B parameter of 1.199 is most likely a result of dative bonding. Although theoretical treatment of nickel carbonyls is difficult and requires high levels of correlation [6], experimentally determined values of the Ni–C bond length and force constant

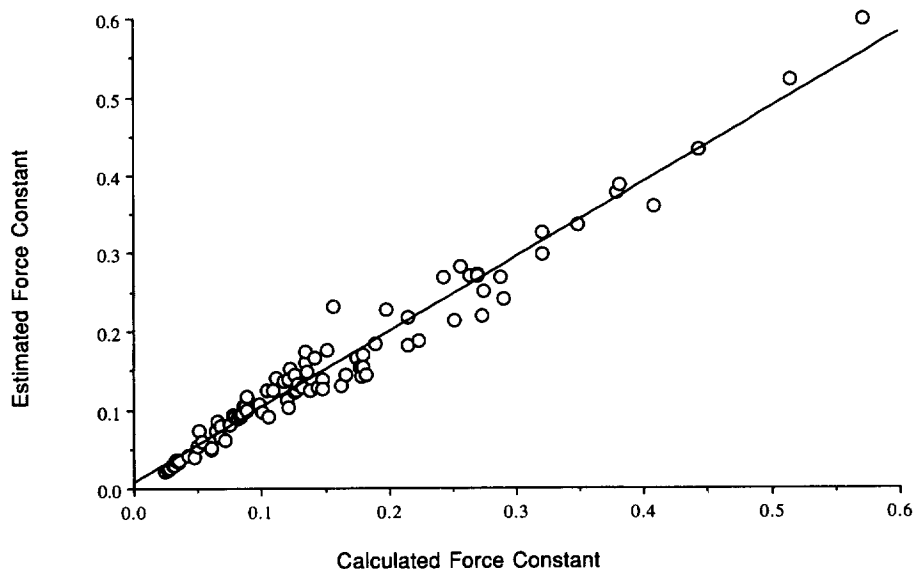


Fig. 1. Comparison of force constants estimated by Badger's rule to force constants computed at the B3LYP level of theory (see text for basis sets).

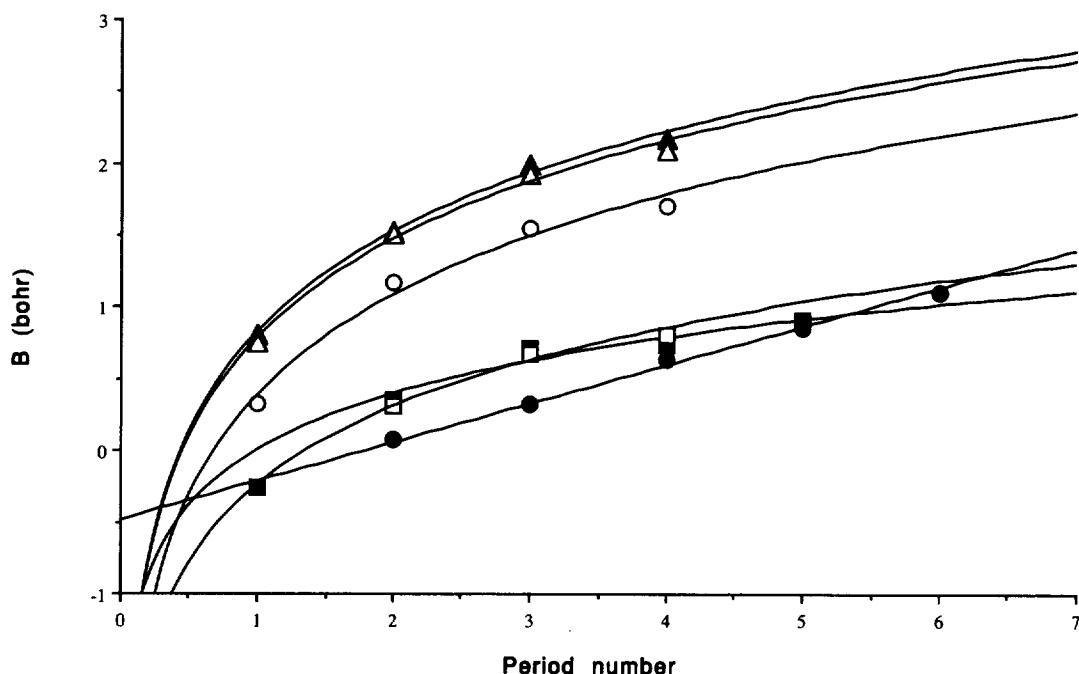


Fig. 2. B vs. row number for the series: X–Br (solid triangle), Ti–X₄ (open triangle), Na–X (open circle), H–X (open square) where X = H, F, Cl, Br; M–H₄ (solid square) where M = C, Si, Ge, Sn; and M–H (solid circle) where M = H, Li, Na, K, Rb, Cs.

by Hedberg et al. [7] also give low results of $B = 1.215$ (bohr). Low values for LiH, 0.08, and NaH, 0.33, also do not appear to be the result of calculational deficiencies. Calculation of B from tabulated experimental data [8] gives even lower values of 0.04 and 0.31.

Within groups of related molecules, the B parameters tend to have a logarithmic dependence upon the period of similar atoms. However, for the alkali metal hydrides, the dependence is linear (Fig. 2). Tentative extrapolation beyond the sixth period of the parameters in Table 2 may be done by fitting an appropriate curve to a plot of B vs. period number for the individual rows of the table.

In general, as the level of theory and size of the basis set increases, the values of B tend to become somewhat smaller. HF/3-21G is the lowest level of theory that can be expected to give reasonable results. MP2 calculations typically give more reliable geometries and force constants. Values of B at the B3LYP levels are similar to those at both the Hartree–Fock and MP2 levels.

Badger's rule previously has been shown to work well for single, double and triple bonds [2,3], however, it does not correctly model other types of

bonding, such as hydrogen bonding, dative bonding and van der Waal's interactions. Fischer and Almlöf give formulas for hydrogen bonding force constants [9]. When using the parameters determined in this work, it should be kept in mind that no calculations were done on transition metal to transition metal bonding nor on any of the lanthanides or actinides.

Fig. 1 compares the force constants (including LiH, NaH and Ni(CO)₄) estimated by Eq. (1) using the average values of B to those computed at the B3LYP levels of theory. The points fall on a line with a slope of 0.96 and a correlation coefficient of 0.964. The average absolute value of the relative error in the estimated force constants is 11.9 percent, with a standard deviation of 9.0 percent. Thus, this simple valence force field provides a reasonable estimate of many bond stretch Hessian elements suitable for use in geometry optimizations.

Acknowledgements

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