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Optimization of parameters for semiempirical methods IV: extension of MNDO, AM1, and PM3 to more main group elements

Abstract The NDDO semiempirical methods MNDO, AM1, and PM3 have been extended to all the remaining non-radioactive elements of the main group, excluding the noble gases. Most of the new elements are of Groups I and II. 44 sets of parameters are presented for the following methods and elements. MNDO: Na, Mg, K, Ca, Ga, As, Se, Rb, Sr, In, Sb, Te, Cs, Ba, Tl, and Bi; AM1: Li, Be, Na, Mg, K, Ca, Ga, As, Se, Rb, Sr, In, Sn, Sb, Te, Cs, Ba, Tl, Pb, and Bi; PM3: B, Na, K, Ca, Rb, Sr, Cs, and Ba. Average errors are presented for heats of formation, molecular geometries, etc.

Keywords Semiempirical methods · MNDO · AM1 · PM3 · Parameter optimization

Introduction

Semiempirical NDDO [1, 2] methods, such as MNDO, [3, 4] AM1, [5] and PM3, [6, 7, 8] involve approximations that include parameters. Values for these parameters have been generated for most of the main group elements, but, except for MNDO lithium, [9] beryllium, [10] sodium [11] and potassium [12] and PM3 lithium, [13] beryllium, [8] and magnesium, [8] parameters for the elements of Groups I and II have not been reported. This deficiency could be attributable both to the paucity of suitable reference data and to the difficulty of developing a method that is of sufficient accuracy to be useful. The lack of such parameters precluded the use of these semiempirical methods for the study of biochemical processes that involve main group metal ions.

A recent modification [14] of the core–core approximation has allowed parameters for a transition metal to be developed. An investigation of the applicability of this modification to MNDO, AM1, and PM3 for main group metals was carried out, and the results were encouraging.

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Method

Semiempirical methods can be defined by the set of approximations used and by the values of the parameters. The basic NDDO approximations, pioneered by Pople, [1, 2] and subsequently modified extensively by Dewar and Thiel, [3] have undergone many small changes. These include changes to the core-repulsion function [5] and the use of two-center core–core terms. [14] As a result of these changes, the current form of the core-repulsion function has become quite complicated, and a summary of the terms used is as follows:

In general, the common part, [3] g_{AB}, of the core–core repulsion function, in eV, between two atoms, A and B, with core charges of Z_A and Z_B, and separated by R ångströms is as shown in Eq. (1).

$$g_{AB} = \frac{eVZ_AZ_B}{\left(\left(\frac{R}{a_0}\right)^2 + (\rho_A + \rho_B)^2\right)^{1/2}} \qquad (1)$$

where

$$eV = 27.2113962, \quad a_0 = 0.529177249 \qquad (2)$$

and

$$\rho_A = eV/2G_{ss} \qquad (3)$$

if G_{ss} is defined. If it is not defined, then ρ_A=0. For some elements, e.g., Na and Mg in MNDO/d, [15] the quantity ρ_A is sometimes explicitly defined, in which case the explicit value is used.

Also, in general, the common part is modified [3] to include a term to represent instantaneous correlation. The most frequently used term is of type:

$$CRF = g_{AB}(1 + e^{-a_Ar} + e^{-a_Br}) \qquad (4)$$

The exceptions [3] are when atom A is hydrogen and atom B is either oxygen or nitrogen, in which case the CRF becomes:

$$CRF = g_{AB}(1 + e^{-a_Ar} + r\,e^{-a_Br}) \qquad (5)$$

If diatomic parameters are used, [14] then the form of the CRF is different, Eq. (6).

$$CRF = g_{AB}(1 + 2a_{AB}e^{-b_{AB}r}) \qquad (6)$$

This expression is different to the equation in [14]—in the original publication, the factor of "2" was apparently inadvertently omitted.

Again, there are exceptions. In AM1, if one atom is hydrogen and the other is molybdenum, [14] then

$$CRF = g_{AB}(1 + 2ra_{H-Mo}e^{-b_{H-Mo}r}) \qquad (7)$$

An alternative function to account for correlation, used in AM1 and PM3, [6, 7] is:

$$\mathrm{CRF} = g_{\mathrm{AB}} + \frac{Z_{\mathrm{A}}Z_{\mathrm{B}}}{r} \left(\sum_k a_{k\mathrm{A}} e^{-b_{k\mathrm{A}}(r-c_{k\mathrm{A}})^2} + \sum_k a_{k\mathrm{A}} e^{-b_{k\mathrm{A}}(r-c_{k\mathrm{A}})^2} \right)$$

(8)

In this expression, one to four sets of Gaussian parameters a, b, and c are defined.

The flexibility allowed by these approximations was found to be sufficient to allow all the elements reported here to be parameterized so that the resulting method was of useful accuracy. Consequently, no new approximations were found to be necessary to allow the NDDO methods to be extended to the elements reported here.

The objective of parameter optimization is to determine the best values for the parameters used in semiempirical methods: that is, to develop a method that most accurately reproduces experimental phenomena for molecules. In this context, the term "method" should be understood as the combination of a set of approximations involving adjustable parameters, and the values of those parameters.

Parameter optimization method

Semiempirical parameter optimization, although historically often regarded as an extremely difficult process, is in fact quite simple in principle. A set of reference data is assembled. Each datum represents a quantity such as a heat of formation, a bond length or angle, a dipole moment, or an ionization potential. Before any data can be used for parameter optimization, they must be rendered dimensionless. As with previous parameterizations, the default weighting factors used here are: heat of formation, ΔH_f: mol kcal^{-1}, geometry gradient: 0.7 mol Å kcal^{-1}, dipole moment: 20 D^{-1}, and I.P. 10 eV^{-1}.

An error function, usually defined as the sum of the squares of the differences of the values of the calculated and reference data, is then evaluated for an initial set of parameters. Several methods exist for generating the initial set of parameters of which the two most common are to use parameters from a previous method and to use parameters derived from a similar element.

Parameter optimization then proceeds by making changes to the values of the parameters so that the error function decreases. Several procedures have been developed for performing this operation. When the parameters for MNDO were originally optimized, a modified Bartels non-linear least squares optimization procedure was used. At that time, 1977, evaluation of the derivatives was considered too arduous with the then-available computer power.

Later optimization procedures did use first derivatives, and more recent optimizations [6, 7, 8] used both first and second derivatives of the reference data with respect to parameters. Analytical evaluation of the derivatives ranged from the trivial, such as the derivative of an ionization potential with respect to a one-electron one-center integral, e.g., a U_{ss} or U_{pp}, to derivatives that were, and remain, intractable, such as the derivative of a bond-length gradient with respect to an orbital exponent. However, with the increase in computer power, all derivatives can now readily be evaluated by finite difference.

Given the availability of accurate first derivatives of the reference data with respect to parameters, evaluation of both first and second derivatives of the error function with respect to parameters is a trivial operation, and allows more sophisticated function minimization procedures to be used.

Several minimization procedures were tried. The simplest, Newton–Raphson, worked efficiently when only a few parameters were being optimized, but became less efficient when the number of parameters increased, becoming essentially useless when more than about ten parameters were simultaneously optimized. Since one objective was to optimize many hundreds of parameters simultaneously, Newton–Raphson was considered unsuitable.

The most efficient method for simultaneously optimizing large numbers of parameters was found to be a modified Broyden–Fletcher–Goldfarb–Shanno (BFGS) procedure. This approach uses an approximation to the inverse Hessian, and updates it as the optimization proceeds. Evaluation of the error function by explicit SCF calculations was then the rate-determining step. However, for small modifications of parameters, a good approximation to the error function could be made by using the first derivatives. This allowed many optimization steps to be performed before the approximation became unusable, at which point an explicit re-evaluation of the error function and derivatives had to be performed. To prevent instability, a dampening function was added, to minimize motion in parameter space, and full function evaluations were performed after the parameters were optimized, or after 2,000 cycles of optimization, whichever occurred first.

Parameter optimization application

Parameters were optimized using a reference data set consisting of molecules and ions of the elements being parameterized. Unlike most previous optimizations, all available reference data were used. This was considered necessary because of the limited amount of reference data on gas-phase systems. Additionally, because of the limited size of the reference data set, constraints were placed on the values that the parameters could assume.

Results

Parameters

Atomic parameters for the various elements and methods are presented in Tables 1, Table 2, and 3. All parameters have the same meaning as originally described, [5] except for the internal orbital exponents, [14] $\zeta_s^{'}$ and $\zeta_s^{'}$, used in AM1 potassium. The effect of the applied boundary conditions can readily be seen in the values of various parameters: most parameters that are near to an integer, e.g., MNDO magnesium G_{pp}, with a value of 10.00003, are the result of the parameter being influenced by a boundary condition. Such conditions are an implicit admission that the reference data set is insufficiently comprehensive to explicitly define the values of the parameters. Diatomic core–core parameters [14] for the three methods are presented in Table 4. In those instances where diatomic parameters are not given, the core–core term described in [3] was used.

Parameters for MNDO sodium and potassium were re-optimized, to allow use of the diatomic core–core parameters. Some parameterizations, such as those for As, Se, Sb, and Te, were performed several years ago, and, although unpublished until now, have been made available in the MOPAC program. [16] These parameters are included here for completeness.

Applications

Average unsigned errors in heats of formation are presented in Table 5. The set of systems surveyed consisted mainly of stable uncharged species. Excited states of atoms and ions were not considered in the

Table 1 MNDO parameters for main group elements

Parameter	Sodium	Magnesium	Potassium	Calcium	Gallium	Arsenic	Selenium	Rubidium
[a]U_{ss}	−5.1235942	−14.8057921	−3.6401731	−12.3919094	−28.3044924	−38.6240790	−49.8117347	−4.3098071
[a]U_{pp}	−3.0124713	−12.7545494	−2.0249253	−9.9348289	−27.2063910	−33.4995395	−38.0475911	−2.7381921
[a]β_s	−1.4916657	−0.0999626	−0.1361851	−8.6404687	−3.9987435	−3.9998231	−12.4685178	−2.2062173
[a]β_p	−0.2208233	−7.6952692	−2.8142350	−9.9515712	−4.3146711	−4.9056176	−5.1744376	−6.2176392
[b]ζ_s	0.8213124	0.9394811	0.7276039	1.0034161	0.6986316	2.5614338	0.7242956	4.0001632
[b]ζ_p	1.0303270	1.3103428	0.9871174	1.3102564	1.8386933	1.6117315	1.9267288	0.9187408
[c]α	5.9940638	0.5354201	0.5616422	0.4999997	2.7577991	1.9381219	2.3513155	0.9976197
[a]G_{ss}	6.9934520	6.9632774	3.7939792	6.5321649	7.5468114	6.7464011	10.3549483	10.7409462
[a]G_{sp}	5.4380530	8.2410934	6.4170233	6.5424442	10.4697612	5.6174985	5.2801360	11.4853623
[a]G_{pp}	6.9285408	10.0000349	5.0972823	6.4627059	8.4599454	6.9333925	7.3611317	8.9878480
[a]G_{p2}	2.4299952	9.0593304	2.1945567	6.3842472	10.4251148	6.3054798	6.1897284	7.7258368
[a]H_{sp}	3.1374231	0.7165063	1.5788130	0.5789676	1.0628013	0.5994346	0.5996560	0.1999294
[a]K_1					0.6265886	−0.2025391	−1.0001121	
[d]L_1					3.0001279	3.0002200	2.7043270	
[e]M_1					1.2564374	1.3902090	0.4993772	

Parameter	Strontium	>Indium	Antimony	Tellurium	Cesium	Barium	Thallium	Bismuth
[a]U_{ss}	−10.8451287	−28.0980892	−42.0643435	−84.2274722	−3.2184078	−10.1125345	−29.7009655	−53.5827147
[a]U_{pp}	−8.3129821	−19.2780588	−35.0626031	−46.5332871	−1.7699113	−8.2347224	−29.5937539	−39.4572213
[a]β_s	−9.9683427	−6.3107479	−0.9999715	−8.5622652	−1.6043600	−9.9994459	−4.9667442	−9.0000249
[a]β_p	−9.9946390	−2.7025837	−4.0920176	−2.6942963	−4.2698040	−9.6197255	−7.7616060	−1.9830269
[b]ζ_s	1.3729266	1.7625740	3.6458835	2.7461609	6.0004170	1.9765973	4.0000447	2.6772255
[b]ζ_p	1.1118128	1.8648962	1.9733156	1.6160376	0.8986916	1.3157348	1.8076332	0.6936864
[c]α	0.5082703	2.3438756	1.9763403	2.2924145	0.4981646	0.8594840	1.3116968	5.7660628
[a]G_{ss}	4.9305520	9.4928794	10.6739308	5.1367706	7.6447851	4.8486178	8.8675337	8.3702778
[a]G_{sp}	4.4249843	7.0094241	7.0477648	11.0720752	3.0454989	4.5659982	12.1148290	7.7974668
[a]G_{pp}	4.0178045	9.6640986	6.7446162	5.8447934	10.0000745	5.0937708	10.6532769	9.8303165
[a]G_{p2}	4.0335640	7.0100315	6.3408531	5.0720495	6.1761092	5.2125824	13.5333191	8.9291355
[a]H_{sp}	0.6272993	0.5995894	0.5997512	0.5997994	0.4647853	0.5237082	0.5997565	0.5999908
[a]K_1		0.9277024	−1.0003602	−0.6033681			−0.7940727	−0.1281535
[d]L_1		0.9999001	0.9992881	1.4127317			0.9999962	3.0003211
[e]M_1		1.1829906	0.0000000	0.4996755			0.4999732	1.7993215

[a]eV   [b]Bohr   [c]Å^{-1} [e]Å   [d]Dimensionless

statistical analysis, but if they had been included, the average errors would have been much higher. For many elements the limited amount of available reference data rendered any statistical analysis based only on well-behaved systems almost meaningless, therefore all available data considered to be accurate was used in the analyses.

Severe difficulties were encountered in reproducing the geometries of compounds involving the alkali metals, which is reflected in the unusually large errors in average unsigned errors in bond lengths, Table 6. Average unsigned errors in angles are given in Table 7. Because of the small number of data available, the reliability of this table is questionable.

Dipole moments for compounds of the alkali metals are reproduced with useful accuracy, Table 8.

After the initial submission of this article, reviewers reported that parameters for AM1 Na, Mg, and Sn, and PM3 Na had already been published. This afforded an opportunity to compare the different types of optimization and the effect of the use of diatomic core–core parameters, a summary of the results for these specific sets are shown in Table 9. Except for PM3 dipoles for sodium (AUE, this work, 1.53 D, 1.52 D [17]) and AM1 dipoles for tin (AUE, this work, 0.62 D, 0.62 D [18]), the AUE are somewhat smaller here than in previously published

work. The sets of reference data used in generating the statistics in Table 9 differ from those in the original papers. It should be emphasized that, since the set used here was essentially identical to the set used in optimizing the parameters, the statistics are unavoidably biased in favor of the current optimization. This unfortunate condition will exist until the number of reference data is increased considerably.

Individual compounds

A comparison of calculated and observed properties for all individual compounds studied is presented in the supplementary materials. Among the more important compounds are the following.

Magnesium porphorin complex

Both MNDO and AM1 correctly reproduce the symmetric environment of the magnesium atom. PM3 yielded an unsymmetric environment.

Table 2 AM1 parameters for main group elements

Parameter	Lithium	Beryllium	Sodium	Magnesium	Potassium	Calcium	Gallium
[a]U_{ss}	−4.9384384	−17.1528584	−5.0711164	−14.6688806	−4.2628511	−12.3085333	−29.7425311
[a]U_{pp}	−3.0959064	−14.6296419	−2.9704119	−11.8763861	−2.6669543	−9.4760505	−27.8983288
[a]β_s	−1.4598822	−4.4963564	−1.1375097	−1.1883090	−0.2601130	−4.2657396	−3.9999888
[a]β_p	−1.5278541	−2.6466323	−2.1005594	−5.2849791	−1.6603661	−6.2934710	−3.9993727
[b]ζ_s	0.7973487	0.7425237	0.7890090	1.0128928	1.2660244	1.1767754	4.0002160
[b]ζ_p	0.9045583	0.8080499	1.1399864	1.1798191	0.9555939	1.2738520	1.3540466
[b]$\zeta_{s'}$					0.7500063		
[b]ζ_p					0.6496923		
[c]α	1.5522111	0.4979614	6.0000025	5.8667260	5.8806897	1.2137738	2.0566626
[a]G_{ss}	5.3999239	7.5260764	6.4751360	6.6824002	10.0000250	6.4320360	8.9143011
[a]G_{sp}	8.9521838	8.5518975	5.4272286	7.1060848	4.8402183	6.0410623	10.9447570
[a]G_{pp}	4.4594975	1.0247326	9.5560913	9.3035830	2.9327889	5.4337615	6.8859524
[a]G_{p2}	10.0000285	9.3833365	5.4192229	9.4772262	2.7340015	5.3548430	8.4778025
[a]H_{sp}	0.3999650	0.3996483	2.8677294	0.7866442	3.0014514	0.6525142	0.5996245
[b]ρ_{core}			1.5305533	1.3507762			
[a]K_1			0.8576729	1.0000046	−1.0000221		0.0541706
[d]L_1			1.3171032	3.0000044	0.9999775		0.9999031
[e]M_1			2.0000497	2.0000043	0.4999782		2.0000642

Parameter	Arsenic	Selenium	Rubidium	Strontium	Indium	Tin	Antimony
[a]U_{ss}	−41.6817510	−41.9984056	−4.4990147	−10.9278146	−28.2223064	−26.6529104	−44.4381620
[a]U_{pp}	−33.4506152	−32.8575485	−2.9263643	−8.5185910	−18.3287837	−12.7840857	−32.3895140
[a]β_s	−5.6481504	−3.1470826	−1.9999892	−9.6008645	−6.1333658	−1.9999126	−7.3823300
[a]β_p	−4.9979109	−6.1468406	−4.4131246	−3.0661804	−0.9999602	−2.1702085	−3.6331190
[b]ζ_s	2.2576897	2.6841570	4.0000187	1.5236848	1.8281576	1.6182807	2.2548230
[b]ζ_p	1.7249710	2.0506164	1.0140619	1.5723524	1.4847500	1.5084984	2.2185920
[c]α	2.2405380	2.6375694	1.1550020	4.6716058	1.8590637	1.6753624	2.2763310
[a]G_{ss}	11.0962258	6.7908891	18.7604025	5.1033321	9.3685202	7.0918140	11.4302510
[a]G_{sp}	4.9259328	6.4812786	18.0931959	4.4927652	6.6873024	2.9999326	5.7879220
[a]G_{pp}	7.8781648	6.4769273	10.8002500	4.2101543	5.9406805	5.3314764	6.4240940
[a]G_{p2}	7.5961088	5.2796993	9.5613216	4.3004995	4.9356943	3.5204737	6.8491810
[a]H_{sp}	0.6246173	4.4548356	0.7084525	0.7724969	0.5998997	2.9523812	0.5883400
[a]K_1	−0.0073614	0.1116681	0.6444472		0.1182997	−0.3446636	−0.5964470
[d]L_1	4.9433993	6.5086644	0.9994819		1.0033833	1.9822018	6.0279500
[e]M_1	1.4544264	1.4981077	2.0004780		1.8646418	1.3433163	1.7103670
[a]K_2	0.0437629	0.0396143					0.8955130
[d]L_2	3.1944613	6.5241228					3.0281090
[e]M_2	2.0144939	2.0751916					1.5383180

Parameter		Tellurium	Cesium	Barium	Thallium	Lead	Bismuth
[a]U_{ss}		−39.2454230	−3.1358230	−10.1164434	−29.8282621	−38.6798569	−42.0556490
[a]U_{pp}		−30.8515845	−1.6791847	−8.0393806	−30.5358091	−26.4559953	−34.9221058
[a]β_s		−8.3897294	−4.4412054	−9.9997673	−6.6096803	−6.5924919	−0.9993474
[a]β_p		−5.1065429	−4.3246899	−9.7724365	−6.5157709	−1.3368867	−1.8948197
[b]ζ_s		2.1321165	5.7873708	1.9136517	3.8077333	2.4432161	4.0007862
[b]ζ_p		1.9712680	1.0311693	1.3948894	1.5511578	1.5506706	0.9547714
[c]α		6.0171167	0.5267821	0.9963852	1.2571916	1.6534073	1.9060635
[a]G_{ss}		4.9925231	3.8928349	4.8572599	9.0641669	8.6199280	10.3839608
[a]G_{sp}		4.9721484	2.9638098	4.4042932	12.5941972	7.6465534	5.7403240
[a]G_{pp}		7.2097852	5.6069289	4.7218273	10.2189635	6.7366709	12.2196363
[a]G_{p2}		5.6211521	3.5192887	4.8406105	13.0987769	5.4967156	11.2050063
[a]H_{sp}		4.0071821	0.3994827	0.5159824	0.5997632	1.2176598	5.0004083
[a]K_1		0.4873378	−1.0009018		−0.5293156	−0.3085992	−1.0004931
[d]L_1		6.0519413	2.4474604		1.2083491	3.0001372	1.5860780
[e]M_1		1.3079857	0.6728225		1.4794195	1.6877190	1.1085026
[a]K_2		0.1520464					
[d]L_2		3.8304067					
[e]M_2		2.0899707					

[a]eV   [b]Bohr   [c]Å^{-1} [d]Dimensionless   [e]Å

Table 3 PM3 parameters for main group elements

Parameter	Boron	Sodium	Potassium	Calcium
$^aU_{ss}$	−50.4776829	−5.0140594	−4.2596475	−11.9608156
$^aU_{pp}$	−37.4119835	−2.9252301	−2.6425087	−8.6350859
$^a\beta_s$	−10.5497263	−3.9486341	−0.4250386	−0.9868271
$^a\beta_p$	−3.9995953	−4.2401809	−3.1998137	−3.9684267
$^b\zeta_s$	1.5312597	2.6618938	0.8101687	1.2087415
$^b\zeta_p$	1.1434597	0.8837425	0.9578342	0.9409370
$^c\alpha$	2.2104163	0.9109177	0.7252158	0.4999979
$^aG_{ss}$	18.2782796	5.7975247	6.7788311	5.9719910
$^aG_{sp}$	15.3330673	10.0000062	9.3472796	4.9607780
$^aG_{pp}$	12.3158582	1.2247903	3.4963514	3.7214897
$^aG_{p2}$	11.1785351	0.9996497	2.7416795	3.7116499
$^aH_{sp}$	0.5997885	0.3999363	1.6592458	0.7928150
$^aK_1$	−0.3518407			
$^dL_1$	3.0008621			
$^eM_1$	0.8241176			

Parameter	Rubidium	Strontium	Cesium	Barium
$^aU_{ss}$	−4.5920539	−10.9183439	−3.2036564	−10.1028101
$^aU_{pp}$	−3.0119211	−7.9835223	−1.7451970	−6.6743838
$^a\beta_s$	12.0894660	−10.0000071	−0.6028761	−10.0000046
$^a\beta_p$	−1.9999268	−5.6755392	−5.9386091	−10.0000103
$^b\zeta_s$	4.0000415	1.2794532	3.5960298	1.9258219
$^b\zeta_p$	1.0134590	1.3912500	0.9255168	1.4519912
$^c\alpha$	0.9985324	1.6467554	0.5238336	0.4999966
$^aG_{ss}$	9.2757213	5.0361465	2.1605658	4.8372407
$^aG_{sp}$	20.0000037	3.9284011	4.1667498	3.1942225
$^aG_{pp}$	13.3694136	3.1533139	5.4140484	2.1243276
$^aG_{p2}$	19.0000035	3.2457312	6.2904939	2.2153940
$^aH_{sp}$	4.9987146	0.7596212	0.3995561	0.3999242

^{a}eV; ^{b}Bohr; ^{c}Å^{-1}; ^{e}Å; ^{d}dimensionless

Methyl magnesium fluoride

Both MNDO and AM1 overestimate the Mg–C distance, 2.08 Å, [19] by about 0.05 Å, and underestimate the Mg–F distance, 1.78 Å, by 0.04 Å.

Ethyl magnesium bromide–diethyl ether complex, $EtMgBr.(Et_2O)_2$

In this Grignard reagent, the ethyl magnesium bromide forms a complex with two molecules of diethyl ether. All three methods underestimate the Mg–Br distance by less than 0.1 Å. MNDO and AM1 reproduce the Mg–O and Mg–C distances accurately, but PM3 underestimates these distances by 0.2 Å.

Dicyclopentadienyl magnesium

The sandwich D_{5d} structure is reproduced, with the Mg–ring distance being overestimated in all three methods by about 0.1 Å.

Cesium sulfate

Cs_2SO_4 forms a D_{2d} structure with the Cs–O distance of 2.8 Å. [20] This structure is reproduced by the three methods, but both MNDO and PM3 underestimate the Cs–O distance as 2.15 Å and 2.65 Å, respectively.

The Cs–C distance in Cs–CP is completely unrealistic; the calculated value being 0.58 Å. This is apparently a consequence of the very small core charge on Cs, +1. In NDDO methods, the core electrons are simply subtracted from the nuclear charge to give a net charge for the nucleus; this approximation works for most elements, because the core–core interaction involves quite large pre-multipliers, but for the higher atomic number Group I elements, problems occur. To a lesser degree, similar problems occur with Group II elements, particularly barium. For these elements, the approximation that the atom is hydrogen-like introduces errors that are too severe to be accommodated by the parameters. When diatomic core–core parameters are used the geometries of many Group I compounds can be predicted with useful accuracy, but when diatomic parameters are absent, as in the case of Cs–P, unrealistic geometries result. Because of this behavior, the results of calculations involving Groups I and II should not be regarded as reliable where values for diatomic parameters are not available.

Calcium hydroxide

In aqueous media, the nearest atom to a calcium ion is likely to be oxygen, therefore the Ca–O distance is of importance in biochemistry. A measure of the accuracy of reproduction of this environment is provided by the

Table 4 Diatomic core−core parameters

Element	Element	MNDO		AM1		PM3	
		$^a\alpha_{M-X}$	$^b\delta_{M-X}$	$^a\alpha_{M-X}$	$^b\delta_{M-X}$	$^a\alpha_{M-X}$	$^b\delta_{M-X}$
Lithium	Hydrogen			2.975116	10.000006		
Lithium	Lithium			2.074231	10.000005		
Lithium	Chlorine			1.779447	1.436235		
Lithium	Fluorine			1.890271	1.542043		
Lithium	Bromine			1.886037	2.214447		
Lithium	Iodine			2.648765	9.992209		
Beryllium	Hydrogen			1.521999	0.535972		
Beryllium	Beryllium			0.999154	0.441202		
Sodium	Hydrogen	2.509533	10.000001	2.430601	9.994724	1.800472	3.171946
Sodium	Carbon	1.600907	1.968197	1.711276	2.226935	1.321600	0.876072
Sodium	Nitrogen	2.137374	7.127566	2.323882	10.000002	0.999895	0.295812
Sodium	Oxygen	1.645246	1.815137	2.161260	4.057658	2.116028	3.392634
Sodium	Fluorine	1.454308	1.176276	2.056819	3.274203	1.860719	1.605474
Sodium	Sodium	1.237658	4.403848	1.612164	9.944446	1.024150	1.126080
Sodium	Sulfur	3.292794	2.813852	1.903681	1.053743	0.999990	0.241710
Sodium	Chlorine	1.808032	2.574233	1.968902	4.053650	1.420756	1.168589
Sodium	Bromine	2.403632	10.000000	2.189596	9.992652	1.517965	1.741658
Sodium	Iodine	2.138290	10.000000	2.130872	10.000000	1.148784	0.747959
Magnesium	Hydrogen	2.225309	3.720059	2.174856	2.832813		
Magnesium	Carbon	2.261280	4.077811	2.216434	2.837201		
Magnesium	Nitrogen	2.235036	2.449707	2.091799	1.504138		
Magnesium	Oxygen	1.861494	1.028465	1.666897	0.472916		
Magnesium	Fluorine	2.020390	1.351638	2.142571	1.227425		
Magnesium	Magnesium	1.836049	10.000011	1.794083	10.000008		
Magnesium	Sulfur	2.042320	2.144097	1.572524	0.571504		
Magnesium	Chlorine	1.827473	1.305523	1.875713	1.195314		
Magnesium	Bromine	2.275335	3.649579	1.939738	1.898893		
Magnesium	Iodine	2.563705	10.000000	2.685633	9.956335		
Potassium	Hydrogen	1.320313	4.298548	2.224557	9.800241	1.027701	0.893642
Potassium	Carbon	0.999445	0.849075	1.687938	3.166630	1.453975	2.009100
Potassium	Nitrogen	2.161504	6.502600	1.938615	7.651496	0.999984	0.425244
Potassium	Oxygen	2.008450	2.658504	1.461751	1.046264	1.470651	0.999945
Potassium	Fluorine	0.999684	0.489361	1.402823	0.811417	0.999898	0.342063
Potassium	Sulfur	3.669853	8.085841	3.439238	9.817827	1.000576	0.584513
Potassium	Chlorine	1.873677	5.877136	2.072076	8.149694	0.999989	0.584823
Potassium	Potassium	1.428561	8.818535	1.267822	9.852489	1.532875	8.250024
Potassium	Bromine	2.029580	8.686070	1.997576	9.709128	1.401604	2.440790
Potassium	Iodine	1.848045	8.419048	2.062884	9.900715	1.402113	2.568324
Calcium	Hydrogen	1.232916	2.523722	1.593033	3.654870	1.427846	1.805489
Calcium	Carbon	0.999988	0.719460	1.005258	0.567133	0.999993	0.320183
Calcium	Nitrogen	0.999988	0.478031	1.003892	0.453895	0.999993	0.275261
Calcium	Oxygen	1.971239	1.362643	2.574888	2.892181	1.934512	0.480203
Calcium	Fluorine	1.519589	0.714119	2.268048	1.986328	1.964914	0.594612
Calcium	Sulfur	0.999943	0.473306	0.999897	0.335089	0.999960	0.212682
Calcium	Chlorine	1.106581	0.445562	1.694685	1.371206	1.669363	0.928683
Calcium	Calcium	0.999160	9.359604	0.999786	4.524140	0.999174	3.160373
Calcium	Bromine	1.217321	0.622015	1.635628	1.769827	1.509690	0.874420
Calcium	Iodine	1.233027	1.073378	2.164489	7.940431	1.513600	0.856865
Rubidium	Hydrogen	2.163911	7.659030	1.999930	7.589965	2.066936	9.999919
Rubidium	Boron			1.999970	6.012783	1.996668	10.000119
Rubidium	Oxygen	3.605597	6.635511	1.999662	2.914922	1.999948	1.817233
Rubidium	Fluorine	2.940757	6.559839	2.914271	8.743147	3.083855	10.000006
Rubidium	Chlorine	2.006252	3.308870	1.999948	3.708034	2.371423	9.970607
Rubidium	Bromine	2.135073	5.523206	1.999755	6.443546	2.071332	7.407687
Rubidium	Rubidium	2.329519	7.321125	1.999854	10.000003	0.539344	2.654922
Strontium	Hydrogen	0.999390	3.279894	1.491059	8.262735	1.385332	7.195639
Strontium	Carbon	1.006168	0.104550	3.009340	5.935637	1.392807	5.455084
Strontium	Nitrogen	1.003353	0.104635	3.004535	6.408169	1.392514	5.293460
Strontium	Oxygen	2.523434	1.384826	2.987339	5.727702	2.471371	2.147711
Strontium	Fluorine	1.779157	1.149661	1.849351	1.086554	2.525416	5.359983
Strontium	Sulfur	1.014322	0.562327	2.051857	4.276806	1.045944	0.594774
Strontium	Chlorine	1.101161	0.419825	2.072171	4.093194	1.473507	1.176805
Strontium	Bromine	0.999859	0.394830	2.168786	8.440324	1.338861	1.082828
Strontium	Strontium	1.004898	0.103370	2.982057	6.335178	1.393785	5.138251
Strontium	Iodine	0.999837	0.819781	2.011009	6.634610	1.730393	3.855491
Cesium	Hydrogen	1.332561	8.705312	0.997604	1.985832	1.448617	6.721688
Cesium	Carbon	1.090683	4.897821	0.999375	0.099375	0.999871	5.579858

Table 4 (continued)

Element	Element	MNDO		AM1		PM3	
		[a]α_{M-X}	[b]δ_{M-X}	[a]α_{M-X}	[b]δ_{M-X}	[a]α_{M-X}	[b]δ_{M-X}
Cesium	Nitrogen	0.999646	0.099792	0.998759	0.205926	0.999559	0.242498
Cesium	Oxygen	3.528675	4.390620	2.249702	1.307467	3.222538	7.547802
Cesium	Fluorine	2.999365	4.453994	0.999854	0.119889	2.748652	3.360596
Cesium	Phosphorus	2.593617	0.190509	0.999228	0.099806	0.999863	0.099894
Cesium	Sulfur	4.000021	4.423858	0.997626	0.766755	0.999607	0.869429
Cesium	Chlorine	1.969222	3.000681	1.061905	0.324568	0.999578	0.288955
Cesium	Bromine	2.046451	4.694115	0.999274	0.416656	0.999651	0.350614
Cesium	Iodine	1.847641	3.998888	1.135145	0.642690	0.998419	0.377054
Cesium	Cesium	0.996356	4.999747	0.994764	3.263516	0.997434	8.549732
Barium	Hydrogen	1.171257	0.099982	1.081595	0.108779	0.999997	0.099997
Barium	Carbon	1.047588	0.099981	1.005494	0.109472	0.999997	0.099997
Barium	Nitrogen	1.000237	0.099981	1.004182	0.109951	0.999997	0.099997
Barium	Oxygen	1.422688	0.383114	1.630584	0.465945	1.249857	0.352542
Barium	Fluorine	1.730509	1.127771	2.230982	2.476341	1.886689	1.528347
Barium	Sulfur	1.505311	1.957151	1.000116	0.714303	0.999862	0.904098
Barium	Chlorine	1.129944	0.557748	1.341436	1.041642	1.490059	1.846584
Barium	Bromine	1.585564	2.326451	1.427436	2.384411	1.628325	3.652542
Barium	Iodine	1.271836	1.714690	1.303416	2.097065	1.461169	2.514512
Barium	Barium	1.000402	0.136939	1.110416	0.101890	0.999997	0.099997

[a]Å^{-1} [b]Dimensionless (see Eq. 6)

Table 5 Average errors in heats of formation (kcal mol^{-1}) (numbers in bold=this work)

Element	MNDO	AM1	PM3	No. in set
Lithium	7.5	**5.3**	13.5	44
Beryllium	14.1	**3.5**	7.9	19
Boron	16.9	13.9	**11.3**	103
Sodium	**6.2**	5.0	6.5	29
Magnesium	**6.7**	7.1	11.4	37
Potassium	7.1	6.1	**2.3**	21
Calcium	4.1	4.8	**4.3**	15
Gallium	**15.2**	25.8	17.0	21
Arsenic	**13.8**	**13.1**	8.6	20
Selenium	**11.7**	**14.6**	16.3	17
Rubidium	**11.1**	**8.6**	**5.7**	11
Strontium	**4.5**	4.3	3.4	12
Indium	**13.0**	10.6	11.9	20
Tin	10.7	**8.5**	8.6	41
Antimony	**12.4**	13.9	12.9	18
Tellurium	**16.7**	21.7	15.0	14
Cesium	**16.2**	**16.4**	**12.4**	26
Barium	**4.3**	**3.6**	**2.7**	10
Thallium	**1.9**	7.2	15.6	8
Lead	11.0	**12.1**	8.5	23
Bismuth	**22.1**	**39.9**	11.4	9

Table 6 Average errors in bond lengths (ångstroms) (numbers in bold=this work)

Element	MNDO	AM1	PM3	No. in set
Lithium	0.050	**0.039**	0.099	24
Beryllium	0.090	**0.062**	0.069	12
Boron	0.107	0.046	**0.076**	101
Sodium	**0.044**	**0.040**	**0.096**	16
Magnesium	**0.053**	**0.053**	0.171	46
Potassium	0.123	**0.104**	**0.114**	15
Calcium	**0.090**	**0.070**	**0.078**	17
Gallium	**0.142**	**0.101**	0.142	26
Arsenic	**0.037**	**0.030**	0.016	12
Selenium	**0.063**	**0.044**	0.040	39
Rubidium	**0.139**	**0.100**	**0.067**	9
Strontium	**0.099**	**0.047**	**0.030**	6
Indium	**0.071**	**0.074**	0.053	9
Tin	0.098	**0.041**	0.035	26
Antimony	**0.212**	**0.143**	0.126	10
Tellurium	**0.162**	**0.083**	0.074	18
Cesium	**0.325**	**0.093**	**0.312**	14
Barium	**0.040**	**0.033**	**0.036**	7
Thallium	**0.092**	**0.091**	0.054	7
Lead	0.103	**0.087**	0.073	17
Bismuth	**0.511**	**0.544**	0.012	3

species Ca(OH)$_2$. The observed Ca–O distance, 2.04 Å, [21] is reproduced within 0.1 Å by all three methods.

Discussion

The use of a diatomic CRF approximation was found to be essential for correctly modeling compounds of the alkali metals. Such compounds range in bonding from 100% covalent, as in the homonuclear diatomics, to very ionic, as in the halides. When purely monatomic parameter approximations were used, the simultaneous modeling of covalent and ionic species was not satisfactory. When diatomic parameters were used, a large improvement in accuracy was obtained.

The accuracy and limitations of the use of diatomic parameters can be observed in the predicted interatomic separations in the alkali metal halides, Table 10. In many instances, the agreement between predicted and observed bond lengths is excellent. This frequently occurs when the number of reference data involving both elements is small. In other cases, exemplified by cesium fluoride, the agreement was unsatisfactory.

Table 7 Average errors in angles (degrees) (numbers in bold=this work)

Element	MNDO	AM1	PM3	No. in set
Boron	3.02	3.38	**5.49**	32
Sodium	**4.96**	**5.32**	**3.43**	4
Magnesium	**3.00**	**2.61**	4.93	4
Potassium	**10.26**	**3.88**	**8.25**	4
Gallium	**0.12**	**1.66**	0.22	1
Arsenic	**6.01**	**2.42**	2.48	10
Selenium	**14.85**	**4.19**	10.04	21
Tin	2.81	**2.03**	1.80	10
Antimony	**9.16**	**2.82**	2.00	5
Tellurium	**21.46**	**7.09**	4.89	5
Cesium	**9.57**	**1.94**	**3.82**	1
Barium	**41.72**	**43.07**	**41.23**	2
Thallium	**22.46**	**26.16**	1.29	1
Lead	3.58	**3.43**	4.75	5
Bismuth	**36.24**	**44.71**	1.22	3

Table 8 Average errors in dipole (debye) (numbers in bold=this work)

Element	MNDO	AM1	PM3	No. in set
Lithium	0.79	**0.51**	0.64	16
Beryllium	**0.05**	**0.55**	**0.26**	1
Boron	0.69	0.59	**0.79**	13
Sodium	**1.02**	**1.21**	**1.63**	5
Potassium	**0.48**	**0.59**	**1.29**	4
Calcium	**0.34**	**0.33**	**1.24**	4
Gallium	**1.00**	**0.64**	1.35	1
Arsenic	**0.95**	**0.37**	0.35	6
Selenium	**1.43**	**0.79**	0.61	10
Rubidium	**0.64**	**0.26**	**0.95**	4
Strontium	**1.60**	**0.12**	**1.42**	2
Indium	**1.08**	**1.70**	0.72	2
Tin	1.04	**0.66**	0.65	10
Antimony	**0.49**	**0.12**	0.42	1
Tellurium	**7.94**	**1.54**	0.22	3
Cesium	**2.18**	**1.05**	**2.02**	5
Barium	**1.48**	**0.87**	**1.35**	4
Thallium	**2.33**	**2.35**	0.35	3
Lead	2.06	**0.92**	0.38	5

Table 9 Average unsigned errors for previously parameterized elements

Method	Element	ΔH_f	Bond length	Dipole
AM1	Na [17]	9.0	0.239	1.31
AM1	Mg [25]	17.6	0.276	–
AM1	Sn [18]	11.1	0.061	0.62
PM3	Na [17]	16.7	0.191	1.53

When the new parameters were used for modeling solids, the results were unsatisfactory. This is illustrated by the alkali metal halides that crystallize in the rock-salt form. Calculations of the solids were performed using the cluster method. [22, 23] This uses Born–von Kármán [24] periodic boundary conditions to simulate the infinite solids. Clusters of 218 atoms, representing cubes with six atoms on each edge, were used. Symmetry was used to accelerate the geometry optimization; there being only one geometric variable, the optimization involved only a

Table 10 Bond lengths and dipole moments for alkali metal halides

Compound	Exp. R(M–X) [26]	Calc. R(M–X) PM3	Exp. dipole [26]	Calc. dipole PM3
Lithium fluoride	1.56	1.58	6.28	5.32
Lithium chloride	2.02	1.88	7.09	6.54
Lithium bromide	2.17	1.80	7.23	6.39
Lithium iodide	2.39	2.19	7.43	7.51
Sodium fluoride	1.93	1.93	8.12	5.13
Sodium chloride	2.36	2.33	8.97	7.70
Sodium bromide	2.50	2.50	9.09	8.01
Sodium iodide	2.71	2.71	9.21	8.82
Potassium fluoride	2.19	2.20	8.56	8.36
Potassium chloride	2.70	2.71	10.24	11.15
Potassium bromide	2.87	3.05	10.63	11.26
Potassium iodide	3.09	3.31	10.82	13.23
Rubidium fluoride	2.27	2.27	8.51	8.73
Rubidium chloride	2.79	2.79	10.48	12.19
Rubidium bromide	2.94	2.94	10.86	11.84
Rubidium iodide	3.18	3.13	11.48	12.55
Cesium fluoride	2.35	1.39	7.85	3.66
Cesium chloride	2.91	2.91	10.36	12.45
Cesium bromide	3.07	3.07	10.82	12.03
Cesium iodide	3.32	3.33	11.69	12.42

single line search. The agreement between the predicted and observed densities was very poor, with errors of 300% being common. This lack of agreement can be attributed to the absence of any solids in the parameter optimization procedure.

In the alkali metal halides, the dipole moments are very sensitive to the interatomic separation, and a poorly predicted geometry invariably results in a poorly predicted dipole. This is again shown in cesium fluoride, where the calculated dipole is in error by over 4 D.

With the completion of the development of parameters for the main group elements, the main emphasis in future work will be to acquire more reference data, and to improve the accuracy of prediction of properties. Hitherto, great difficulty has been encountered in developing computational models, mainly because of the lack of precursor geometries. The central task of parameterizing the approximations used in semiempirical methods was made more complicated by the propensity of molecular structures to spontaneously change into something unphysical during the parameter optimization process. This was usually a consequence of the initial values of the parameters being too far from the optimum. Now that parameters and geometries are available for compounds of all non-radioactive elements of Groups I to VII, future developments can be focused on increasing the accuracy of prediction by the development of more physically realistic approximations and by improved parameter optimization methods.

Limitations

The validity of application of the parameters to metallic systems such as solid metals has not yet been determined.

Table 11 References for elements of main group (*=this work)

Element	MNDO	AM1	PM3	Element	MNDO	AM1	PM3
Hydrogen	[4]	[5]	[7]	Gallium	*	*	[8]
Lithium	[9]	*	[13]	Germanium	[27]	[28]	[8]
Beryllium	[10]	*	[8]	Arsenic	*	*	[8]
Boron	[29]	[30]	*	Selenium	*	*	[8]
Carbon	[4]	[5]	[7]	Bromine	[31]	[32]	[7]
Nitrogen	[4]	[5]	[7]	Rubidium	*	*	*
Oxygen	[4]	[5]	[7]	Strontium	*	*	*
Fluorine	[33]	[32]	[7]	Indium	*	*	[8]
Sodium	*	*	*	Tin	[34]	*	[8]
Magnesium	*	*	[8]	Antimony	*	*	[8]
Aluminum	[29]	[35]	[7]	Tellurium	*	*	[8]
Silicon	[36]	[37]	[7]	Iodine	[38]	[32]	[7]
Phosphorus	[39]	[40]	[7]	Cesium	*	*	*
Sulfur	[41]	[42]	[7]	Barium	*	*	*
Chlorine	[43]	[32]	[7]	Thallium	*	*	[8]
Potassium	[12]	*	*	Lead	[44]	*	[8]
Calcium	*	*	*	Bismuth	*	*	[8]

Solid metals contain a Fermi surface, and current semiempirical programs cannot model such systems. This does not imply that the parameters are not suitable for the study of metals, only that the applicability of the parameters for such work has not been determined, due to software limitations.

The validity of applicability of the parameter sets reported here to compounds involving bonding between atom pairs other that those listed in Table 4 has not been determined, and is likely to be poor. Thus the properties of the hypothetical species Na–K are unlikely to be reproduced accurately, because diatomic core–core parameters involving both Na and K have not been determined.

References for main group elements

With the development of these parameters, all 34 elements of the main group, with the exceptions of the radioactive elements and the noble gasses, are now available. References for elements parameterized are shown in Table 11.

Conclusion

With the publication of the 44 sets of parameters, the mapping of the more important elements of the main group is completed for the semiempirical methods MNDO, AM1, and PM3. Average errors in heats of formation are somewhat higher than for the other elements. No specific reason was found for this, although it is probable that the error lies in the set of approximations used or in the parameter optimization procedure. In developing the parameters reported here, the parameters for elements previously optimized were held constant. As these parameters were defined without using any of the compounds reported here, it is not surprising that the average values for errors are increased. One obvious way to avoid this problem would be to simultaneously optimize all parameters for all of the main group elements.

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