



Sparkle/PM6 Parameters for all Lanthanide Trications from La(III) to Lu(III)

Ricardo O. Freire[†] and Alfredo M. Simas^{*,‡}

*Departamento de Química, Universidade Federal de Sergipe,
49.100-000, São Cristóvão, SE, Brazil and Departamento de Química Fundamental,
Universidade Federal de Pernambuco, 50.740-540, Recife, PE, Brazil*

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Abstract: PM6 is the first semiempirical method to be released already parametrized for the elements of the periodic table, from hydrogen to bismuth ($Z = 83$), with the exception of the lanthanides from cerium ($Z = 58$) to ytterbium ($Z = 70$). In order to fill this gap, we present in this article a generalization of our Sparkle Model for the quantum chemical semiempirical calculation of lanthanide complexes to PM6. Accordingly, we present Sparkle/PM6 parameters for all lanthanide trications from La(III) to Lu(III). The validation procedure again considered only high-quality crystallographic structures and included 633 complexes. Sparkle/PM6 unsigned mean errors $UME_{(Ln-L)}s$, corresponding to all the interatomic distances between the lanthanide ion and the atoms directly coordinated to it, range from 0.066 to 0.086 Å for Gd(III) and Ce(III), respectively. These minimum and maximum $UME_{(Ln-L)}s$ across the lanthanide series are comparable to the Sparkle/AM1 values of 0.054 and 0.085 Å for Ho(III) and Pr(III), respectively, as well as to the values for Sparkle/PM3 of 0.064 and 0.093 Å for Gd(III) and Pr(III), respectively. Moreover, for all 15 lanthanide ions, these interatomic distance deviations follow a γ distribution within a 95% level of confidence, indicating that these errors appear to be random around a mean, freeing the model of systematic errors, at least within the validation set. Sparkle/PM6 presented here, therefore, broadens the range of applicability of PM6 to the coordination compounds of the rare earth metals.

Introduction

Parametric method number 6, PM6,¹ is the latest in a series of semiempirical methods which encompass MNDO,^{2,3} AM1,⁴ PM3,^{5–8} and RM1.⁹ The accuracy of PM6 in predicting enthalpies of formation, yielding an unsigned mean error of 4.4 kcal.mol^{−1} for a representative set of 1373 compounds, exceeds those of Hartree–Fock (7.4 kcal.mol^{−1}) or B3LYP DFT (5.2 kcal.mol^{−1}) methods. PM6 has also been successfully used for modeling proteins and a variety of their properties.¹⁰ Moreover, PM6 has been further shown to be capable of reproducing the geometries and the enthalpies of formation of several solids with useful accuracy.¹¹

The Sparkle Model is a semiempirical approach to the quantum chemical calculation of lanthanide complexes, originally introduced by our research group in 1994.^{12,13} It replaces the lanthanide ions by a Coulombic charge of $+3e$, superimposed to a repulsive exponential potential of the form $\exp(-\alpha r)$, which was introduced to mimic the effect of the size of the ion. Thus, the Sparkle Model assumes that the angular effects of the f-orbitals are negligible and does not take them into account, being, thus, a spherically symmetric model. The Sparkle Model was improved in a subsequent article¹⁴ by the addition of two Gaussian functions to the core–core repulsion energy term, and by including the lanthanide mass, which allowed the calculation of vibrations and thermochemical quantities.¹⁵ Major and significant improvements to the parametrization procedure were then carried out, eventually leading to Sparkle/AM1,¹⁵ the first semiempirical quantum chemical model to be parametrized

* Corresponding author. E-mail: simas@ufpe.br.

[†] Universidade Federal de Sergipe.

[‡] Universidade Federal de Pernambuco.

for the whole lanthanide series.^{16–24} More recently, in order to allow the user a choice for the modeling of the organic motif of the complexes, Sparkle/PM3 was subsequently introduced.^{25–31}

The Sparkle Model was designed to reproduce the coordinating polyhedra of the complexes. That is because the geometry of a lanthanide coordination compound is its single most important feature for complex design.³² Indeed, for example, when designing a highly luminescent complex, one aims at achieving high-energy transfer rates from the ligands to the central metal ion, followed by a subsequent intense emission of light. For that purpose, the interaction between the ligands and the central metal ion can be described by the ligand field parameters, which can be calculated from the knowledge of the geometry of the coordination polyhedron. Within the simple overlap model,^{33,34} the ligand field parameters depend on the third, fifth, and seventh powers of the lanthanide–ligand interatomic distances, thus requiring an accurate knowledge of these distances. Likewise, for the design of contrast agents for magnetic resonance imaging, an accurate knowledge of the distance between the gadolinium ion and the oxygen atom of the coordinating water molecule is required. That is because the important dipolar relaxation mechanism has a dependency on the inverse sixth power of this distance. Again, any inaccuracies in this distance are greatly amplified when one tries to determine the relaxation rate of solvent protons, known as relaxivity.³⁵ A larger relaxivity implies that the required contrast agent may be administered in lower doses or that the imaging can be carried out in regions of lower contrast agent concentrations.

PM6 has been published and released already parametrized for 70 elements, from hydrogen to bismuth, with the exception of the lanthanides from cerium to ytterbium ($Z = 58$ and 70 , respectively).

Therefore, in order to broaden the range of applicability of PM6, we generalize in this article the Sparkle Model by introducing Sparkle/PM6 parameters for all lanthanide trications, from La(III) to Lu(III).

Results and Discussion

PM6 is a neglect of diatomic differential overlap (NDDO) method modified by the adoption of a slightly improved version of Voityuk's core–core diatomic parameters³⁶ to improve the predicted enthalpies of formation and geometries as well as rare gas interactions. On the other hand, the Sparkle Model does not require diatomic parameters, and therefore, for PM6, we maintained the same monatomic Sparkle core–core potential $E_N(A,B)$ with only two Gaussian functions, as fully described before.¹⁵

Although PM6, when released, already had parameters for lanthanum and lutetium, we decided to also make available PM6 sparkles for the trivalent ions of these atoms as well, to make the set consistent with Sparkle/AM1 and Sparkle/PM3.

Sparkle/PM6 parameters were obtained via the same parametrization procedure carried out to obtain the Sparkle/AM1¹⁵ and Sparkle/PM3 parameters.³¹ As such, we only used high-quality crystallographic structures

(R -factor $< 5\%$) obtained from the Cambridge Structural Database (CSD),^{37,38} and for the case of promethium, structures obtained by ab initio calculations,²¹ having selected a total of 633 complexes. From these, we took, as training sets, the same 15 subsets of 15 complexes for each lanthanide trication, previously chosen for the parametrization of Sparkle/AM1,^{16–24} and carried out the optimization following the same methodology as described before.¹⁵

The Sparkle/PM6 parameters found for all 15 lanthanide trications are shown in Table 1. In order to proceed with the validation, we used as geometry accuracy measures the average unsigned mean error for each complex i , UME_i , defined by

$$UME_i = \frac{1}{n_i} \sum_{j=1}^{n_i} |R_{ij}^{CSD} - R_{ij}^{calc}| \quad (1)$$

where n_i is the number of atoms in the coordination polyhedron of the lanthanide ion. Two cases were examined: (i) $UME_{(Ln-L)}$, where we considered only the interatomic distances between the lanthanide ion, Ln, and the atoms directly coordinated to it, L, and (ii) UMEs of all the edges of all faces of the pyramids defined by the lanthanide ion in the apex as well as all interatomic distances between all atoms of the coordination polyhedron.

Once again, it is important to assess whether Sparkle/PM6 provides a good and reliable representation of lanthanide complexes, free of systematic errors, at least within the validation set of complexes. For that to be true, the $UME_{(Ln-L)}$ s and the UMEs of all distances of all complexes of the test set should be randomly distributed about the mean, whose value can be used as a measure of the accuracy of the model. Therefore, $UME_{(Ln-L)}$ s and the UMEs should follow the probability density function of the γ distribution, since UMEs are positive and defined in the domain $(0, \infty)$. We then proceeded by obtaining a fit of the UMEs to a γ distribution function, from which the mean and variance could be determined. The quality of the γ distribution fit can be assessed via the one-sample nonparametric Kolmogorov–Smirnov test³⁹ in order to verify statistically whether the distribution of the UME values could be represented by a γ distribution indexed by the estimated mean and variance. If the p -value of the test is larger than 0.05, the γ distribution fit is indeed justified within a 95% confidence interval, and the mean and variance can be used as accuracy measures of the model.

The Supporting Information contains tables with the individual $UME_{(Ln-L)}$ s and UMEs for all 633 complexes. Table 2 summarizes these data for the $UME_{(Ln-L)}$ s for each lanthanide trication. The p -values of the γ distribution fits are all well above 0.05, implying they are all statistically valid. The average value of all $UME_{(Ln-L)}$ means is 0.0741 Å, whereas the average value of the respective variances is 0.0012 Å². One can see that these values are relatively constant throughout the table, with the maximum $UME_{(Ln-L)}$ being 0.0856 Å for Ce(III) and the minimum being 0.0663 Å for Gd(III). The corresponding low value for Pm(III), 0.0619 Å, is not strictly comparable with the others because

Table 1. Parameters for the Sparkle/PM6 Model for All Lanthanide Trications from La(III) to Lu(III)

Sparkle/PM6					
	La ³⁺	Ce ³⁺	Pr ³⁺	Nd ³⁺	Pm ³⁺
α	2.0955474333	2.1249588196	2.4693712260	4.1738480733	3.0374070006
GSS	55.7614959637	58.8260906171	58.3343604075	57.6974644976	59.5665725491
a_1	0.9198962192	1.7329167054	2.8321015232	1.1507966088	1.8134017776
b_1	7.1956586116	7.4140930052	7.1195524904	6.4949658378	9.0994056545
c_1	1.8688421745	1.7149281546	1.6208236553	1.5653255583	1.6148716177
a_2	0.3395617280	0.0764294472	0.0541169724	0.1889516026	0.2759193756
b_2	8.5194840290	8.4974750829	7.8230014741	10.9231117908	7.2120871121
c_2	3.1236739454	3.0778367381	3.1133411960	3.0169407149	3.0287226366
	Sm ³⁺	Eu ³⁺	Gd ³⁺	Tb ³⁺	Dy ³⁺
α	4.0858458124	2.0467722838	2.1346333468	2.5139941133	2.5510632015
GSS	56.8573294165	55.6632255486	56.8944696903	55.2205687662	55.8786332882
a_1	1.5645679440	0.2712333739	0.2517865588	0.5222813525	1.1809130487
b_1	6.4255324886	7.3743656586	8.7505991931	7.9527873623	8.9849822704
c_1	1.4885991013	1.7955662564	1.7313405711	1.7550018623	1.6756952638
a_2	0.1021969444	0.3493713916	0.1221903028	0.3099626210	0.4066395540
b_2	9.4102061689	7.7881047906	7.4979582981	6.6812787003	8.9799453811
c_2	3.1094973204	2.9632616015	2.9344373061	2.9759649920	2.9787279400
	Ho ³⁺	Er ³⁺	Tm ³⁺	Yb ³⁺	Lu ³⁺
α	3.4814819284	3.6603230421	2.3042905227	4.2104920412	3.2076166779
GSS	56.0010800433	58.4870426290	56.3699484190	56.3592753390	56.2871833842
a_1	0.3389541104	0.4687052850	0.7757838661	1.0542080628	0.6496316332
b_1	8.1824420999	9.3819581436	8.3570694122	8.5454710978	9.2468459960
c_1	1.6446707189	1.7306657473	1.6489766048	1.4993488570	1.5344631779
a_2	0.1333201849	0.2107436963	0.2905574744	0.1983232376	0.2355401411
b_2	8.7112042124	8.4256041357	7.6933919381	8.4702758246	7.3208383861
c_2	2.9809112221	2.7714227710	2.9316355211	2.8575372636	2.9270906286

Table 2. Means and Variances of the γ Distribution Fits for the UME_(Ln-L)s Computed for the *N* Complexes for Each Lanthanide Trication^a

UME _(Ln-L)				
lanthanide ion	<i>N</i>	mean (Å)	variance (Å ²)	<i>p</i> -value
La ³⁺	73	0.0739	0.0011	0.732
Ce ³⁺	36	0.0856	0.0020	0.687
Pr ³⁺	47	0.0779	0.0014	0.994
Nd ³⁺	57	0.0744	0.0011	0.679
Pm ³⁺	15	0.0619	0.0015	0.947
Sm ³⁺	37	0.0748	0.0010	0.956
Eu ³⁺	88	0.0775	0.0013	0.159
Gd ³⁺	64	0.0663	0.0008	0.249
Tb ³⁺	35	0.0743	0.0007	0.961
Dy ³⁺	26	0.0798	0.0005	0.443
Ho ³⁺	28	0.0695	0.0006	0.838
Er ³⁺	38	0.0670	0.0028	0.761
Tm ³⁺	15	0.0734	0.0007	0.973
Yb ³⁺	44	0.0777	0.0013	0.993
Lu ³⁺	30	0.0778	0.0015	0.266

^a The last column shows the *p*-values of the one-sample nonparametric Kolmogorov–Smirnov tests,³⁹ carried out for each lanthanide ion, in order to verify statistically that its value is above 0.05, indicating that the distribution of the UME_(Ln-L) values can indeed be represented by a γ distribution indexed by the estimated mean and variance. *N* refers to the number of complexes used in the comparison.

it was computed based on geometries obtained from ab initio calculations²¹ and not from crystallographic measurements, since Pm is a synthetic element which does not possess a stable nucleus.

Table 3 also summarizes the data for the UMEs for each lanthanide trication. In this case, the average value of all means is 0.192 Å, and the average value of all variances is 0.0066 Å². Once again, one can see that these values are relatively constant throughout the table, with the maximum

Table 3. Means and Variances of the γ Distribution Fits for the UMEs Computed for the *N* Complexes for Each Lanthanide Trication^a

UME				
lanthanide ion	<i>N</i>	mean (Å)	variance (Å ²)	<i>p</i> -value
La ³⁺	73	0.213	0.0091	0.735
Ce ³⁺	36	0.190	0.0073	0.988
Pr ³⁺	47	0.212	0.0089	0.632
Nd ³⁺	57	0.198	0.0086	0.895
Pm ³⁺	15	0.165	0.0047	0.583
Sm ³⁺	37	0.188	0.0066	0.262
Eu ³⁺	88	0.195	0.0046	0.957
Gd ³⁺	64	0.186	0.0066	0.460
Tb ³⁺	35	0.191	0.0062	0.620
Dy ³⁺	26	0.204	0.0039	0.418
Ho ³⁺	28	0.214	0.0053	0.957
Er ³⁺	38	0.204	0.0102	0.948
Tm ³⁺	15	0.174	0.0048	0.892
Yb ³⁺	44	0.169	0.0041	0.666
Lu ³⁺	30	0.183	0.0084	0.819

^a The last column shows the *p*-values of the one-sample nonparametric Kolmogorov–Smirnov tests,³⁹ carried out for each lanthanide ion, in order to verify statistically that its value is above 0.05, indicating that the distribution of the UME values can indeed be represented by a γ distribution indexed by the estimated mean and variance. *N* refers to the number of complexes used in the comparison.

UME being 0.214 Å for Ho(III) and the minimum being 0.169 Å for Yb(III). These data imply that Sparkle/PM6 is well balanced across the lanthanide series.

Figure 1 presents a histogram comparing UME_(Ln-L)s for all three Sparkle Models: Sparkle/AM1, Sparkle/PM3, and Sparkle/PM6. The UME_(Ln-L)s represent the accuracy of the model in terms of the distances between the lanthanide ion and the coordinated atoms, important for the design of both luminescent complexes and contrast agents for MRI. The

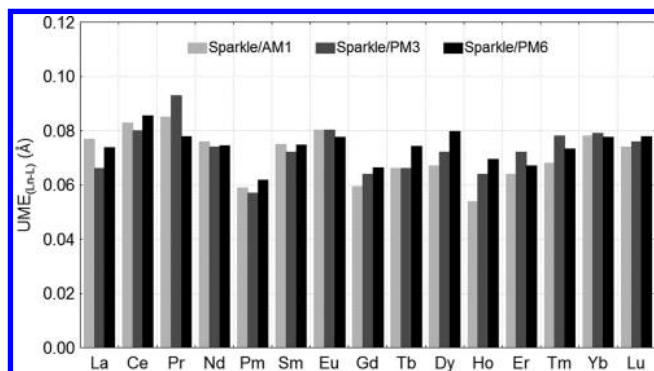


Figure 1. $UME_{(Ln-L)}$ s obtained using all three versions of the Sparkle Model: Sparkle/AM1, Sparkle/PM3, and Sparkle/PM6, for all complexes of the validation set and lanthanide trications, from La(III) to Lu(III). The UMEs are calculated as the average of the absolute value of the difference between the experimental and calculated interatomic distances between the lanthanide ion and the directly coordinating ligand atoms, summed for all complexes for each of the lanthanides.

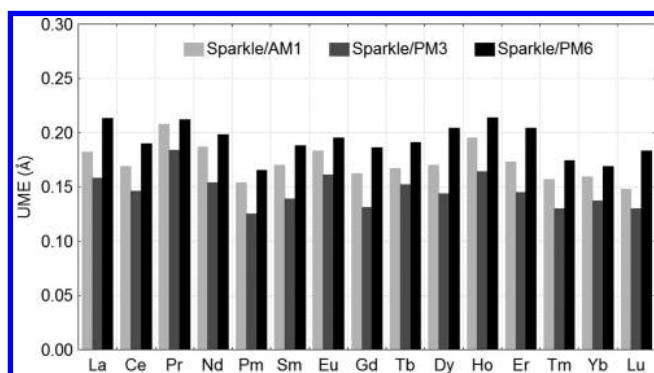


Figure 2. UMEs obtained using all three versions of the Sparkle Model: Sparkle/AM1, Sparkle/PM3, and Sparkle/PM6, for all complexes of the validation set and lanthanide trications, from La(III) to Lu(III). The UMEs are calculated as the average of the absolute value of the difference between the experimental and calculated interatomic distances between all atoms in the coordination polyhedron (lanthanide ion included), summed for all complexes for each of the lanthanides.

accuracy trends in this measure are similar for all three models across the lanthanide series, making them equivalent parametrizations. Figure 2 also presents a histogram comparing UMEs for all three Sparkle Models. In this case, there are more variations among the models, although their behavior is constant across the lanthanide series; the most accurate one being Sparkle/PM3, followed by Sparkle/AM1, and finally Sparkle/PM6. These trends probably reflect aspects of the original parametrizations of each method, not for the lanthanide but mainly for the types of atoms normally found in the coordination polyhedron.

In order to employ any of the Sparkle Models in MOPAC2009,⁴⁰ one must use the keyword SPARKLE together with the keyword of the chosen method: AM1, PM3, or PM6.⁴¹ Actually, to use Sparkle/PM6 the keyword SPARKLE only is normally sufficient, since PM6 is the default method of MOPAC2009. On the other hand, the PM6 article reports parameters for lanthanum and lutetium as regular PM6 atoms with orbitals, parameters which are also

Table 4. Sparkle/AM1, Sparkle/PM3, Sparkle/PM6, and PM6 Unsigned Mean Errors^a

Model	unsigned mean errors for specific types of distances (Å)					
	Ln-Ln	Ln-O	Ln-N	L-L'	Ln-L and Ln-Ln	Ln-L, Ln-Ln, and L-L'
Lanthanum(III)						
Sparkle/AM1	0.176	0.086	0.048	0.208	0.077	0.182
Sparkle/PM3	0.104	0.060	0.083	0.179	0.066	0.158
Sparkle/PM6	0.208	0.076	0.062	0.240	0.074	0.213
PM6	2.392	0.711	0.494	0.796	0.544	0.714
Lutetium(III)						
Sparkle/AM1	0.222	0.084	0.047	0.170	0.074	0.148
Sparkle/PM3	0.176	0.083	0.054	0.145	0.076	0.130
Sparkle/PM6	0.201	0.089	0.048	0.212	0.078	0.183
PM6	0.788	0.163	0.059	0.272	0.124	0.227

^a For all distances involving the central lanthanide ion, Ln, and the ligand atoms of the coordination polyhedron, L and L', and the specific cases when L is either oxygen or nitrogen for the 73 La(III) complexes and 30 Lu(III) complexes considered.

present and implemented in MOPAC2009. So, for the cases of lanthanum and lutetium, complexes can also be computed from pure PM6 parameters. Table 4 presents a comparison among all three Sparkle Models and the pure PM6 for such complexes with respect to several geometry accuracy measures. Clearly the geometry errors of pure PM6 for these two lanthanide atoms are a few times larger than the corresponding ones for all three Sparkle Models. Thus, only if properties other than geometries are required, the usage of pure PM6 for these two elements would be justified. However, due to the magnitude of the errors, even in these cases one could perhaps consider the possibility of optimizing the geometry with Sparkle/PM6 and then computing the other properties of interest with pure PM6 at the sparkle geometries.

As indicated above, Sparkle/PM6 is already implemented in MOPAC2009⁴⁰ and has been tested independently by Seitz and Alzakhem⁴² with respect to its ability to predict the average bond lengths of Ln-OH₂ for the technologically important central lanthanides, Ln = Eu, Gd, and Tb. These authors studied two classes of complexes: the first composed of pyridine-like ligands with 172 complexes, and the second featured ligands with the cyclen motif with 51 complexes. They concluded that Sparkle/AM1 is best for complexes with pyridine-like ligands, whereas Sparkle/PM6 outperforms the other two Sparkle Models in cyclen-derived species. This assertion clearly illustrates and justifies the importance of having all three Sparkle Models available because the individual characteristics of each underlying semiempirical method (AM1, PM3, or PM6) may be more applicable to one or another specific situation.

Conclusions

Sparkle/PM6 stands as another option in the suite of semiempirical models applicable to the quantum chemical calculation of lanthanide complexes. Sparkle/PM6 is an accurate and statistically valid tool for the prediction of the geometrical features of lanthanide coordination polyhedra and, by design, is expected to perform best with ligands with nitrogen or oxygen as coordinating atoms present in the vast majority of all coordination compounds of the trivalent rare earth metals.

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Supporting Information Available: Instructions on how to run lanthanide complexes Sparkle calculations (<http://www.sparkle.pro.br>) with MOPAC 2009 (<http://openmopac.net>). Additional tables containing UME_(Ln-L)s and UMEs for all 633 complexes of the validation set. Additional histograms comparing all three Sparkle Models with respect to various classes of coordinating bonds. Sample MOPAC 2009 input (.mop) and output (.arc) files for one representative complex for each of the lanthanide ions, from La(III) to Lu(III). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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