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13. ABSTRACT (Maximum 200 words)

Elemental parameter sets have been completely developed and validated for sulfur (S), silicon (Si), and phosphorous (P). They are a significant improvement over previous models. Extensive work has been completed on SAM1 parameters for iron (Fe), preliminary results are available. Substantial obstacles have been overcome in the iron work and a clear route to the objective has been established. The theoretical framework is in place and all that is required is completion of the parameterization process. The experience we have gained will allow us to parameterize SAM1 for other transition metals very quickly. The primary question of this research as to whether the Dewar-style semiempirical methodology could be extended to transition metals has been answered in the very definite affirmative.

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# Objectives for the Period 2/93 – 2/94

## Year 1:

1. Prepare literature base and update MBSP for S, P, and Fe.
2. Parameterize SAM1 for S, P, and Fe.
3. Test and evaluate parameters.
4. Apply SAM1 to problems of chemical interest for S, P, and Fe.
5. Prepare and present results at ACS meeting.
6. Submit results for publication in the scientific literature.

## Objectives Accomplished

All of the objectives listed above have been accomplished except the publication of results. Additionally, SAM1 parameters for Si were obtained during the same period. A number of publications are in progress (see below) and will be submitted before the end of 1994.

### *SAM1 Parameters for Si, S, P*

The parameterizations for these main group elements have been quite successful. The addition of *d*-orbitals seems to have made a substantial difference in the overall quality of results and especially in the results for hypervalent systems. The errors for the parameterizations are listed below in averaged form:

Elements	Number of Examples <sup>1</sup>	Type of Error <sup>2</sup>	Procedure		
			SAM1	AM1	PM3
Si	62	MU	6.09	7.33	6.56
		SD	2.92	5.80	7.53
S	76	MU	6.45	7.09	9.33
		SD	2.07	4.00	7.06
P	60	MU	9.97	16.33	15.82
		SD	1.90	4.80	6.21

1. The total of the number examples is greater than the total number of species due to overlap in the categories.

2. MU=mean unsigned error; MS=mean signed error, SD=standard deviation, RMS=root mean square error.

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The improvement in error for the heats of formation is substantial, especially in the case of phosphorous. Even more notable than the raw improvement in the results is the reduction in the standard deviation of the errors. This indicates that the spread of the results has been greatly reduced, lending greater reliability to the model's predictions. Work is presently underway on testing of these parameters for a variety of chemical situations.

### *SAM1 Parameters for Fe*

The success of our new method for SAM1 in the case of iron (Fe) is a major scientific breakthrough. We have expanded the traditional Dewar-style semiempirical methods to transition metals for the first time, making these highly efficient computational methods available to a wider audience. A tremendous amount of code work and scientific development went into the expansion of AMPAC to allow treatment of the new element (and those that will follow). The work that had to be done included:

- re-coding of AMPAC to handle very large open-shell multiplicities such as are routinely encountered with transition metals
- development of new CI (configuration interaction) algorithms and approaches, again to handle the large open-shell systems
- extrapolation of initial values for the parameters from which to begin searches
- further extensive grid searches for initial values for the parameters from which to begin searches
- energy separation of the parameters describing the one-electron/one-center energies
- ordering of the atomic orbital levels
- partially automated approach to CI for easier calculation and determination of the minimum level of CI required for a particular system

At present, we have located two sets of SAM1 iron parameters that appear to be roughly equivalent. We have released one set to a number of beta testers

for feedback. A decision will be made on which set will finally be released to users when all of that data has been analyzed. Some selected preliminary results for iron are listed below:

Molecule	Spin	Error in:	
		$\Delta H_f$	Geometry
FeH	4	96.3 (113.9)	FeH: 1.54 (1.57)
FeCH <sub>3</sub>	4	72.1 (71)	-
Fe <sub>2</sub>	7	178.0 (180)	FeFe: 2.01 (2.40)
FeO	4	14.1 (60)	FeO: 1.60 (1.62)
FeOH	4	30.1 (32)	-
Fe(OH) <sub>2</sub>	3	-63.4 (-79)	C <sub>2v</sub> , FeO: 1.81 (1.8)
Fe(CO)	3	68.4 (63.9)	-
Fe(CO) <sub>2</sub>	3	3.5 (0.2)	-
Fe(CO) <sub>3</sub>	3	-41.4 (-55.8)	-
Fe(CO) <sub>4</sub>	3	-101.2 (-104.5)	-
Fe(CO) <sub>5</sub>	1	-157.1 (-175.4)	D <sub>3h</sub> , FeC: 1.91, 1.88 (1.83, 1.81)
Fe <sub>2</sub> (CO) <sub>9</sub>	1	-354.1 (-319)	FeFe: 2.60 (2.52)
Fe <sub>3</sub> (CO) <sub>12</sub>	1	-402.5 (-419)	-
FeO <sub>4</sub> C <sub>10</sub> H <sub>14</sub>	1	-191.0 (-198)	-
FeO <sub>6</sub> C <sub>12</sub> H <sub>21</sub>	1	-314.5 (-297)	-
FeF <sub>2</sub>	5	-80.3 (-93.1)	-
FeCl <sub>2</sub>	5	-46.6 (-33.7)	FeCl: 2.04 (2.17)
FeBr <sub>2</sub>	5	-17.9 (-9.9)	FeBr: 2.20 (2.31)
FeI <sub>2</sub>	5	28.0 (14.5)	FeI: 2.26 (2.43)
Fe-Porphyrin	1	-	D <sub>4h</sub> , FeN: 2.04 (1.97)
Ferrocene	1	59.72 (58)	D <sub>5h</sub> , FeCp: 1.89 (1.65), FeC: 2.27 (2.06)
Average (MU)	15.6	1.06	2.01
# Molecules	26	15	2

### *Other Work with SAM1*

We have also completed an extensive analysis of frequencies using the new SAM1 model. This will also be added to the literature.

## ***Publications***

### *Completed:*

Holder, A. J.; Dennington, R. D.; Jie, C. *Tet.* 1994, 50, 627; "An Addendum to SAM1 Results Previously Published".

### *In Preparation:*

Holder, A. J.; Dennington, R. D.; Jie, C. *J. Am. Chem. Soc.*; "SAM1: A New Generation of Semiempirical Theoretical Models".

Holder, A. J.; Dennington, R. D.; Jie, C. ; Dobbs, K.D. *J. Am. Chem. Soc.*; "SAM1 Semiempirical Parameters for Iron".

Holder, A. J.; Dennington, R. D.; Jie, C. *Organometallics*; "SAM1 Semiempirical Parameters for Silicon".

Holder, A. J.; Dennington, R. D.; Jie, C. *Inorganic Chemistry*; "SAM1 Semiempirical Parameters for Sulfur".

Holder, A. J.; Dennington, R. D.; Jie, C. *Inorganic Chemistry*; "SAM1 Semiempirical Parameters for Phosphorous".

Holder, A. J.; Dennington, R. D. *J. Comput. Chem.*; "SAM1's Performance for Frequency Calculations".

Holder, A. J.; Dennington, R. D., Venkatchalam, R. *Organometallics*; "SAM1 Semiempirical Parameters for Aluminum".

### *Personnel*

Andrew J. Holder (Ph.D., U. of Southern Mississippi): *Principal Investigator*

Roy D. Dennington, II (Ph.D., U. of Texas): *PostDoctoral Associate*

Caoxian Jie (M.S., U. of Beijing): *PostDoctoral Associate*

Revathy Venkatachalam: *Graduate Student*

## ***Interactions***

### ***Presentations:***

- (1) Marquette University: "Applications and Development of Modern Semiempirical Methodology", Feb. 26, 1993 in Milwaukee, WI. *Invited Lecture*
- (2) Minnesota Supercomputer Center: "Applications and Development of Modern Semiempirical Methodology", March 3, 1993 in Minneapolis, MN. *Invited Lecture*
- (3) 5th International Conference on Mathematical and Computational Chemistry: "SAM1: A Next Generation Semiempirical Model Including *d*-Orbitals", May 17, 1993 in Kansas City, MO. *Contributed Paper*
- (4) Eli Lilly and Co.: "Development and Applications of Modern Computational Methods", July 28, 1993 in Indianapolis, IN. *Invited Lecture*
- (5) American Chemical Society 1993 Fall National Meeting: "SAM1: A General Description and Performance Evaluation for Hydrogen Bonds", August 22, 1993 in Chicago, IL. *Invited Speaker at ACS Symposium.*
- (6) Wright-Patterson AFB: "Development and Applications of Modern Computational Methods", September 14, 1993 in Dayton, OH. *Invited Lecture*
- (7) Univ. of Missouri-Kansas City: "Development and Applications of Modern Computational Methods", October 19, 1993. *Invited Lecture*
- (8) Univ. of Southern Mississippi: "Development and Applications of Modern Computational Methods", February 16, 1994. *Invited Lecture.*
- (9) DowElanco, Indianapolis, IN: "The State-of-the-Art in Semiempirical Methods", February 24, 1994. *Invited Lecture.*
- (10) 1994 Spring American Chemical Society National Meeting: "SAM1: A Next Generation Semiempirical Method.", March 14, 1994. *Invited Plenary Lecture.*
- (11) Southwestern Baptist University: "Development of Semi-Empirical Methods of Drug Design", April 7, 1994. *Invited Lecture.*

- (12) Southwest Missouri State University: "Development and Applications of Modern Computational Methods", April 8, 1994. *Invited Lecture.*
- (13) Florida Sections ACS Meeting, Orlando, FL: "Development and Applications of Modern Computational Methods", May 6, 1994. *Invited Lecture.*
- (14) Gordon Conference on Computational Chemistry, New Hampton, NH: "SAM1 Semiempirical Parameters for Transition Metals", July 3-8, 1994. *Contributed Poster.*

*Consultations:*

- (1) Wright-Patterson AFB: September 13, 14 1993 in Dayton, OH. *Lecture and meetings.*
- (2) Numerous contacts on the phone and via e-mail with the groups of Dr. Douglas Dudis and Ruth Pachter at Wright-Patterson AFB.
- (3) Numerous contacts on the phone and via e-mail with the group of Dr. George Famini at Aberdeen Proving Ground..