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13. ABSTRACT (Maximum 200 words)

The goal of this research was to develop efficient methods for the determination of structures of complex molecular systems. Both the optimization strategy (1), and the generation of accurate potential energy functions (2) were addressed. Under (1), the PI concentrated on the role of coordinates adapted to molecular potential surfaces. His coordinates are widely used for medium-sized molecules where their rapid convergence greatly outweighs their extra cost. However, for large systems they become expensive. A natural/redundant coordinate optimization was developed with favorable computational cost and storage requirements. An efficient optimization method in inverse distance coordinates was implemented for Van der Waals clusters and for supramolecular optimization. Under (2), the PI further developed the localized correlation technique. He created a new program which allows correlated ab initio calculations on asymmetric molecules of unprecedented size. He also parametrized distant (dispersion-like) pair correlation energies; their empirical inclusion greatly speeds up correlated calculations on large systems. Vibrational force fields were developed by scaling density functional force fields. These force fields accurately predict not only structures but also vibrational frequencies. A new definition of force constants in redundant coordinates was introduced, simplifying the parametrization and scaling of force fields.

14. SUBJECT TERMS
Optimization, Molecular Geometry, Electron Correlation, Localized Orbitals, Force Fields, Vibrational Spectra

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Computationally Efficient Models for the Calculation of Structures and Properties of Materials

I. INTRODUCTION

The aim of computational modeling of molecular systems at the atomic and electronic level is to computer design useful materials and molecules. This will certainly be a major contributor to technology in the near future, as computer power continues to expand, and larger systems become amenable to accurate simulation.

Both aspects of molecular simulation are addressed: finding the minima and stationary points on the hypersurface, using calculated energies and gradients, and the generation of the latter at a given molecular geometry, i.e. the calculation of the energy hypersurface,

II. KEY RESULTS

The key results of the research performed under this grant are the following:

(1) We have developed a program for the efficient optimization of large molecules using internal valence coordinates. This method reduces the number of iterative cycles by almost an order of magnitude. It avoids the explicit construction and inversion of large matrices and uses a novel incomplete Cholesky decomposition method.

(2) We have developed a method for the efficient optimization of clusters using distance coordinates.

(3) We have developed models for dispersion forces, using accurate localized *ab initio* pair correlation energies.

(4) We have developed an efficient local MP2 (second-order Moller-Plesset theory) program with favorable scaling, permitting calculations on molecules with ~1000 basis functions with no symmetry.

(4) We have implemented (together with Werner's group) the first analytical derivatives for localized MP2 wavefunctions.

(5) We have determined scaling factors for vibrational force fields obtained by Density Function Theory.

(6) We have succeeded in defining force constants directly in primitive valence coordinates, and developed scaling techniques for them.

III. OPTIMIZATION METHODS

Optimization of molecular geometries is the first and most fundamental task in simulating the properties of complex molecular systems. Optimization of large molecules raises fundamentally new problems, compared to small systems, such as the existence of multiple minima, and the fact that the computer resources needed in the optimization, which are negligible for smaller systems, become significant.

We have been stressing for some time that abstract mathematical techniques, i.e. those which do not consider the specific properties of molecular potential energy surfaces, are mature and unlikely to contribute much to molecular geometry optimization in the future. The most natural way to include information on the problem at hand is to use coordinates adapted to the physical characteristics of the potential energy surface. For covalent molecular structures, two coordinate systems yield the best performance. Curvilinear *natural internal coordinates*[1] are the optimum choice for moderately large systems. We have confirmed this recently for *ab initio*[2] calculations in a comprehensive comparison of various optimization techniques at the *ab initio* level. These calculations use Baker's test set[3] and either a molecular mechanics force field (CVFF[4]) starting Hessian or the model Hessian recently introduced by Lindh *et al.*[5], Cartesian or natural internal coordinates, the Rational Function/Augmented Hessian[6,3] or the Geometry DIIS[7] optimization methods, with or without updating the Hessian by the BFGS method. These methods have also been incorporated in the efficient MOLPRO suite of programs[8]. The results are summarized in [10]. The best methods need a little more than 6 steps on the average to converge for the 30 test molecules which range from simple molecules like ammonia to caffeine and methone. However, the definition of natural internal coordinates is complex and logic-intensive. Automatic computer programs[9] take care of this problem but they occasionally fail for molecules with complex topology. For this reason, redundant valence coordinate optimization, introduced by the present P.I.[10], and widely implemented by other researchers[11,12] is the current standard.

Both natural internals and redundant valence coordinates suffer from the fact that the optimization itself is relatively time-consuming. This is a secondary consideration in most

ab initio calculations, as the generation of the potential energy surface is usually much more demanding. However, it is important for molecular mechanics force fields and semiempirical methods where simple optimization using Cartesians is the standard. Although often requiring a large number of iterations, the computational requirement of the optimization itself is small, in line with the inexpensive nature of the force fields. Recently, however, it has become desirable to combine the advantages of the two methods, for several reasons. Quantum mechanical calculations can now treat *quite large* systems, and the relatively steep $O(N^3)$ scaling of the optimizer may soon become a bottleneck. Conversely, it would be desirable to have the fast convergence of the algorithms used in *ab initio* programs also for molecular mechanics calculations if the computational cost of the optimization step could be reduced. The greatest need for a fast and inexpensive optimization method is, however, posed by the emerging quantum mechanics - molecular mechanics (QM/MM) methods. In these methods the active site of a large molecule is described by quantum mechanics while the rest is modeled by much less expensive molecular mechanics (empirical force fields). The quantum mechanical part requires rapidly convergent methods. However, the cost of the optimization must be low in view of the size of the whole system.

Much of our effort has been spent in extending the applicability of natural internal coordinate optimization to large molecules (using mostly empirical model surfaces). This has been a greater challenge than we anticipated, and has been successfully accomplished only at the very end of the grant. The large number of independent variables introduces new computational challenges, and requires the modification of the algorithms, as the computational expense associated with the optimization itself became important. Results will be presented below for the performance of our new code. It appears that this is a significant breakthrough, as molecular modeling is widely used in biochemical and pharmaceutical, but also in materials science research.

In the following, the essential results from the key paper[13] are discussed at a greater length, as the paper, at this writing, still has not appeared. Both the paper and the computer program were ready in 1996 but we were somewhat disappointed by its

performance. We withdrew the paper when we discovered the complete solution and resubmitted it only recently.

The key steps in *curvilinear* geometry optimization of molecular systems are as follows:

⇒ Define a suitable set of coordinates $\mathbf{q}$ (in our case internal valence coordinates, i.e. bond lengths, angles and torsions) and calculate the first-order transformation matrix $\mathbf{B}$ connecting them with the Cartesians $\mathbf{x}$: $\mathbf{q} = \mathbf{Bx}$.

⇒ Calculate $\mathbf{A}$, the right Penrose inverse of $\mathbf{B}$: $\mathbf{A} = \mathbf{B}^T(\mathbf{BB}^T)^{-1}$.

⇒ Transform the Cartesian row vector of forces $\mathbf{f}$ to internal forces φ: $\varphi = \mathbf{fA}$.

⇒ Relax the molecule, resulting in a change in the internal coordinates $\Delta \mathbf{q}$.

⇒ Transform back to Cartesians iteratively, using the first-order formula $\Delta \mathbf{x} = \mathbf{A}\Delta \mathbf{q}$.

The usual method of implementing these operations results in a computational work which scales with the cube of the number of degrees of freedom, $O(N^3)$. To reduce this steep scaling, we use the fact that the $\mathbf{B}$ matrix is sparse. We never form the $\mathbf{A}$ matrix. Rather, the transformation of the forces is accomplished by solving iteratively the system of equations $(\mathbf{B}(\mathbf{B}^T\varphi^T)) = \mathbf{Bf}^T$ by the conjugate gradient method. The principal operation here is multiplication by the sparse $\mathbf{B}$ matrix which scales roughly as $O(N)$. The back transformation to Cartesians is done similarly. The performance problem referred to above was caused by slow convergence of the conjugate gradient (CG) algorithm, leading to an iteration count comparable with the number of degrees of freedom. This was obviously due to strong couplings in the matrix $\mathbf{G} = \mathbf{BB}^T$, since in weakly diagonally dominant cases (e.g. the coupled-perturbed Hartree-Fock method), CG converges in 10-15 steps independently of the size of the problem. The solution was to generate an incomplete Cholesky decomposition[14] of $\mathbf{G}$. Due to the sparsity of both $\mathbf{B}$ and $\mathbf{G}$, this step scales only linearly both in space and in time. Note that the usual incomplete Cholesky decomposition methods[15] are inapplicable because they do not yield positive definite factors.

To test our method with a realistic potential energy surface, we implemented a documented force field for organic and bioorganic structures (SYBYL)[16] and coupled our natural coordinate optimization method with it. We used an earlier published version of the current SYBYL force field[17] of Tripos, Inc; it differs somewhat from the current

commercial program. The resulting program allows the study of the optimization process in internal coordinates for large structures.

Tables I and II illustrate the efficiency of the new procedure for the geometry optimization of alpha helical alanine polypeptides, H-[NH-CH(CH$_3$)-CO-]$_n$OH with n=5 to 50. The largest system has over 1500 degres of freedom. Table I shows the average number of CG iterations and the corresponding timings for the optimization. It also shows the average number of elements retained in the approximate Cholesky factors. It demonstrates that the fraction of computer time spent in the optimization routines declines steadily as the size of the system grows and becomes insignificant for 1500 degrees of freedom [(alanine)$_{50}$]. The fraction of nonzero elements in the incomplete Cholesky decomposition also diminishes as the system grows. Similar results were obtained for a number of large organic systems, e.g. taxol, streptomycin, daunomycin etc.

Another important problem in optimization is posed by the emerging area of molecular clusters. These are often held together by largely non-directional forces: Van der Waals forces or metallic forces. These systems are best treated by using distance coordinates, or even better inverse power distance coordinates[18]. The optimization of Lennard-Jones particles (particles interacting by a potential of the form ar^{-12}-br^{-6}) is a well-defined mathematical problem, frequently used as a standard to compare optimization techniques. We have shown that a redundant system of inverse distance coordinates significantly improves the convergence rate of the optimization, compared to Cartesians. Such coordinates have not been used before for optimization, and one of our goals was to see if the redundancy leads any computational difficulties. An intersting observation is that inverse distance coordinate optimizations tend to converge to lower local minima than Cartesian ones; this may be useful for global optimization.

III. MOLECULAR POTENTIAL ENERGY FUNCTIONS
III.1. Calculation and Modeling of Local Pair Correlation Energies

Although Density Functional Theory (DFT) became the most popular correlated electronic structure method, there is still wide interest in accurate wavefunction-based methods because DFT cannot describe some effects (e.g. the London dispersion force or

multiplet splittings), and because of the somewhat empirical foundation of DFT. Dispersion forces are particularly important in determining the structures of larger systems like biomolecules and many materials, as they are always attractive and thus add up. However, their calculation is quite difficult because dispersion is a purely correlation effect. Neither SCF wavefunctions nor current density functional theory is able correctly to account for dispersion effects[19]. Popular empirical force fields model dispersion forces with a simple inverse sixth power expression. However, the accuracy of this simple model is questionable, particularly for such important phenomena as, say, π stacking interactions. We have carried out two projects for the efficient evaluation of these terms. First, it is clear that only a localized representation of the molecular orbitals is capable of separating the dispersion terms from other correlation effects. We are able to calculate correlated wavefunctions, starting from the simplest MP2 (second order many-body perturbation theory with the Moller-Plesset partitioning) to the CEPA and coupled cluster level[20]. These calculations yield *ab initio* pair correlation energies in localized orbital basis. These, as expected, diminish roughly as the inverse sixth power of the distance between the centers of the orbitals. The objective of the first project was simply to calculate the localized correlation energy components (pair correlation energies) at a reasonably good *ab initio* level, and parametrize them as functions of the properties of the localized orbitals: their sizes, shapes and distances. We have calculated local MP2 (LMP2) pair correlation energies for about 50 small and medium-sized molecules, resulting in over 10,000 pair correlation energies. These *ab initio* results were used to train a neural network to reproduce the more distant intramolecular pair correlation energies[21]. We also used an analytical model which gave similar performance. The energies predicted are quite accurate in comparison with directly calculated values. E.g. for lactic acid, cyclopentenedione, toluene, and aniline the sum of the distant pair correlation energies is accurate to about 1-2 %, both at equilibrium geometries and at distorted ones[21]. Fig. 1 compares the calculated and estimated pair energies for 1-4 interactions (pairs separated by two bonds) in a number of small molecules.

In the second project, our goal is to accelerate the direct calculation of (configuration-based) correlation energies. In spite of the great progress made by density

functional theories, these methods are still deficient in some areas, the dispersion interaction being one of these. After years of slow progress, the development of modern high-speed workstations stimulated much effort in this field[22,23,24]. Most of these developments follow the local correlation method originally introduced by the P.I.[25,26]; Murphy *et al.* and Carter combine this with the pseudospectral technique of Friesner. An ingenious alternative technique, based on the Laplace transform form of the correlation energy, was introduced by Häser and Almlöf[27], and we have examined this method concerning its suitability for calculating localized correlation energies[28]. We have found, however, that the Laplace transformation of the orbitals destroys localization to a significant degree, although only for large values of the Laplace transform variable where the orbitals are small. We have thus stayed with the original local correlation method[25,26]. A weakness of the latter was that it used the traditional integral transformation step, and thus it offered significant computational advantages only for higher level (MP4 and coupled cluster) methods but not for lower level (MP2) calculations where the transformation constitutes most of the work. We have now developed a *direct* and *local* integral transformation and MP2 program which can be applied to systems of unprecedented size[29]. We have already performed many calculations in the range 700-1000 basis functions, and are currently working on parallelizing the code. Fig. 2 shows the scaling of the local MP2 program with molecular size for a series of calculations on fragments of the glycine crystal.

The essence of the method is to use localization of the orbitals in the transformation step to omit insignificant terms in the transformation. Empirically, the MP2 calculation only scales with the *square* of the basis set size, although with a quite steep prefactor. Nevertheless, for very large calculations the cost of the MP2 calculation is less than that of the SCF[29]. We plan to improve this method further by simplifying the calculation of the correlation energy for the *weak pairs*, i.e. between distant orbitals. For correlation between distant orbitals, the dominant $(C_6 R^{-6})$ correlation effects should be concentrated in just a few (in most cases 6, i.e. 3 per localized orbital) virtual orbitals; these are the 6 dominant pseudo-natural orbitals of the pairs[30]. A new insight is that *these orbitals are essentially the same for the interaction of a given orbital with any other distant orbital.*

In a large system, the majority of the interactions can thus be described very simply, only the intraorbital and close interorbital correlation effects need a large local correlation space. We intend to include this extension in our program.

We have provided the first implementation of analytical gradients for the local MP2 method, in collaboration with Werner's group[31]. This was a technically very demanding project.

III.2. Molecular Force Fields

We have continued systematic determination of vibrational force fields for a organic molecules using density functional methods, in order to generate improved empirical force fields. Good initial force fields greatly accelerate the convergence of *ab initio* geometry optimization, and are indispensable for predicting vibrational spectra. Our database of molecular vibrational force fields includes about 150 molecules at present, and is growing. We, and others, have shown that density functional theory, in particular the Becke 3-parameter functional, is excellent for generating force fields. Even they need, however, empirical scaling for full accuracy in the prediction of vibrational spectra. We have determined transferable scale factors for DFT-based force fields[32] and applied them to a number of spectroscopic[33] and chemical problems, like the identification of chlorinated dioxins[34], the true structure of azulene[35], the molecular rearrangement of benzofuroxan[36], and the inner hydrogen migration in porphyrin[37]

An important result is the first satisfactory definition of force *constants in redundant* internal coordinates, and scaling in redundant primitive valence coordinates[38]. We anticipate that this will greatly aid the parametrization of *ab initio* force fields. We can now omit the cumbersome fitting procedure (e.g. Ref. 4) and calculate potential function parameters *directly* in valence coordinates. We have already used this method for macrocyclic molecules like porphyrins and phthalocyanines.

Table I. Geometry optimization of alanine α helix oligopeptides. The following data are shown: the number of optimization cycles, total optimization time (seconds) on a 390 node of an IBM SP2, the fraction of the time spent in the major compute modules, and the density (the fraction of nonzero elements) in the LU decomposition

molecule[a]	cycles	total time	force field %	LU %	linear eq. %	Density %
ala5	36	57.21	26.2	6.8	6.2	54.35
ala10	60	332.7	46.0	4.2	8.3	32.62
ala15	71	948.2	59.1	3.7	7.6	22.80
ala20	88	2249	64.9	2.8	7.4	17.53
ala25	83	3872	72.5	2.2	6.3	14.31
ala30	71	5290	76.5	2.1	6.0	12.05
ala40	44	7484	80.6	2.2	5.9	9.92
ala50	58	18713	79.7	2.2	6.2	7.99

[a] Number of atoms = $10n+3$ where n is the number of alanine units. The number of degrees of freedom is $30n+3$, 153 for ala5 and 1503 for ala50.

Table II. Comparison of optimizations of alanine α helix oligopeptides using natural internal and Cartesian coordinates. The final energy (kcal/mol), number of gradient and energy evaluations, and maximum residual force [kcal/(mol Å)] are shown for Cartesian optimization implemented in the SYBYL program, and natural internal coordinate optimization in the FYFF program. SYBYL uses the current TRIPOS force field while FYFF is based on an older, published version of same force field; this explains the difference in the energies. See text.

	Sybyl				Fyff			
	E final	N gradient	N energy	Max. force	E final	N gradient	N energy	Max. force
ala5	0.266	367	2214	0.143	-.283	36	154	0.114[a]
ala10	-8.929	361	2178	0.071	-9.711	60	239	0.176
ala15	-18.055	358	2154	0.121	-19.222	71	279	0.141
ala20	-27.193	359	2162	0.169	-28.741	88	316	0.152
ala25	-36.341	339	2037	0.218	-38.261	83	317	0.142
ala30	-45.466	335	2018	0.210	-47.782	71	268	0.145
ala40	-63.602	325	1949	0.153	-66.822	44	171	0.122
ala50	-81.605	239	1438	0.133	-85.864	58	228	0.112

[a] 1 kcal/molÅ ≈ 0.0008433 atomic units ≈ 0.0069478 aJ/Å

Calculated LMP2 Correlation Energies (mHartree)

0.0

−0.5

−1.0

−1.5

−2.0

Alanine O/O

Norbornadiene (1.1) C−C/C−C
Norbornadiene C−C/C−C

Aminopyridine (1.1) N−C/C−C

−2.0   −1.5   −1.0   −0.5   0.0
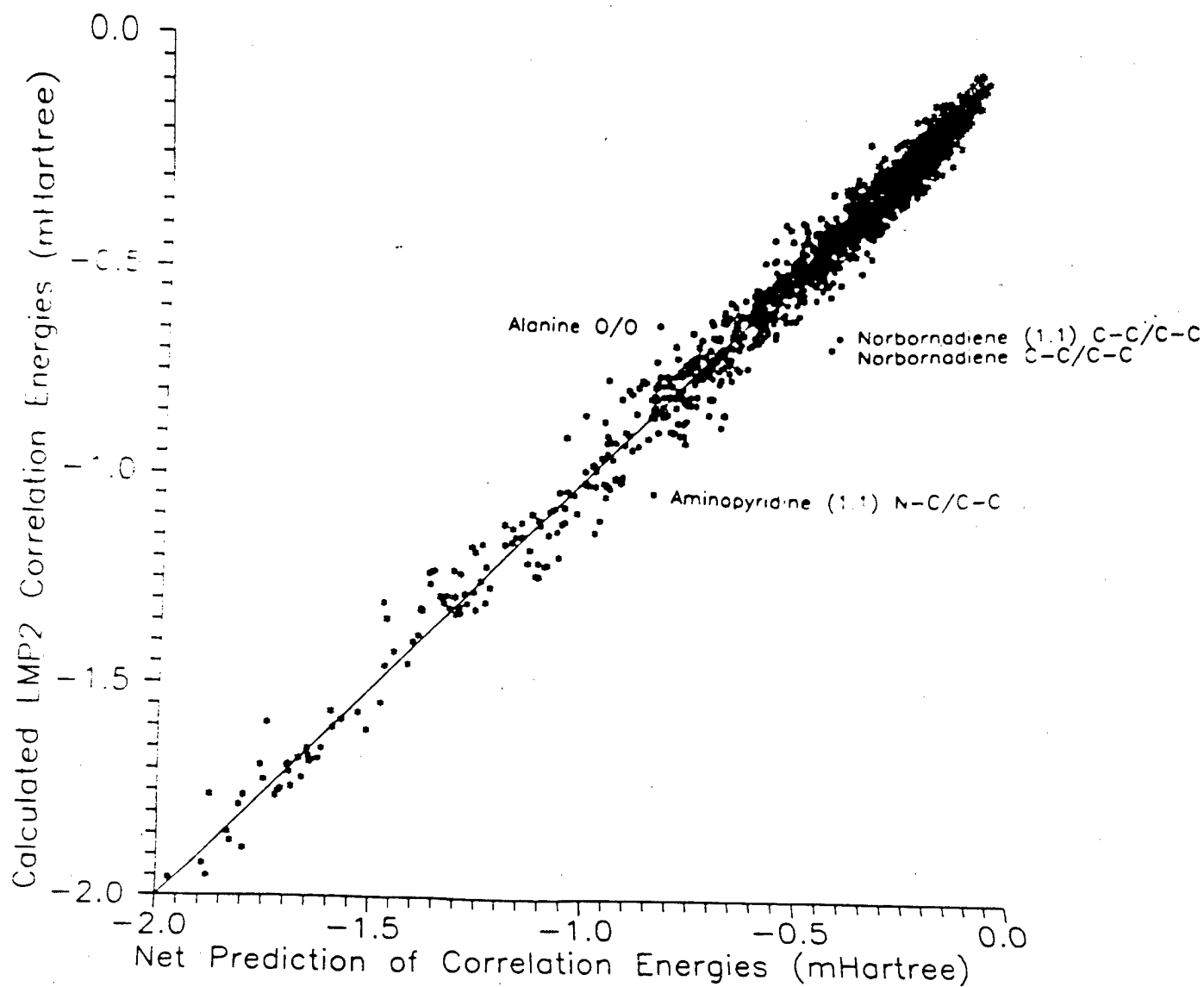
Net Prediction of Correlation Energies (mHartree)

Fig. 1. Correlation between calculated and modeled *ab initio* pair correlation energies[21]
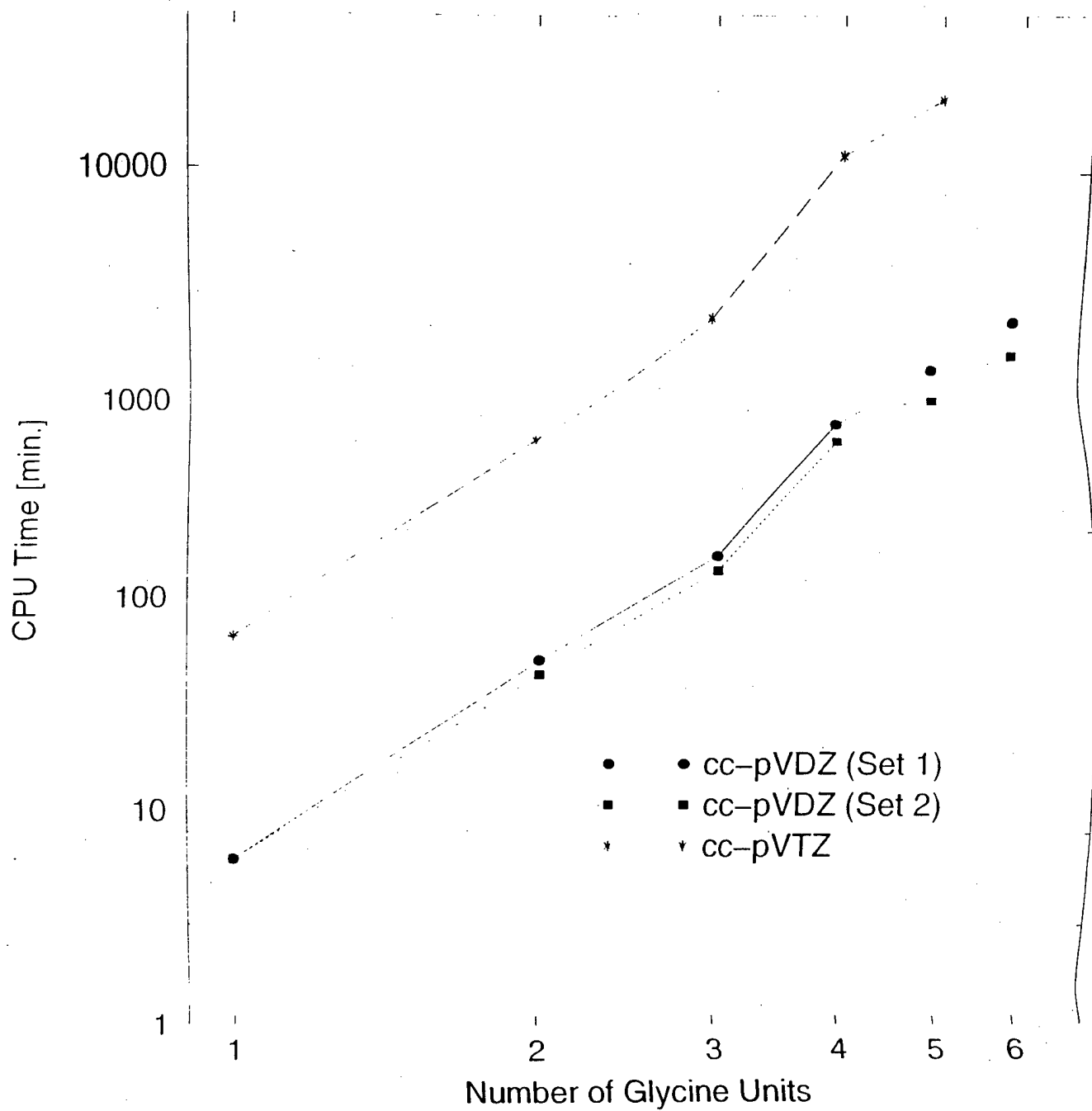
Fig. 2. Scaling of the local correlation treatment for (glycine)$_n$ clusters (n=1-6). The number of basis functions varies between 95 to 570 for the cc-pVDZ basis, and between 195 and 1170 for the cc-pVTZ basis.

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[a] Papers published under this grant are in bold face

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UNIVERSITY of ARKANSAS

MEMORANDUM

TO: Dr. Peter Pulay
     Department of Chemistry & Biochemistry

FROM: Jane L. Treat
       Associate Director

DATE: January 26, 1998

RE: CCN 0402-17012-21-0000
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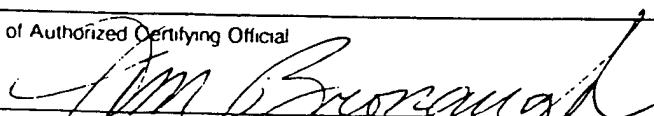☐ The following subcontract(s) was/were let on the referenced contract:

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4. Employer Identification Number	5. Recipient Account Number or Identifying Number	6. Final Report	7. Basis
71-6003252	0402-17012-21-0000	☒ Yes ☐ No	☐ Cash ☒ Accrual

8. Funding/Grant Period (See Instructions) From: (Month, Day, Year) 01/15/94	To: (Month, Day, Year) 07/14/97	9. Period Covered by this Report From: (Month, Day, Year) 01/15/97	To: (Month, Day, Year) 07/14/97

10. Transactions:

	I Previously Reported	II This Period	III Cumulative
a. Total outlays	151,609.84	31,226.42	182,836.26
b. Recipient share of outlays	- 0 -	- 0 -	- 0 -
c. Federal share of outlays	151,609.84	31,226.42	182,836.26
d. Total unliquidated obligations			- 0 -
e. Recipient share of unliquidated obligations			- 0 -
f. Federal share of unliquidated obligations			- 0 -
g. Total Federal share (Sum of lines c and f)			182,836.26
h. Total Federal funds authorized for this funding period			182,844.00
i. Unobligated balance of Federal funds (Line h minus line g)			7.74

11. Indirect Expense

a. Type of Rate (Place "X" in appropriate box)
☐ Provisional   ☒ Predetermined   ☐ Final   ☐ Fixed

b. Rate	c. Base	d. Total Amount	e. Federal Share
41 % MTDC	130,155.37	51,093.00 MAX	51,093.00 MAX

12. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation

13 Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.

Typed or Printed Name and Title	Telephone (Area code, number and extension)
Jim Bronaugh, Project/Program Mgr	501-575-4853

Signature of Authorized Certifying Official	Date Report Submitted
Jim C Bronaugh	10/09/97

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Standard Form 269A (REV 4-88)
Prescribed by OMB Circulars A 102 and A 110

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