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## Modern Iterative Minimization Techniques for Quantum Chemistry

In recent years, advances in computer technology and theoretical modelling of quantum many-body systems have made it possible for theory to begin addressing real materials problems and issues using only the atomic numbers of the constituent atoms as experimental input. Theoretical investigations of this type are commonly described as being "*ab initio*." They can be extremely useful in providing a fundamental understanding of the physical and chemical phenomena underlying materials behavior, can help guide experimental research, and can even probe into regimes that are inaccessible to experiment.

*Ab initio* investigations typically begin with a calculation of the total energy of a material system. This is because nearly all physical properties of materials are related to total energies or to differences between total energies. Since a material system is essentially an interacting many-body system of electrons and nuclei, such a calculation involves minimization of the total energy with respect to its electronic and nuclear coordinates. Because of the large difference in mass between the electrons and nuclei, and the fact that the forces on the particles are the same, the electrons respond essentially instantaneously to the motion of the nuclei. Thus the nuclei can be treated adiabatically leading to a separation of electronic and nuclear coordinates in the many-body wavefunction. This "Adiabatic Principle" then reduces the many-body problem to the solution of the dynamics of the electrons in some frozen-in configuration of the nuclei.

Even with this simplification, the many-body problem remains formidable. Further simplifications, however, can be introduced that allow total

energy calculations to be performed accurately and efficiently. One efficient method that has proved to be very useful in the study of solids involves the following approximations: *density functional theory*<sup>1,2</sup> to model the electron-electron interactions, *pseudopotential theory*<sup>3-5</sup> to model the electron-ion interactions, and *supercells*<sup>6</sup> to model systems with non-periodic geometries.

Very briefly, the essential concepts are the following:

(i) Density functional theory<sup>1,2</sup> allows one, in principle, to map exactly the problem of a strongly interacting electron gas (in the presence of nuclei) onto that of a single particle moving in an effective non-local potential. Although this potential is not known precisely, local approximations to it seem to work remarkably well. Presently, we have no *a priori* arguments to explain why these approximations work. Density functional theory was revitalized in recent years only because theorists were able to perform total energy calculations using these potentials and show that they could reproduce a variety of ground state properties within a few percent of experiment. Thus the acceptance of local approximations to density functional theory has only emerged, *a posteriori*, after many successful investigations of many types of materials and systems. Generally, total energy differences between related structures can be believed to within a few percent and structural parameters to within a tenth of an Å.

(ii) Pseudopotential theory<sup>3-5</sup> allows one to replace the strong electron-nuclei potential with a much weaker potential—a pseudopotential—that

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## NEW PRODUCTS

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### SunSoft Introduces ToolTalk

SunSoft, a subsidiary of Sun Microsystems, Inc. has unveiled its first product, **ToolTalk**, a new software package that allows easy communication between UNIX applications and the first component of a comprehensive software environment to be announced by Sun later this year. The product assures application interoperability with other vendors' software. By the end of the year, ToolTalk is scheduled to be available for SPARC computers and other platforms which include, DEC, Hewlett-Packard, IBM, Integraph, and Sun. ToolTalk is to be shipped in the fourth quarter, with prices to be available at that time. Developer copies are available now. Product inquiries should be directed to SunSoft corporate headquarters (415-336-0678). ■

### Alliant Announces Pax Compiler Availability from Intel

In conjunction with a recent announcement from Intel Corp., Alliant Computer Systems Corp. notes that its parallel **FORTRAN and C compilers** are available this quarter from Intel for use with the i860 RISC microprocessor family. Significant performance enhancements include on-chip support for the Alliant-developed *Concurrency Control Architecture (CCA)*, a technology that provides synchronization and control functions for multiprocessing computer systems, a feature not found on other RISC microprocessors. This technology was licensed to Intel when the two companies formed a strategic alliance in 1989. The Alliant compilers and the CCA are key components of the **PAX (Parallel Architecture eXtended)** specification, a unified hardware and software standard for technical computing co-developed by the Companies. For more information, contact Alliant Computer Systems Corp., One Monarch Dr., Littleton, MA 01460 (508-486-4950). ■

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describes all the salient features of a valence electron moving through the solid. This is shown schematically in Figure 1. Thus the original solid is now replaced by pseudo-valence-electrons and pseudo-ion cores. These pseudo-electrons experience exactly the same potential outside the core region as the original electrons but have a much weaker potential inside the core region. The fact that the potential is weaker is crucial, however, because it makes the solution of the Schrödinger equation much simpler. This simplicity, in turn, makes the study of complex, low symmetry configurations of atoms much more tractable. Use of plane waves as basis functions, for example, is a very efficient way to accurately and systematically investigate systems with very low symmetry.

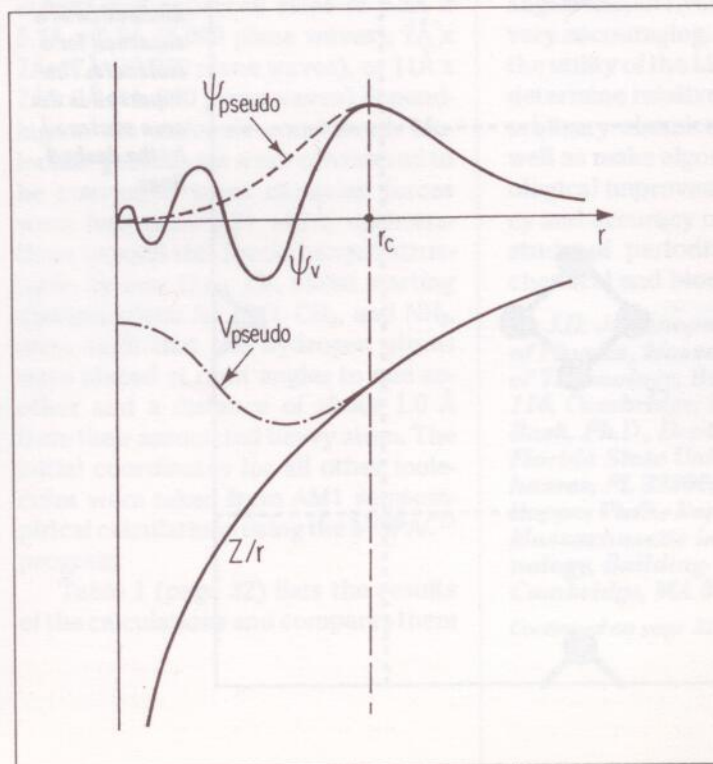
(iii) The super cell approximation<sup>6</sup> allows one to deal with aperiodic configurations of atoms within the framework of Bloch's theorem. One simply constructs a large unit cell containing the configuration in question and

repeats it periodically. This is shown schematically in Figure 2 (Page 30) for the case of a simple molecule. By studying the properties of the system for larger and larger unit cells, one can gauge the importance of the induced periodicity and systematically filter it out.

Using all these ideas a typical calculation would then proceed as follows: (1) freeze the ion cores at a certain configuration; (2) choose an appropriate plane wave basis; (3) choose a starting potential; (4) diagonalize the Hamiltonian to generate a new potential; (5) repeat step (4) until the potential is self-consistent; (6) include ion-ion interactions and calculate the total energy and forces on the ions; (7) move ions along forces for a short distance; (8) repeat steps (2) through (7) until the equilibrium configuration is reached.

The limiting aspects of this approach are the amount of memory available to set up a large matrix and the time spent in diagonalizing it.

A few years ago, Car and Parrinello<sup>7</sup> described a new method for performing  
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**Figure 1.** Schematic illustration of all-electron (solid lines) and pseudo-electron (dashed lines) potentials and their corresponding wavefunctions. The radius at which all-electron and pseudo-electron values match is designated  $r_c$ .

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ing *ab initio* total energy calculations that provided a different way of performing steps (3) to (6) described above. The scheme created a great deal of excitement because it promised to achieve global minimization of the total energy with respect to both electronic and ionic coordinates, thus implying that structural determination in solids could now proceed essentially by simulated annealing.

The basic idea is to minimize the total energy functional using a molecular dynamics approach. In the usual molecular dynamics approach one is given a system of particles with coordinates  $c\{\vec{X}_i\}$  and some total-interaction potential  $V(\{\vec{X}_i\})$ . One then begins with the system at some high temperature and gradually cools down to what is hopefully the configuration  $\{\vec{X}_i\}_0$  that minimizes  $V$ . This is shown in Figure 3 (page 31). In the Car and Parrinello scheme, the total energy functional

$F = F(\{\alpha_i\})$  where  $\alpha_i$  represents the coefficients of the plane wave basis and the set of ionic coordinates. Thus one now thinks of each  $\alpha_i$  as a coordinate of some "particle". To minimize  $F$  one adds a kinetic energy to these "particles" and gradually cools the system down to  $\{\alpha_i\}_0$ . Thus, in principle, one is reduced to solving a simple classical EOM problem. It should be emphasized, however, that  $F$  is physically meaningful *quantum mechanically* only when the  $\alpha_i$ 's, corresponding to the plane-wave coefficients, have zero kinetic energy.

The molecular dynamics method developed by Car and Parrinello<sup>7</sup> has transformed the philosophy of local density approximation pseudopotential plane wave (LDAP-PW) calculations. The method can be used to perform calculations for systems containing on the order of 100 atoms in supercells with sides no longer than about 20 Å. However, severe difficulties are encountered when attempting to use the molecular dynamics meth-

od to perform calculations on much larger systems. The problem lies with the discrete nature of the minimization procedure. Recently, conjugate gradients methods have been developed<sup>8-10</sup> that overcome the difficulties encountered with the molecular dynamics technique by using a *continuous* minimization procedure. Conjugate gradients methods have again transformed the philosophy of LDAP-PW. Using these methods calculations can be performed for systems containing many hundreds of atoms and length scales greater than 20Å.

The molecular dynamics and conjugate gradients methods allow LDAP-PW calculations to be performed for much larger systems than is possible using conventional matrix diagonalization methods. They also allow, for the first time, tractable *ab initio* quantum mechanical simulations to be performed for systems at finite temperature. While these abilities offer the obvious advantage of permitting more complex systems to be studied, there is yet another benefit to be gained by using these new computational methods. At one time it was believed that noble and transition metal atoms and first row elements such as oxygen are intractable with pseudopotentials in a plane wave representation. Recent work<sup>4,5</sup> has shown that pseudopotential calculations can be performed for systems containing these atoms for a large but manageable number of plane waves in the basis set. Molecular dynamics and conjugate gradients methods allow very large plane wave basis sets to be used in pseudopotential calculations. These methods therefore permit LDAP-PW calculations to be performed for a considerably larger variety of systems than previously possible.

LDAP-PW's characteristics of simplicity, generality, and efficiency naturally lead to the consideration of its use to study large heterogeneous non-periodic systems such as biological

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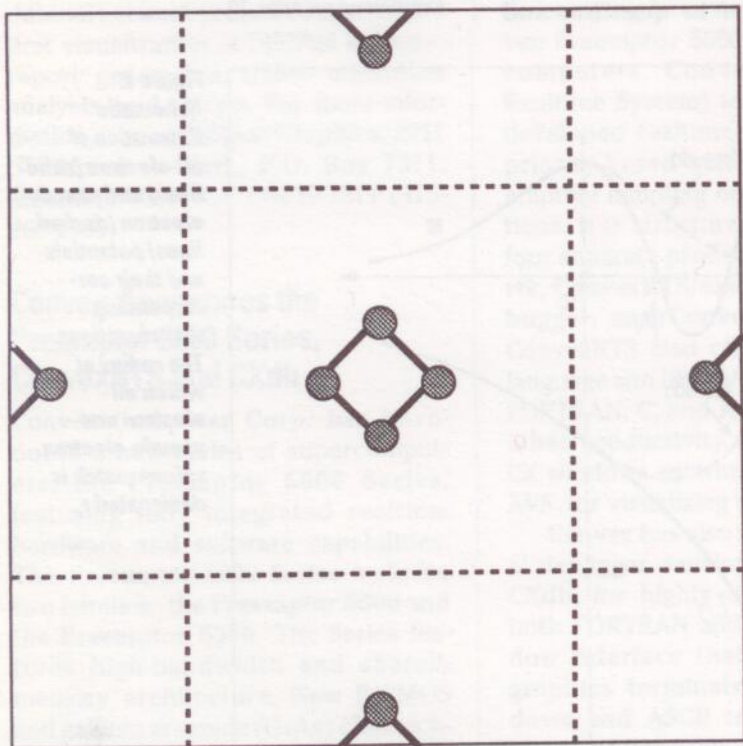


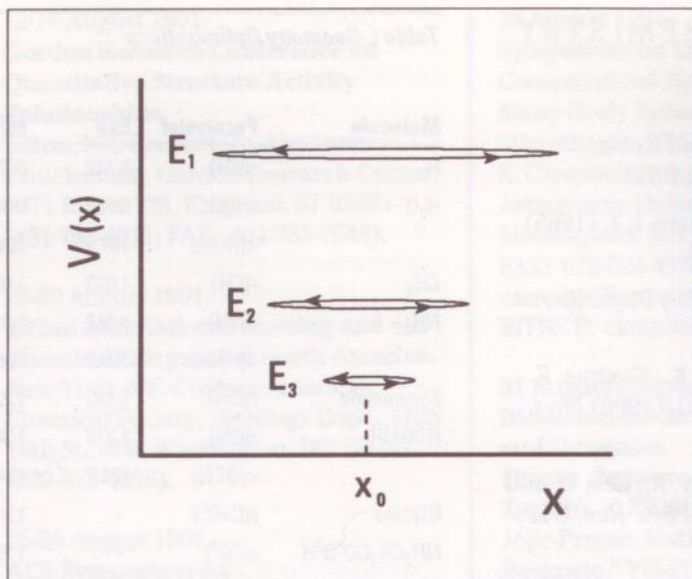
Figure 2  
Schematic illustration of a supercell for a molecule. The supercell is the area enclosed by the dashed lines.

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molecules that may consist of extended organic fragments, metal ions, and solvent water molecules. As a first step in this direction, this article presents the results of tests of the ability of this *ab initio* quantum mechanical method to reproduce structural properties of molecules with a variety of sizes and combinations of functional groups consisting of first-row elements.<sup>11</sup> These include the simple molecules  $H_2$ ,  $H_2O$ ,  $CH_4$  and  $NH_3$  that are constituents of the "biotic-soup" of the primordial atmosphere;<sup>12</sup> neutral glycine which is the simplest amino acid, and formamide which models the peptide-bond between amino acids in a protein. Formamide and glycine are illustrated in Figures 4 and 5 (page 32) respectively.

The supercell approximation allows one to use plane waves as basis functions very easily, but care must be taken to minimize potential artifacts due to interactions between molecules in adjacent unit cells. Because one is attempting to calculate properties of molecules in the gas phase, two restrictions are imposed on the supercell environment: (1) the supercell size is chosen so that there is no van der Waals overlap between molecules in adjacent cells, and (2) rotations and translations of a molecule within the supercell are eliminated by constraining three atoms to remain in a plane, two of these to remain in a line, and one of these atoms to be fixed in space. This constraint is necessary because, without it, electrostatic interactions between cells would cause polar molecules to orient in a way that would align their dipoles. Such large rotations cause a practical problem of inefficient optimization of ionic positions, but have little effect on resultant internal geometries. The internal coordinates of molecules given different orientations in the supercell are found



**Figure 3.** Schematic illustration of annealing procedure in molecular dynamics. The system is started at a high temperature with total energy  $E_1$ . The trajectory at this energy allows the system to sample a large amount of phase space. As the system is gradually cooled to  $E_2$ ,  $E_3$ , etc., the system settles down to a minimum energy configuration.

to differ by less than 1%. Calculated geometries are also found to be insensitive to supercell size as long as the unit cell is large enough to include the molecule together with the van der Waals radii of their atoms.

The calculations were performed at 544.232 electron volt (eV) energy cutoff (except for the  $H_2$  at 816.35 eV cutoff) and supercell sizes of  $5.5\text{\AA} \times 5.5\text{\AA} \times 5.5\text{\AA}$  (5,000 plane waves),  $7\text{\AA} \times 7\text{\AA} \times 7\text{\AA}$  (10,000 plane waves), or  $11\text{\AA} \times 7\text{\AA} \times 5\text{\AA}$  (11,000 plane waves) depending on the molecule considered. Molecular geometries were considered to be converged when cartesian forces were less than  $0.01 \text{ eV/\AA}$ ; optimizations beyond this level changed structures by less than 1%. Initial starting configurations for  $H_2O$ ,  $CH_4$ , and  $NH_3$ , were such that the hydrogen atoms were placed at right angles to one another and a distance of about  $1.0 \text{ \AA}$  from their associated heavy atom. The initial coordinates for all other molecules were taken from AM1 semi-empirical calculations using the MOPAC<sup>13</sup> program.

Table 1 (page 32) lists the results of the calculations and compares them

with both experimental values and MP2/6-31G\* Hartree-Fock calculations.<sup>14</sup>

Overall agreement of LDAP-PW with experiment: MP2 calculations is excellent;  $0.019 : 0.01 \text{ \AA}$  and  $0.6 : 0.4$  degrees for bond lengths and angles respectively. For these molecules the MP2 results differ from experiment by  $0.011 \text{ \AA}$  and  $0.3$  degrees for bonds and angles respectively. These results are very encouraging. Future work will test the utility of the LDAP-PW approach to determine relative energy changes for arbitrary chemical transformation as well as make algorithmic and methodological improvements to the efficiency and accuracy of the method for the study of periodic and non-periodic chemical and biochemical systems.

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Table I. Geometry Optimizations

Molecule	Parameter	Exp	MP2	$\Delta^1_{\circ}$	LDAP-PW	$\Delta^2_{\circ}$	$\Delta_G$
H <sub>2</sub>	r(HH)	0.742	0.738	0.004	0.776	0.034	0.038
H <sub>2</sub> O	r(OH)	0.958	0.969	0.011	0.976	0.018	0.007
	<(HOH)	104.5	104.0	0.5	104.0	0.5	0.0
CH <sub>4</sub>	r(CH)	1.092	1.090	0.002	1.102	0.01	0.012
NH <sub>3</sub>	r(NH)	1.012	1.017	0.005	1.028	0.016	0.011
	<(HNN)	106.7	106.3	0.4	105.7	1.0	0.6
Formamide	r(C=O)	1.193	1.224	0.031	1.217	0.024	0.007
HCONH <sub>2</sub>	r(CN)	1.376	1.361	0.015	1.365	0.011	0.004
	<(OCN)	124.7	124.8	0.1	124.9	0.2	0.1
Glycine	r(C=O <sup>1</sup> )	-	1.218	-	1.204	-	0.014
NH <sub>2</sub> CH <sub>2</sub> CO <sup>1</sup> O <sup>2</sup> H	r(CO <sup>2</sup> )	-	1.358	-	1.345	-	0.013
	r(CC)	-	1.515	-	1.535	-	0.020
	r(NC)	-	1.451	-	1.460	-	0.009
	<(O <sup>1</sup> CO <sup>2</sup> )	-	123.2	-	123.7	-	0.5
	<(O <sup>2</sup> CC)	-	111.4	-	111.9	-	0.5
	<(O <sup>1</sup> CC)	-	125.4	-	124.4	-	1.0
	<(CCN)	-	114.9	-	114.8	-	0.1

All experiment and MP2 values are taken from reference 14 except those of glycine which were optimized using GAUSSIAN 90 at MP2/6-31G\*.  $\Delta^1_{\circ}$  and  $\Delta^2_{\circ}$  are the deviations of the MP2 and LDAP-PW calculations from experiment, and  $\Delta_G$  is the deviation of LDAP-PW from the MP2 values.

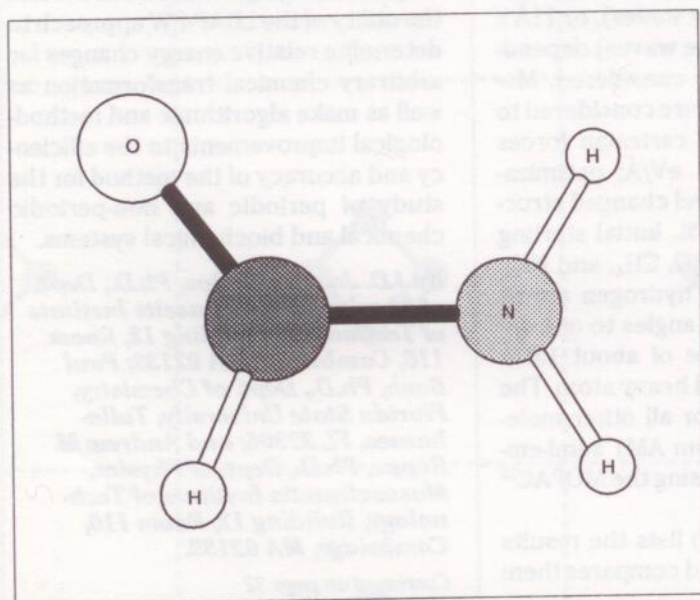


Figure 4. Ball and stick model of formamide: HCONH<sub>2</sub>. The shaded sticks highlight the conjugated  $\pi$ -bonding system.

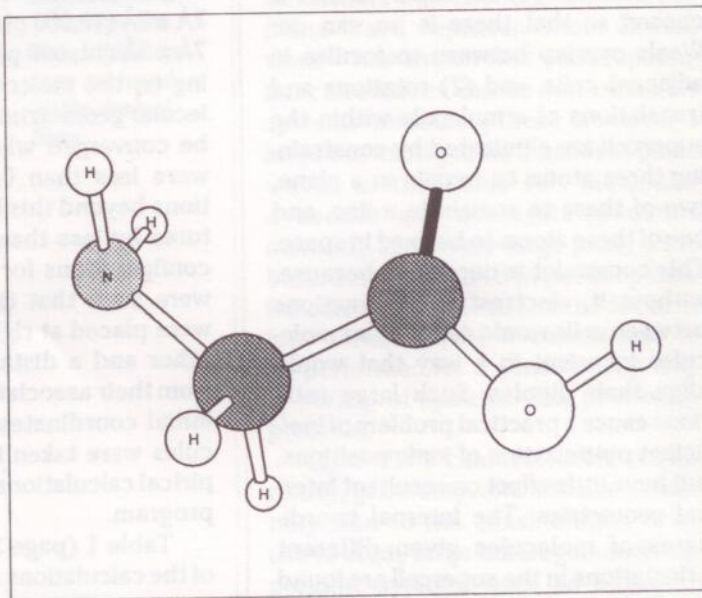


Figure 5. Ball and stick model of glycine: NH<sub>2</sub>CH<sub>2</sub>CO<sup>1</sup>O<sup>2</sup>H. The shaded stick represents a double bond.

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23-25 September 1991.

**The Montreux International Chemical Information Conference & Exhibition.**

Annecy, FRANCE. Contact Harry Collier, Infonortics Ltd., 9A High St., Calne, Wiltshire SN11 0BS, UK.

24-27 September 1991.

**Polymer Modelling and Simulation Workshop.**

Lowell, MA. Contact Continuing Education-Special Programs, 1 University Ave., University of Lowell, Lowell, MA 01854-2881 (508-934-4664).

29 September-1 October 1991.

**Computer Law: Practicing on the Front Line.**

Toronto, CANADA. Contact Barbara Fieser, Executive Director, Computer Law Association, 8303 Arlington Blvd., Ste. 210, Fairfax, VA 22031 (703-560-7747; FAX: 703-207-7028).

30 September-2 October 1991.

**SUP'EUR FALL '91.**

Rome, ITALY. Contact TWT CONVENTIONS/SUP'EUR FALL '91, Palazzo Specchi, Via degli Specchi n. 3, 00186 Rome, ITALY (39-6-6833776, 6548352; FAX: 39-6-6873091).

4-7 October 1991.

**CENIT Asia '91.**

HONG KONG. Contact Hannover Fairs USA, Inc., 103 Carnegie Center, Princeton, NJ 08540 (609-987-1202).

6-9 October 1991.

**Society of Petrochemical Engineers.**

Dallas, TX. Contact Society of Petroleum Engineers, Meetings and Exhibits Dept., P. O. Box 833836, Richardson, TX 75083-3836 (214-669-3377; FAX: 214-669-0135).

6-11 October 1991.

**1991 Joint Meeting**

**FACSS/Pacific Conference.**

Anaheim, CA. Contact FACSS, P. O. Box 278, Manhattan, KS 66502-0003.

7-9 October 1991.

**Second Symposium on High Performance Computing.**

Montpellier, FRANCE. Contact CNUSC, SHPC Secretariat, 950, rue de Saint Priest, BP 7229, 34184 Montpellier Cedex 4, FRANCE (33-67-14-14-14; FAX: 33-67-52-37-63; e-mail: SHPC@FRMOP11.Bitnet).

11-14 November 1991.

**ICCAD 91, IEEE International Conference on Computer Aided Design.**

Santa Clara, CA. Contact IEEE Computer Society (202-371-1013).

14 November 1991.

**2nd W. M. Keck Center for Computational Biology Symposium.**

Houston, TX. Contact Kathleen Matthews, Chair, Dept. of Biochemistry & Cell Biology, Rice University, P. O. Box 1892, Houston, TX 77251 (713-527-4015; FAX: 713-285-5154).

17-22 November 1991.

**Annual AIChE Meeting.**

Los Angeles, CA. Contact Yoram Cohen, Dept. of Chemical Engineering, 5531 Boelter Hall, University of California, Los Angeles, CA 90024 (213-825-8766; FAX: 213-206-4107) or Richard Parnas, Building 224, Rm. A-209, National Institute of Standards and Technology, Gaithersburg, MD 20899 (301-975-5805; FAX: 301-869-3239 or 301-975-2128).

18-22 November 1991.

**SUPERCOMPUTING 1991.**

Albuquerque, NM. Contact Raymond L. Elliott, MS B-260, P. O. Box 1663, Los Alamos National Laboratory, Los Alamos, NM 87545 (505-667-1449).

2-7 December 1991.

**Materials Research Society Meeting.**

Boston, MA. Contact David Sours, Materials Research Society, 9800 McKnight Rd.—Ste. 327, Pittsburgh, PA 15237 (412-367-3003; FAX: 412-367-4373).

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