

## 2-year Report on the HPRN-Network:

### Molecular Properties and Molecular Materials: MOLPROP

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## Part A

# Research Results

## A.1 Scientific Highlights

We describe below the scientific highlights from each of the nodes, emphasizing the contracted work plan, the midterm milestones and the collaborative aspects.

**P1 KTH-Stockholm** The Stockholm partner has continued to focus on the development and application of response methodology for non-linear optical properties. The research efforts devoted to various *optical limiting* processes have given rich results, especially concerning the goal to derive useful materials for laser protection. In addition to the multi-dimensional and multi-branched structures, reported on in the 1-year report, we have now derived a series of metallo-porphyrines and platinum containing compounds with outstanding optical limiting properties. A strong effort on the methodological development paved the way for these results, in particular a non-linear density functional theory based on the quasi-energy ansatz, including all modern exchange-correlation functionals. This development also concerned full and approximate relativistic algorithms and effective core potentials, and a dynamical, density matrix based, theory for pulse propagation in multi-photon active media. The main collaborators in this work are Oslo, Odense and Pisa nodes. The research adheres mostly to the second milestone of the mid-term review.

**P2 U-Valencia** This node has implemented the calculation of SCF and MP2 energies from Cholesky-decomposed two electron integrals. The work on van der Waals complexes has continued together with the Santiago node. A new collaboration line has been opened with the Stockholm YR using coupled cluster methods together with ECP and Douglas-Kroll relativistic methods for calculations of heavy metal compounds. A joint project with the Modena node is started, focusing on coupled cluster studies of the polarizabilities and hyperpolarizabilities of benzene isomers. In collaboration with the Mainz node, we determine the NMR spectra of HCP and CH<sub>3</sub>CP at the coupled cluster level.

**P3 U-Santiago de Compostela** During the second year of the network, this node continued working on the development of a gauge-invariant coupled cluster model using the time-dependent Lagrangian response approach and nonorthogonal orbital rotations. Now we are dealing with the implementation of the model using the Cholesky decomposition in order to reduce the scaling. We work together with the nodes in Valencia and Odense. The applications we carried out dealt with the evaluation of molecular properties using the coupled cluster method and augmented correlation consistent basis sets. We studied (hyper)polarizabilities, second virial coefficients and intermolecular potential energy surfaces and corresponding dynamics of the helium-, neon-, and argon-molecule van der Waals complexes. This work has been carried out together with the nodes in Pisa, Aarhus, Valencia and Odense.

**P4 U-Mainz** At the node in Mainz, analytic second derivatives for excitation energies calculated at the CCSD linear response theory level are currently implemented (by Dan Jonsson). The nodes at Mainz and Pisa (A. Rizzo) developed a coupled-cluster response theory approach for the determination of effective quadrupole centers and applied this scheme to CO, OCS, and N<sub>2</sub>O. In collaboration with the node in Valencia (with T.B. Pedersen), the possibility to compute temperature effects on molecular properties (e.g. NMR shieldings) has been implemented.

Together with the node in Valencia, highly accurate coupled-cluster calculations for the NMR spectrum (shieldings and coupling constants) of HCP have been carried out. In collaboration with the node in Helsinki a program for calculating current densities within the gauge-including atomic-orbital framework has been written and is now applied to investigate ring current effects. Together with the nodes in Odense and Oslo an extensive study concerning the accuracy of calculated equilibrium geometries as well as the accuracy of geometries derived from experimental rotation constants has been performed.

**P5-Modena** The analytic procedure of continuous transformation of the origin of the current density-diamagnetic term to zero for the calculation of magnetic susceptibility and nuclear magnetic shielding has been implemented within the DALTON code. This work is done in collaboration with the Odense node. The graphical codes implemented in the first year of activity have been used for representing streamlines and modulus of the current density induced by a magnetic field in the electrons of a series molecules: 2- and 4-pyrones, 1-2 dithiin and its derivatives, heteropentalenes and s-indacene. The aromaticity of these systems has been discussed in relation to magnetic properties. This work is carried out jointly with the Valencia node. Calculation of electric dipole polarizabilities in dipole velocity and acceleration forms at the coupled-cluster level is being carried out in collaboration with the Oslo node. A new efficient coupled Hartree-Fock computational scheme for parity-violating energy differences in enantiomeric molecules, based on the density matrix formalism, has been developed.

**P6 CNR-Pisa** The work has concerned studies of electric and magnetic, optical properties in molecules, in collaborations with other nodes. Study of interaction induced properties in neon using a Coupled Cluster approach. (Collaboration with the node of Santiago de Compostela). Study of the effect of triple excitations on the Electric Field Gradient induced birefringence of polar molecules (Collaboration with the node of Mainz). Study of the Raman and Raman Optical activity spectra of Carbohydrates, using Hartree Fock Response theory (Involving the YR). Study of the effect of relativity on the Raman Scattering of small molecules (Involving the YR). Analysis of the behavior of Density Functional Theory employed for the study of properties at the nuclei (Nuclear potential, electric field and its gradient at the nucleus, Sternheimer shieldings and polarizabilities of the EFG at the nucleus (Collaboration with the nodes of Oslo and Stockholm).

**P7 U.Helsinki** The MOLPROP collaboration between the Helsinki node and the Arhus group of the Odense node has focused on development of computational approaches for calculation of optical and dynamical properties of strain-induced quantum dots. The methods are being implemented into a new *ab initio* program package. A main goal is to find a quantum dot system with such a size and shape for which the recombination dipole moment is large but the lines are still narrow enough for identifying individual transitions. The present methods have successfully been used for studying nanotechnologically important semiconductor quantum dots containing electrons and holes. The collaboration with the Odense group of the Odense node consists mainly of investigations of optical properties of Bi compounds using their relativistic 4-component RPA method. The collaboration with the Mainz node involves the development of a computational method to calculate the magnetically induced current density employing gauge-including atomic orbitals.

**P8 U.Odense** Calculation of frequency dependent polarizabilities using the coupled cluster approximate triples model (CC3) has been implemented with reduced scaling. We have demonstrated that most accurate equilibrium geometries are obtained based on experimental vibration ground state constants and calculated vibration-rotation interaction constants. A new large-scale CI module has been incorporated in the relativistic four-component second-order MCSCF program. Theory for a more correct account for the free particle g-factor in EPR has been implemented in the relativistic EPR program. Theory and implementation for MCSCF calculations of near-resonant absorption with account for finite lifetimes has been finished. QM/MM methods have been developed and imple-

Table 1: Essential collaboration between nodes

<i>Node</i>	<i>Stockholm</i>	<i>Valencia</i>	<i>Santiago</i>	<i>Mainz</i>	<i>Modena</i>	<i>Pisa</i>	<i>Helsinki</i>	<i>Odense</i>	<i>Oslo</i>
Stockholm	-	X				X		X	X
Valencia	X	-	X	X	X			X	
Santiago		X	-			X		X	
Mainz		X		-		X	X	X	X
Modena		X			-				
Pisa	X		X	X		-		X	X
Helsinki				X			-	X	X
Odense	X	X	X	X		X	X	-	X
Oslo	X			X		X	X	X	-

mented at the Hartree-Fock, MCSCF and Coupled Cluster levels. These methods enable calculations of properties up to third order. Heterogeneous solvation models have been developed and implemented at the Hartree-Fock and MCSCF levels and these methods enable calculations of properties up to fourth order.

**P9 U-Oslo** The Oslo node has worked on the implementation of multipole methods in Dalton. A fully working, efficient implementation of the tree-code algorithm is now in place (scales as  $N\log N$ ), and some optimization is being carried out on the fast multipole method (scales as  $N$ ). Test calculations on systems containing several hundred atoms show that the classical contribution to the Coulomb energy can now be calculated very efficiently. In collaboration with the Stockholm node, quadratic response has been implemented at the LDA, GGA, and hybrid DFT levels of theory. In collaboration with the Aarhus node, very accurate calculations have been carried out molecular structure and vibrational energy levels, yielding important information about the performance of ab initio models. In collaboration with the Modena node, work is being carried out on the calculation of polarizabilities in different gauges.

## A.2 Joint Publications

The partner collaboration is listed. Young researchers hired by MOLPROP are in boldface. Other young researchers are in italic.

1. **P1, P9**. O. Vahtras, O. Loboda, B. Minaev, H. Ågren and *K. Ruud*, Ab Initio Calculations of Zero-Field Splitting Parameters, Chem. Phys, 279, 133 (2002).
2. **P1, P4, P9**. O.Loboda, B. Minaev, O. Vahtras, B.Schimmelpfennig, *K. Ruud*, **D. Jonsson**, H. Ågren, Ab Initio Calculations of Zero-Field Splitting Parameters in Linear Polyacenes, Chem. Phys. Letters, submitted (2002).
3. **P1, P6**. V. Carravetta and H. Ågren, An ab initio method for computing multi-atom resonant photoemission, Chem. Phys. Lett. 354, 100 (2002).
4. **P1, P6**. K. Kaznatcheyev, A. Osanna, C. Jacobsen, *O. Plashkevych*, O. Vahtras, H. Ågren, V. Carravetta, and A.P. Hitchcock, Inner-shell absorption spectroscopy of amino acids. J. Chem. Phys., 00, 000 (2002).
5. **P1, P9**. **P. Salek**, O. Vahtras, T. Helgaker, H. Ågren, Density-functional theory of linear and nonlinear time-dependent molecular properties, submitted to J. Chem. Phys.

6. **P1, P9. P. Salek**, O. Vahtras, J. Guo, Y. Luo, T. Helgaker, H. Ågren, Calculations of two-photon absorption cross sections by means of density functional theory, submitted to *J. Phys. Chem.*
7. **P3, P1. B. Jansik**, A. Sanchez de Meras, B. Schimmelpfennig and H. Ågren. A coupled cluster study of the structures of the lanthanum trihalides LaF<sub>3</sub> and LaCl<sub>3</sub>, Submitted to *J. Chem. Soc. Dalton Transactions*.
8. **P2, P8.** A. Sanchez de Meras, *I. Garcia Cuesta* and H. Koch. A coupled cluster calculation of the spectrum of urea, *Chem. Phys. Lett.* 348 (2001) 469.
9. **P2, P3. T.B. Pedersen**, *J. L. Cacheiro*, B. Fernandez and H. Koch Rovibrational structure of the Ar-CO complex based on a novel 3-dimensional ab initio potential, *J. Chem. Phys.* in press
10. **P3, P8. T.B. Pedersen**, B. Fernandez, H. Koch, Gauge Coupled Cluster response theory using optimized nonorthogonal orbitals', *J. Chem. Phys.* 114, 6983 (2001).
11. **P3, P8. T.B. Pedersen**, B. Fernandez, H. Koch, J. Makarewicz, The helium-, neon-, and argon-cyclopropane van der Waals complexes: Ab initio ground state intermolecular potential energy surfaces and intermolecular dynamics, *J. Chem. Phys.*, 115, 8431 (2001).
12. **P3, P8. T.B. Pedersen**, *J. Lopez Cacheiro*, B. Fernandez, H. Koch, Rovibrational structure of the Ar-CO van der Waals complex from a 3-dimensional coupled cluster potential, *J. Chem. Phys.*, accepted.
13. **P3, P6, P8.** A. Rizzo, C. Hättig, B. Fernandez and H. Koch, The effect of intermolecular interactions on the electric properties of helium and argon. Part III: Quantum statistical calculations of the dielectric second virial coefficients, *J. Chem. Phys.*, accepted.
14. **P4, P6.** A. Rizzo and J. Gauss, CCSD(T) Shielding Polarizabilities, *J. Chem. Phys.* 116, 869 (2002).
15. **P4, P8, P9. F. Pawlowski**, P. Jørgensen, J. Olsen, *F. Hegelund*, T. Helgaker, J. Gauss, K.L. Bak and J.F. Stanton, Molecular Equilibrium Structures from Experimental Rotational Constants and Calculated Vibration-Rotation Interaction Constants, *J. Chem. Phys.* 116, 6482 (2002).
16. **P5, P2. R. Soriano Jartin**, *I. Garcia Cuesta*, A. Sanchez de Meras, and P. Lazzeretti, Calculation of electric dipole polarizability of benzene isomers. Connections with aromaticity, in preparation.
17. **P5, P2. R. Soriano Jartin**, *I. Garcia Cuesta*, A. Sanchez de Meras, and P. Lazzeretti, Calculation of magnetic properties of heteropentalenes aromaticity, in preparation.
18. **P6, P4. M. Pecul** and A. Rizzo Linear response coupled cluster calculation of Raman scattering cross sections. *J. Chem. Phys.*, 116 (2002), 1259.
19. **P6, P4. M. Pecul** and A. Rizzo A Full Configuration Interaction calculation of the density dependence of the <sup>3</sup>He shielding constant, *Mol. Phys.*, 100 (2002), 447.
20. **P6, P3, P8.** A. Rizzo, S. Coriani, B. Fernandez and O. Christiansen, A coupled cluster response study of the electric dipole polarizability, first and second hyperpolarizabilities of HCl. *Phys. Chem. Chem. Phys.*, 4 (2002), 2884-90.
21. **P6, P8.** S. Coriani, **M. Pecul**, A. Rizzo, P. Jørgensen and M. Jaszunski, Ab initio study of magnetochiral birefringence. Submitted, *J. Chem. Phys.*

22. **P6, M. Pecul**, A. Rizzo and J. Leszczynski, The Vibrational Raman and Raman Optical Activity Spectra of D-lactic acid, D-lactate, and D-glyceraldehyde: ab initio calculations, Submitted, *J. Phys. Chem. A*.
23. **P7, P8 M. Braskén, S. Corni**, M. Lindberg, J. Olsen, and D. Sundholm, Full Configuration Interaction Studies of Phonon and Photon Transition Rates in Semiconductor Quantum Dots, *Mol. Phys.* 100 (2002) 911.
24. **P7, P8. S. Corni**, J. Olsen, *M. Braskén*, M. Lindberg, and D. Sundholm, Size Dependence of the Electron-Hole Recombination Rates in Semiconductor Quantum Dots, *Phys. Rev. B* (submitted, April 2002).
25. **P6, P8. K. Hald**, A. Halkier, P. Jrgensen and S. Coriani. Orbital non-relaxed CCSD(T) calculation of first-order one-electron properties. *J. Chem. Phys.*, submitted.
26. **P8, P9. F. Pawlowski**, A. Halkier, P. Jrgensen, K.L. Bak, T. Helgaker and Wim Klopper. Accuracy of spectroscopic parameters of diatomic molecules from ab initio calculations. *J. Chem. Phys.*, submitted.
27. **P8. K. Hald, F. Pawlowski**, P. Jrgensen and C. Hättig. Calculation of frequency dependent polarizabilities using the coupled cluster approximate triples model (CC3). *J. Chem. Phys.*, submitted.
28. **P8, P1. P. Norman**, D. M. Bishop, H.J.Aa. Jensen and J. Oddershede Near-resonant absorption in the time-dependent self-consistent field and multiconfiguration self-consistent field approximations *J. Chem. Phys.* Volume 115, pp. 10323 (2001).
29. **P8, P9. R. Cammi, L. Frediani**, B. Mennucci, J. Tomasi, *K. Ruud* and K. V. Mikkelsen. A second-order, quadratically convergent multiconfigurational self-consistent field polarizable continuum model for equilibrium and nonequilibrium solvation *J. Chem. Phys.* Volume 117, pp. 13-26 (2002)
30. **P8, P9. H. Larsen**, J. Olsen, P. Jorgensen, and T. Helgaker, Direct optimization of the atomic-orbital density matrix using the conjugate-gradient method with a multilevel preconditioner, *J. Chem. Phys.* 115, 9685 (2001).
31. **P8, P9. H. Larsen**, T. Helgaker, J. Olsen, and P. Jorgensen, Geometrical derivatives and magnetic properties in atomic-orbital density-based Hartree-Fock theory, *J. Chem. Phys.* 115, 10344 (2001).

## Part B

# Comparison with the joint program of work

## B.1 Research Objectives

As during the first year of the MOLPROP network, the research objectives - both the low and the high end objectives - were maintained during the second year without any significant changes. Thus theoretical work referring to basic science as well as applications of the theory has progressed. This holds for all the milestone items; The 4th order property toolbox (milestone nr 1); Non-linear optical properties and materials (milestone nr 2); Relativistic theory (milestone 3); New correlation models, in particular new coupled cluster and density functional theory

models, with reduced scaling (milestone 4). Molecular property algorithms have continuously been developed and applied in a variety of contexts. This goes for optical, magnetic and optical properties, both linear and non-linear.

New hyperfine coupling modules have been implemented for applications of magnetic resonance phenomena (NMR and EPR spectroscopies), in order to produce diagnostics and structure-property relations of molecular compounds. This has taken place both at the ab initio (MCSCF and coupled cluster) and density functional levels of theory. One can here mention coding of zero-field splitting parameters, thereby completing calculations of the full spin Hamiltonian; paramagnetic NMR shieldings and hyperfine couplings; use of current densities to compute shieldings and ring currents. The implementation of relativistic 4-component calculations for EPR parameters is a particularly rewarding example. Theory for a more correct account of free particle g-factor in EPR has been implemented, etc. The computation and the viewing of current densities have progressed along the planned lines of research.

The reduced scaling demand has also been met to a large extent; an algorithm with  $N\log N$  scaling has been derived and implemented for the Coulomb integral part, thereby removing a severe bottleneck. More work has been devoted to an iterative algorithm for relaxing the density, thereby further reducing the scaling for very large systems. Correlated techniques have been developed within the coupled cluster methodologies, including new CC3 models and Cholesky decomposition to reduce scaling.

A large step forward has been taken for density functional theory (DFT), and properties computed for this theory: We have during the year derived and implemented a DFT theory for linear and nonlinear response functions using an explicit exponential parametrization of the density operator. The response functions were derived using the Ehrenfest principle and the quasi-energy principle, including all modern correlation-exchange functionals, in particular hybrid functionals at the general gradient-approximation level and fractional exact Hartree-Fock exchange. This makes possible accurate calculations of materials properties, like two-photon absorption and phosphorescence, of technologically interesting compounds, and makes an excellent connection to the high-end goals of the network.

We emphasize also the development with the relativistic methodologies (milestone 3). Higher order properties have been computed using fully relativistic (4-component) wave functions, but also with simplifying relativistic schemes, e.g. the Douglas-Kroll technique and relativistic effective core potentials. The advanced four-component Dirac method now also encompasses multi-configurational self-consistent field wave functions and a new large-scale CI module. Another rewarding development within this network research is the integration between relativistic theory and DFT techniques.

Concerning milestone 2, we have further advanced the quantum dot research: The presented methods have successfully been used for studying nanotechnologically important semiconductor quantum dots containing electrons and holes. In the case of optical limiting, the research has already arrived at some new compounds that have been suggested for synthesis, in particular metallo-porphyrins which are predicted to show optical limiting capability in the whole visible range of the spectrum. Other compounds based on heavy element components have been derived. Research on second harmonic generation has also been pushed forward. Extended systems have also been studied through the development and applications of solvent models, which give possibilities for future large scale applications using the property toolbox. Heterogeneous solvation models have thus been developed and implemented at the Hartree-Fock and MCSCF level; these models enable calculations of properties up to fourth order. This includes the so-called polarized continuum model as well as a "QM-MM" (Quantum mechanics - molecular mechanics) methodology.

## B.2 Research Method

The aim with the MOLPROP research has been develop its own research tools. In this sense there will continuously be changes of the research method, or methods, employed. These methods file under the broad context of first principle “ab initio” methods for molecular modeling. They have during the passed year been further advanced, with some obvious corrections and improvements of the original planning. The main project objective for the research methods thus remains as stated, namely to develop them as such, using the tools of quantum theory, algebra and numerical analysis. The method development has followed the proposed hierarchical way with the goal to converge computational results in a controlled manner. This holds especially for the coupled cluster methodology, on which much efforts are devoted in the network (5 nodes).

The proposed research method of density functional theory (DFT), which at the time of the contract was quite new to us, has been pursued along the planned line with an implementation that matches our “ab initio” toolbox to a considerable extent. This development, which has broadened the scope of the network, fits well with our experience with ab initio time-dependent response theory, and together with the proposed linear scaling technologically, it now forms a basis for “high end” applications on the outlined technically relevant problems. In this respect our research methodology has developed as proposed, or, in fact, even advanced further than that.

A strong focus is maintained on the response methods for calculations of *linear and non-linear properties and spectra*. with a wide variety of applications involving linear and non-linear electromagnetic properties, being time-dependent or time-independent, originating from hyperfine interactions or external fields. Some of the properties have a very strong potential for technical applications and for material science. Several new types of such properties have during the passed year been collected in the gauge-invariant fourth order property toolbox, referring to both variational (SCF, MCSCF, DFT) and perturbational (MP, coupled cluster) wave functions. Among them we can also mention the magnetic resonance parameters (NMR and EPR) for which we produced new algorithms and codes.

## B.3 Work Plan

### B.3.1 Breakdown of tasks

In the following we comment briefly the work plan, in particular any changes from the Technical Annex.

#### B.3.1.1 Gauge-invariant fourth order property toolbox

New properties have been coded in particular fine- and hyperfine structure properties and properties for excited states.

#### B.3.1.2 Relativistic formulations

The Dirac-Fock implementation of non-linear electric properties is now working. Several simplifying relativistic models have been implemented and applied.

### B.3.1.3 Linear scaling and density functional theory

New *linear scaling* scaling algorithms have been derived and coded; an NlogN algorithm for the Coulomb integral part, and an algorithm for iterative density optimization is tested in model calculations. The goal to derive a new *time-dependent density functional code* has already been fulfilled. Solvent models have been implemented, "PCM", "QCMM" and "semiclassical" models.

### B.3.1.4 Response theory in the time domain

No results during year 2.

### B.3.1.5 Direct dynamics

We have derived time-dependent wave packet techniques for nuclear dynamics and implemented these for computations in connection with femto-second spectroscopy. Applications for X-ray Raman scattering used to interpret pulsed synchrotron radiation experiments. The excited state EOM-CC method has produced gradients and Hessians for excited states. An efficient code for RPA excited state gradients have been derived.

### B.3.1.6 Nuclear magnetic spin resonance

Much work has been accomplished within the coupled cluster and the density functional technologies. Theory and code for paramagnetic NMR shieldings have been derived.

### B.3.1.7 Electron spin resonance

The full spin Hamiltonian is now available including A- and g-tensors, and zero-field parameters. Open shell response functions have been derived in Hartree-Fock and DFT. Fully relativistic calculations of g-tensors are now possible.

### B.3.1.8 Non-uniform fields

The graphical codes implemented in the first year of activity have been used for representing streamlines and modulus of the current density induced by a magnetic field in the electron clouds of a series of molecules. These codes give qualitative interpretations of paths whereby the spin and density information passes through the molecules.

### B.3.1.9 Chirality and dichroism

Dichroic properties -either natural or field induced- have been further studied by the proposed response theory techniques. In particular, one can mention a new efficient coupled Hartree-Fock computational scheme for parity-violating energy differences in enantiomeric molecules, based on the density matrix formalism.

### B.3.2 Joint program of work

Table 2: Professional effort of each team

<i>Task</i>	1	2	3	4	5	6	7	8	9
Node									
Stockholm	X	X	X	X	X		X		X
Valencia	X		X			X			
Santiago	X		X				X		
Mainz	X		X			X			X
Modena	X					X		X	X
Pisa	X			X		X			X
Helsinki		X		X			X		
Odense	X	X	X	X		X	X		X
Oslo	X		X	X	X	X			X

### B.3.3 Schedule

In Table 1 we specify the degree of fulfillment of the Schedule outlined concerning months 1-24 in section 3.2 of the technical Annex. In the rightmost column a comment is given and a digit 0-5, where 5 denotes what we regard as a perfect fulfillment of the plan.

### B.3.4 Milestones

The degree of milestone fulfillment was commented already in Part A (Scientific Highlights). We recapitulate the main points here.

#### B.3.4.1 Fourth order property toolbox

Several new properties have been included in the toolbox, which basically now is completed for electric field properties. Relativistic and density functional properties are included as a bonus.

#### B.3.4.2 Non-linear optical properties and materials

The midterm milestone for optical limiting has been completed, and some results have been obtained for second harmonic generation. The method development and a large part of the coding has been completed. Remaining work will focus on straight applications.

#### B.3.4.3 Relativistic formulations

i) 1-component theory - fulfilled; ii) Electric properties 2-component theory - fulfilled to a large extent; iii) Full one-electron implementation for 4-component theory - fulfilled.

Table 3: Schedule and fulfillment of tasks during months 1-24

<i>Months</i>	<i>Projects</i>	<i>Comment</i>
<b>1- Fourth order Toolbox</b>		
1-12	MCSCF and CC third and fourth order properties	Going well - 4
1-12	CC applications of excited state properties	New algorithms derived - 5
13-24	EOM-CC second derivative program	Almost implemented - 4
<b>Relativistic Formulations</b>		
1-18	Relativ. RPA - including applications	Done to the point - 5
6-24	Relativ. 4-component 2nd order MCSCF - CI	Formulation + code - 4
<b>Reduced Scaling correlated methods</b>		
1-12	TD-DFT spectra and properties	Formulated, implemented - 5
1-18	Reduced Scaling in CC	Some reduction obtained - 3
13-24	Linear Scaling in response properties	NlogN prepared - 3
<b>NLO properties and materials</b>		
1-12	Multi-photon and optical limiting	Rich results - 5
1-12	SHG and Kerr materials	Some results - 2
13-24	2D charge-transfer systems	Compounds predicted - 4
13-24	Optical smart windows	Started but delayed - 2
<b>Direct Dynamics</b>		
1-12	Interface to EOM-CC	The EOM-CC part developed - 4
13-24	Use of evolution operator techniques	Not started - 1
<b>Nuclear Magnetic Resonance</b>		
1-12	CC hierarchy for spin-spin couplings	Well met - 4
13-24	Relativistic approaches	With perturbation theory - 3
<b>Electron Spin Resonance</b>		
1-12	Benchmarking	Much development - 5
13-24	London orbital implementation	Not yet - 1
<b>Non-uniform fields modeling</b>		
1-12	Topological features of current densities	New program - 4
13-24	NM dipole induced current densities	New results - 4
<b>Chirality and Dichroism</b>		
1-12	MCD and Magnetic Optical Dichroism	Several Papers - 4
13-24	EF induced chiral absorption	Paper out - 4

#### B.3.4.4 Reduced scaling in correlated methods

NlogN scaling obtained in the Coulomb part for density functional and Hartree-Fock based properties. New low-scaling algorithms for iterative density matrix optimization. Reduction has been achieved for coupled cluster models through the Cholesky decomposition scheme.

#### B.3.5 Research effort of the participants

Table 4: Professional research effort on the network project (man-months) during 01-05-15 to 02-05-15

<i>Participant</i>	<i>YR Months delivered</i>	<i>From other sources</i>	<i>Total individuals</i>
1	25	34	7
2	10.5	26	5
3	1.5	18	3
4	12	17	3
5	9	12	3
6	11	20	3
7	11.5	15	2
8	16	64	12
9	19.5	33	6
Totals	116	239	42

## B.4 Organization and Management

### B.4.1 Network organization

Remains as reported last year. Thus: The possibilities of the international telecommunications have been exploited as much as possible. A link has been created from the main CORDIS homepage to a local home page (<http://www.theochem.kth.se/molprop/>) for special and detailed network information. This home page has frequently been used by the participants as a working array to report on employments, organized meetings, meeting attendance, visits, and other network activities. A special part (sealed with a password) of the home page contains financial network information for the node leaders. The home page also provides links to the individual URL addresses of the partners. MOLPROP announcements and information are canalized through this home page (as a complement to the CORDIS page). The home page is thus constantly updated by the partners, but with the coordinator obviously having the overall responsibility.

Secondly, we have used the page/ mailing list that already exists for the DALTON program system, which is the main common main software system of the network. Much of the actual scientific activity, correspondence, results presentations, benchmarking, program discussions, dissemination and updates takes place in connection with the "DALTON" program and through the use of its home page (<http://www.kjemi.uio.no/software/dalton/dalton.html>).

#### B.4.1.1 List of partner home pages

1. P1- Hans Ågren, Royal Institute of Technology, Stockholm  
URL: <http://www.theochem.kth.se/html/agren/>
2. P2- Alfredo M.J. Sanchez de Meras, Universitat de Valencia  
URL: <http://www.uv.es/~uvalen/eng/>
3. P3- Berta Fernandez Rodriguez, Universitat de Santiago de Compostela  
URL: <http://www.usc.es/qfweb/grupes.html.qch>
4. P4- Jürgen Gauss, Universität Mainz  
URL: <http://www.uni-mainz.de/FB/Chemie/AG-Theoretische/>
5. P5- Paolo Lazzaretti, University of Modena  
URL: <http://www.chimica.unimo.it/lazzeretti.html>
6. P6- Antonio Rizzo, Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R., Pisa  
URL: <http://www.icqem.pi.cnr.it/rizzo/ar.html>
7. P7- Dr. Dage Sundholm, University of Helsinki  
URL: <http://www.chem.helsinki.fi/~sundholm/>
8. P8- Hans Jørgen Aa. Jensen, University of Southern Denmark  
URL: <http://www.sdu.dk/Nat/Chem/staff/sci/Hja.html>
9. P9- Trygve Helgaker, University of Oslo  
URL: <http://www.uio.no/~trygve/>

## **B.4.2 Network meetings**

### **B.4.2.1 2001-10-13/12 Winter School in Theoretical Chemistry 2001 in Helsinki**

Time : 10-13 December, 2000.

Place: Helsinki

Title: Condensed Phase Dynamics Lectures: 17 hours of lectures plus poster presentations

66 PARTICIPANTS: Including all MOLPROP hired YRs

The full program can be found at: <http://www.chem.helsinki.fi/Info/WinterSchool/ws2000.html>

The full participant list can be found at: <http://www.chem.helsinki.fi/Info/WinterSchool/part2001.html>

The signed participant list can be found at: <http://www.chem.helsinki.fi/Info/WinterSchool/ws2001-molprop.gif>

This was the second of the yearly Winter Schools organized by partner 7, and with participation from the MOLPROP network. It focuses each year on a subject that is relevant to the network goals and with strong participation of the MOLPROP YRs. This year it had a somewhat broad scope: Condensed Phase Dynamics.

### **B.4.2.2 2002-01-24/25 MOLPROP Midterm Review Meeting in Copenhagen**

Time : 24-25 January, 2002.

Place: Copenhagen

Lectures: 6 tutorials, 14 YR presentations, 5 main Discussion/ Group work sessions

58 Participants.

58 researchers, 16 seniors, and 42 young researchers associated to the Network were gathered at this midterm review meeting. That includes all YRs hired by the network. The midterm review meeting contained a general network presentation by the coordinator, young researcher presentations, a set of parallel tutorials, a seniors meeting on organizational issues, and a meeting with the EU official about the status of the network and a future outlook. Time was also set aside for group work and group presentations focusing on different aspects of the network research goals. Future directions of the work was debated and some revisions and augmentations of the work plan were suggested. Exchange of information was provided, especially concerning a detailed plan for manning the remaining YR employments. All 14 hired YRs presented themselves and, briefly, their roles in the network.

A full program can be found at: <http://www.theochem.kth.se/molprop/midterm/>

### **B.4.2.3 2002-01-25/26 MOLPROP Second Network Coordination meeting in Copenhagen**

Time : 25-26 January, 2002.

Place: Copenhagen

Lectures: 21 lectures

58 Participants. The 58 researchers (16 seniors, and 42 young researchers) stayed in Copenhagen for the Second Network Coordination Meeting. 21 scientific presentations were made by young researchers (fourteen 30 minute

talks and seven 20 minute talks). The topics covered those which were at the front in the network research. Young researchers were also selected for chairing the different sessions.

Full program can be found at: <http://www.theochem.kth.se/molprop/midterm/>

### B.4.3 Networking

Meeting attendances are reported under B.4.2 "Network meetings".

#### B.4.3.1 Twinning Program

The twinning program includes node-to-node visits by the hired YRs for carrying out collaborative research and for general information about research work in a foreign country. During year 2 it was carried out as described below:

1. During 19/11 - 9/12 Mark Watson from the Oslo node visited Stockholm. He gave a seminar on Linear Scaling methodology, and participated in group seminars and discussions with other PhD students at the institute.
2. During 12/12 - 23/12 Rafael Soriano from the Modena group visited Stockholm. He worked in collaboration with Oscar Rubio on some issues of molecular phosphorescence and fluorescence.
3. During 19/11 - 10/12 Pawel Salek from the Oslo group visited Stockholm. He gave a seminar on DFT Response Theory and participated in group seminars and discussions. He performed DFT response calculations together with a PhD student in the Stockholm group.
4. Branoslav Jansik from the Stockholm node paid two twinning visits to the Valencia node during 7-22/1 2002 and 1- 13/3 2002, for working on the Lanthanum halide project.
5. Visit of Dan Jonsson to Pisa (26-11-01 to 7-12-01) to work on the coupled-cluster calculations of mixed electrical and magnetic properties.
6. Visit of Thomas Bondo Pedersen from Valencia to Mainz (26-11-01 to 8-12-01) to work on vibrational corrections to molecular properties.
7. Oscar Rubio Pons from the Stockholm node paid a twinning visit to the Modena node 7-21/1 2002.
8. Visit of Dr. Magdalena Zofia Pecul to Aarhus, node of Odense, for the duration of one month, for training and research. Ab initio studies of magnetochiral birefringence.
9. During 7/1-27/1 2002 Stefano Corni from Helsinki visited Aarhus (Odense node).
10. During 14/1-3/2 2002 Michael Patzschke from Helsinki visited Odense to work with the DIRAC relativistic program.
11. Filip Pawlowski from the Odense node paid a twinning visit to Oslo 7-22/1 2002 in order to study common Coupled Cluster methodology.

12. Filip Pawlowski spent the week 14/1 - 18/4 at the Oslo node, working on the accurate calculations of vibrational frequencies (benchmarking) with T. Helgaker and P. Jorgensen. He gave a group seminar.
13. Peter Macak from Stockholm spent the week 12.11.01 - 18.11.01 at the Oslo node, working with Helgaker on gradients of excited-state surfaces. He gave a group seminar.

#### B.4.3.2 Other MOLPROP visits

Other MOLPROP visits were executed according to the following:

1. Kenneth Ruud, (YR) Oslo node visited Stockholm 21-29/11 2001 for merging the HSROHF and the spin-spin coupling codes.
2. Vincenzo Carravetta (Pisa) visited Stockholm to work on the DALTON STEX code, and coorganize a Swedish-Italian workshop in Stockholm including MOLPROP students.
3. Matthias Stein (YR) from the technische Universität in Berlin visited Stockholm during 1-14 June 2001 to discuss and collaborate on EPR g-tensor calculations of bio-radicals.
4. Visit of Dr. Rizzo (Pisa) to Stockholm from April 29th to May 10th 2002, for collaboration on interaction electric and magnetic properties of heavy atomic systems (relativistic effects).
5. 2001-12-01: Dr. Henrik Koch (Odense) visited Valencia, following up on the implementation of the Cholesky decomposition code.
6. Visit of Alfredo Sanchez (Valencia) to Modena (17-21/10 2002) to start joint applications in the field of high order properties
7. Visit of Alfredo Sanchez (Valencia) to Mainz (29/6 - 4/7 2001) to work on applications of CCSD response to calculate NMR parameters
8. Berta Fernandez from Santiago de Compostela visits the node in Valencia 2002-06-08.
9. Visit of Berta Fernandez, Santiago de Compostela, to Pisa, 8th-15th of April 2002. Collaboration of interaction electric and optical properties of Neon.
10. Visit of Jonas Juselius (YR) from Helsinki to Mainz (08-04-02 to 26-04-02) to work on the calculation of current densities in the connection of ring current models
11. Visit of Jonas Juselius (YR) from Helsinki to Mainz (11-11-01 to 29-11-01) to work on the calculation of current densities in the connection of ring current models.
12. Visit of Jurgen Gauss (Mainz) to Aarhus (19/3 -22/4 2002) to work on a benchmark study on vibrational frequencies
13. Visit of Dan Jonsson (Mainz, YR) to Oslo from 2001-03-29 to 2001-04-15 to work on the implementation of integral direct response theory for high-spin restricted open-shell HF within the Dalton program package.
14. Visit of Dr. Rizzo (Pisa) to Oslo April 25th to 29th 2002, for collaboration on DFT determination of Electric Field and EF gradient properties at the nuclei.

15. Visit of Dr. Rizzo (Pisa) to Dept of Chemistry of the University Aarhus, June 1st to June 28th, for a collaboration with Prof. Jorgensen (node of Odense) on the ab initio study of magnetochiral birefringence.
16. Jeppe Olsen (Odense) visited Helsinki 3.6.2002-6.6.2002. Development of the quantum dot program
17. Jeppe Olsen (Odense) visited Helsinki 12.9.2001-18.9.2001. Development of the quantum dot program.
18. Dage Sundholm (Helsinki) visited the Odense (Aarhus) node for work on quantum dots (20.01.2002-24.01.2002).
19. Helena Larsen (Odense, YR) visited the Oslo node 27/5-3/6 2001 to work with Trygve Helgaker.
20. Visit of Trygve Helgaker (Oslo) to Aarhus 02.02.02 - 08.02.02, work on benchmarking with P. Jorgensen and J. Olsen.
21. Visit of Trygve Helgaker (Oslo) to Odense 25.08.01 - 26.08.01, to work on the DIRAC program with with H.J.Jensen.
22. Visit of Trygve Helgaker (Oslo) to Cambridge 12.06.01 - 15.06.01 to work with Mark Watson.
23. Visit of Trygve Helgaker (Oslo) to Aarhus 07.09.01 - 12.09.01. Work on frequencies with Filip Pawlowski.

## **B.5 Training**

### **B.5.1 Vacancies**

Vacancies in the YR program have been advertised on the MOLPROP home page, with links from the personal home pages of the individual scientists in the network and from the pages of the institutions to which they belong. Proper advertisement has also been made through the channels provided by CORDIS. The frequent meeting attendance by MOLPROP members has given special possibilities to announce the positions.

### **B.5.2 Recruitment of YRs**

Despite some initial recruitment problems and the early commencement date, most recruitments were made at the beginning of the second year, and now the network runs on full manpower. As seen in the hiring table below the prognosis is very bright and ends at 283 months, well above the contracted 252 months.

### **B.5.3 Scheme of Hiring of Young Researchers**

### **B.5.4 Integration of YRs**

In addition to the 13 twinning actions involving the hired YRs, there has been a strong participation of YRs in the visit program, see section B.4.3. The participation of the YRs in the 3 network meetings amounted to about 42 in the Midterm review meeting and also in the second coordination meeting (including all the hired YRs). Furthermore all hired YRs participated in the Helsinki Winter school. Many publications have been produced involving the YRs; 19 such publications have been obtained during the year with node-to-node collaboration, see A.2. The total number of publications from the hired YRs amount to over 30 during the year.

Table 5: Hiring-Months of Young Researchers 01-05-15 to 02-05-15\*

Participant	Contract deliverable of Young Researchers to be financed by the contract (person-months)			Young Researchers financed by the contract so far (person-months)		
	Pre-doc (a)	Post-doc (b)	Total (a+b)	Pre-doc (c)	Post-doc (d)	Total (c+d)
P1-Stockholm	25 (31.5)		25 (31.5)	24		24
P2-Valencia		10.5 (10.5)	10.5 (10.5)		24	24
P3-Santiago		1.5 (13.5)	1.5 (13.5)		24	24
P4-Mainz		12 (14)	12 (14)		24	24
P5-Modena	9 (9)		9 (9)		24	24
P6-Pisa		11 (12.5)	11 (12.5)	24		24
P7-Helsinki	11.5 (13)		11.5 (13)		24	24
P8-Odense	14.5 (18)	1.5 (1.5)	16 (19.5)	36	12	48
P9-Oslo	9 (9)	10.5 (10.5)	19.5 (19.5)	36		36
Total	69 (80.5)	47 (62.5)	116 (143)	120	132	252

\* Total months during 00-05-15 to 02-05-15 in parenthesis.

Table 6: Hiring Scheme

<i>Node</i>	<i>PhD/Post – Doc</i>	<i>c/r<sup>1</sup></i>	<i>Period</i>	<i>NrMonths<sup>2</sup></i>
Stockholm	PhD	c	1/11 2000 - 31/10 2002	24
Stockholm	PhD	c	1/9 2001 - 15/5 2003	21
Stockholm	PhD	c	1/1 2002 - 15/5 2003	16
Valencia	Post-Doc	c	1/7 2001 - 15/5 2003	23
Santiago	Post-Doc	c	1/7 2000 - 30/6 2001	12
Mainz	Post-Doc	c	1/3 2001 - 15/5 2003	26
Modena	PhD	c	15/9 2001 - 15/5 2003	20
Pisa	Post-Doc	c	1/4 2001 - 30/3 2002	12
Pisa	PhD	r	1/8 2002 - 15/5 2003	10
Helsinki	PhD	c	1/9 2001 - 15/5 2003	20
Helsinki	PhD	c	1/6 2002 - 15/5 2003	11
Odense	PhD	c	1/2 2001 - 15/5 2003	28
Odense	Post-Doc	c	1/4 2002 - 31/3 2003	12
Odense	PhD	c	1/3 2002 - 28/2 2003	12
Oslo	Post-Doc	c	1/7 2001 - 30/6 2002	12
Oslo	PhD	c	15/8 2001 - 14/8 2002	12
Oslo	Post-Doc	c	1/5 2002 - 30/4 2003	12
Total	PhD			174
Total	Post-Doc			109
Grand-total				283

1. c= contracted, r=recruited

2. Half-months are included/excluded each second time.

### B.5.5 Special measures

Apart from the integration of the YRs in the specified network research projects, we have actively stimulated the YRs to participate in the meetings (especially the 3 network meetings), and to give talks or posters at these meetings. 35 oral presentations were made by YRs the MOLRPOP network meetings alone. All this have been accounted for in the foregoing. We have also tried to activate the YRs as much as possible in the editing and preparation of the research papers which they coauthor.

We emphasize that a full twinning program has been executed involving all the hired YRs, although not following the detailed plan of the contract Annex. This is mainly due to that the recruitment dates came out so differently.

### **B.5.6 Equal opportunities**

We do have made special efforts to recruit female students, however, since the recruitment situation initially was problematic we were forced to take a somewhat pragmatic view in this context. Node 6 has recruited a female post-doctor.

### **B.5.7 Multidisciplinarity**

The fields covered by the network projects are quite versatile; mathematics, numerical analysis, quantum mechanics, and scientific computing. We have objectives covering basic science as well as materials applications. We have tried to emphasize this in the network meetings and visits involving the YRs, so they are trained (at least) in computing and programming as well as in theory.

### **B.5.8 Industrial connections**

No connections utilized so far.

## **B.6 General Comments**

We, ourselves, consider the network to be a success in all aspects; science, training, meetings, visits, and collaboration in general. There has been a lot of enthusiasm and good spirits among the partners. This owes to some extent to the close connections that already were established between most of the nodes, but also, as we feel, to that we succeeded to form new connections and to well integrate every node, every YR in the network. These facts have also greatly alleviated the coordination of the network.

The early difficulty of recruitment has completely been overcome, and, as can be understood by the tabulation in the foregoing section, the prognosis is that the network will deliver well beyond the contracted number of man-months. We have great confidence in the further success of the network.