

3rd Year and Final Reports on the HPRN-Network:

Molecular Properties and Molecular Materials: MOLPROP

Network Data:

Contract Number:	HPRN-CT-2000-00013
Commencement Date:	15-05-00
Duration of contract:	36 months
Period of the 3rd Year Report:	12 months from 02-05-15 to 03-05-14
Period of the Final Report:	36 months from 00-05-15 to 03-05-14

Network Coordinator Data:

Prof. Hans Ågren
Theoretical Chemistry
Royal Institute of Technology
Roslagstullsbacken 15
SE-10691 Stockholm, Sweden
Tel: +46 55378416
Fax: +46 55378590
E-mail: agren@theochem.kth.se
URL-Ågren: <http://www.theochem.kth.se/html/agren>
URL-MOLPROP: <http://www.theochem.kth.se/molprop>

Contents

A	Research Results	7
A.1	Scientific Highlights - 3rd Year Report	7
A.1	Scientific Highlights - Final Report	9
A.2	Joint Publications - 3rd Year Report	16
A.2	Joint Publications - Final Report	19
B	Comparison with the joint program of work	24
B.1	Research Objectives - 3rd year Report	24
B.2	Research Method - 3rd year Report	27
B.3	Work Plan - 3rd year Report	27
B.3.1	Breakdown of tasks - 3rd year Report	27
B.3.1.1	Gauge-invariant fourth order property toolbox	28
B.3.1.2	Relativistic formulations	28
B.3.1.3	Linear scaling and density functional theory	28
B.3.1.4	Response theory in the time domain	28
B.3.1.5	Direct dynamics	28
B.3.1.6	Nuclear magnetic spin resonance	28
B.3.1.7	Electron spin resonance	29
B.3.1.8	Non-uniform fields	29
B.3.1.9	Chirality and dichroism	29
B.3.2	Schedule and Milestones - 3rd year Report	29
B.3.2.1	Fourth order property toolbox	30

B.3.2.2	Non-linear optical properties and materials	30
B.3.2.3	Relativistic formulations	30
B.3.3	Research effort of the participants - 3rd year Report	31
B.1	Research Achievements - Final Report	31
B.1.1	Research Objectives - Final Report	31
B.1.2	Research Method - Final Report	33
B.1.2.1	Development of high-level correlation methods	33
B.1.2.2	Relativistic methods	33
B.1.2.3	Linear Scaling methods	34
B.1.2.4	Methods for modelling of characterizing technologies	34
B.1.3	Breakdown of tasks - Final Report	35
B.1.3.1	Gauge-invariant fourth order property toolbox	35
B.1.3.2	Relativistic formulations	35
B.1.3.3	Linear scaling and density functional theory	35
B.1.3.4	Response theory in the time domain	35
B.1.3.5	Direct dynamics	36
B.1.3.6	Nuclear magnetic spin resonance	36
B.1.3.7	Electron spin resonance	36
B.1.3.8	Non-uniform fields	36
B.1.3.9	Chirality and dichroism	37
B.1.4	Schedule and Milestones - Final Report	37
B.1.4.1	Fourth order property toolbox	37
B.1.4.2	Non-linear optical properties and materials	37
B.1.4.3	Relativistic formulations	37
B.1.4.4	Reduced scaling in correlated methods	39
B.1.5	Research effort of the participants - Final Report	39

B.4 Organization and Management - 3rd Year Report	39
B.4.1 Network organization - 3rd Year Report	39
B.4.2 Network meetings - 3rd Year Report	40
B.4.2.1 2002-06-24 - 2002-07-06 SOSTRUP Summer School in Molecular Properties in Arhus	40
B.4.2.2 2002-10-04 - 2002-10-05 MOLPROP meeting in Valencia	41
B.4.2.3 2002-09-12 - 2002-12-12 Winter School in Theoretical Chemistry in Helsinki	41
B.4.2.4 2003-04-23 - 2003-04-25 MOLPROP meeting on Density Functional Theory in Stockholm	41
B.4.2.5 2003-04-26 - 2003-04-26 MOLPROP Final Meeting in Stockholm	42
B.4.3 MOLPROP visits - 3rd year Report	42
B.4.3.1 Summer Schools, Meetings	44
B.2 Organization and Management - Final Report	44
B.2.1 Network organization - Final Report	44
B.2.2 Communication Strategy - Final Report	44
B.2.3 Dissemination of results - Final Report	46
B.2.3.1 List of partner home pages	46
B.2.4 Network Meetings and Schools - Final Report	47
B.2.4.1 2000-05-28 - 2000-05-29: First MOLPROP network meeting	47
B.2.4.2 2000-12-11 - 2000-12-15 Winter School in Theoretical Chemistry 2000	47
B.2.4.3 2000-01-25 - 2000-01-27 First MOLPROP Workshop Meeting in Santiago de Com- postela	48
B.2.4.4 2001-12-10 - 2001-12-13 Winter School in Theoretical Chemistry in Helsinki	48
B.2.4.5 2002-01-24 - 2002-05-25 MOLPROP Midterm Review Meeting in Copenhagen . . .	49
B.2.4.6 2002-01-25 - 2002-01-26 MOLPROP Second Network Coordination meeting in Copen- hagen	49
B.2.4.7 2002-06-24 - 2002-07-06 SOSTRUP Summer School in Molecular Properties in Arhus	49
B.2.4.8 2002-10-04 - 2002-10-05 MOLPROP meeting in Valencia	50

B.2.4.9	2002-12-9 - 2002-12-12 Winter School in Theoretical Chemistry in Helsinki	51
B.2.4.10	2003-04-23 - 2003-04-25 MOLPROP meeting on Density Functional Theory in Stockholm	51
B.2.4.11	2003-04-26 - 2003-04-26 MOLPROP Final Meeting in Stockholm	51
B.2.5	Networking Activities - Final Report	52
B.2.5.1	Node-to-node visits	52
B.5	Training - 3rd Year Report	55
B.5.1	Vacancies	55
B.5.2	Recruitment of YRs - 3rd Year Report	55
B.5.3	Integration of YRs - 3rd Year Report	56
B.5.4	Special measures - 3rd Year Report	56
B.5.5	Equal opportunities - 3rd Year Report	56
B.5.6	Multidisciplinarity - 3rd Year Report	56
B.5.7	Industrial connections - 3rd Year Report	56
B.6	Difficulties - 3rd Year Report	57
B.7	Adjustments to costs previously reported - 3rd Year Report	57
B.3	Training Overview - Final Report	58
B.3.1	Training Activities - Final Report	58
B.3.1.1	Training instruments	58
B.3.1.2	Summer Schools	58
B.3.1.3	Twinning Program	59
B.3.1.4	Workshop and Visit program.	60
B.3.1.5	Tutorials over the net - Coherent training	60
B.3.1.6	Use of softwares as platforms for training and transfer of knowledge.	60
B.3.1.7	Other Measures	61

B.3.2 Final result for hiring of young researchers - Final Report	61
B.3.3 What happened with the YRs after appointment ? - Final Report	61
B.3.4 Importance of MOLPROP training for YR careers	64
B.4 Industry connections - Final Report	64
B.5 Recommendations - Final Report	65

Part A

Research Results

3rd Year Report

A.1 Scientific Highlights - 3rd Year Report

We describe below the scientific highlights from each of the nodes during the 3rd year, emphasizing the contracted work plan, the midterm milestones and the collaborative aspects. The latter are marked by boldfacing.

P2 KTH-Stockholm

The Stockholm node has continued to develop time-dependent density functional theory (DFT) in collaboration with the **Oslo node**. A special edge during the 3rd year of work refers to open-shell spin restricted DFT. The corresponding linear response code predicts molecular g-tensors and excitation spectra with a higher accuracy than hitherto possible. Higher order response with so-called triplet operators have also been included into the toolbox. New core RPA-, complex polarization propagator-, and spin restricted static exchange DFT algorithms have been derived for X-ray spectra together with the **Pisa node**. Further progress in the dynamical density matrix based code for pulse propagation in multi-photon active media has been accomplished and new applications of this code have been presented. The drug solubility problem was addressed in collaboration with the **Odense node**.

P2 U-Valencia

During the 3rd year the code developed during the whole period has been basically finished. At present, the Cholesky decomposition of the two-electron integrals can be routinely carried out and used to compute energy and molecular properties. Collaboration with the **Santiago and Odense nodes**. Referring to applications, we have finished the calculation of the electronic spectra of TCNE and TTF, determined the RMN spectra of small phosphoalkines (with **Mainz node**) and some magnetic properties of hetero-pentalenes (with **Modena node**).

P3 U-Santiago de Compostela

During the 3rd year we have been dealing with applications regarding the evaluation of molecular properties mainly for van der Waals complexes. The work was done in collaboration with the **nodes in Pisa and Odense**. We are dealing now with the evaluation of these properties for the corresponding rare gas mixtures. Other main applications of the coupled cluster code were the evaluation of the interaction energy surfaces for the Ar-CO and the benzene-N₂ van der Waals complexes (together with the **node in Valencia**). Regarding the code we dealt with the development and programming of the CCSD(T) code using the Cholesky decomposition (with the **node in Valencia**).

P4 U-Mainz

During the third year, the implementation of analytic second derivatives calculated at the CCSD level (by YR Dan Jonsson) has been almost completed. Together with the **node in Pisa**, high-level coupled-cluster calculations have been completed for the electric-field gradient induced birefringence and the Cotton-Mouton effect. In a collaborative effort with the **node in Helsinki**, electron-correlated schemes have been implemented to compute current-densities with the gauge-including atomic orbital framework. Together with the **node in Odense** the use of quantum chemical calculations for the determination of highly accurate equilibrium geometries from experimental rotational constants has been further explored. Further calculations concerning the NMR spectra of HCP and its derivatives have been carried out together with the **node in Valencia**.

P5 U-Modena

During the third year: (1) The CTOCD scheme for calculation of NMR magnetic shielding has been implemented in the DALTON code. Coupled cluster calculations are carried out in collaboration with the **Odense and Valencia nodes**: (2) The graphical codes implemented in the first and second 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. This work is carried out jointly with the **Valencia node**. (3) Calculation of electric dipole hypershieldings at the nuclei have been carried out in collaboration with the **nodes of Oslo and Valencia**.

P6 CNR-Pisa

The following collaboration projects have been carried out: Study of electric and magnetic, optical properties in molecules, in collaboration **with Santiago, Oslo, Stockholm and Mainz**: Study of the effect of triple excitations on the magnetizabilities and hypermagnetizabilities of noble gases (with **Mainz**): Study of the Raman, Raman Optical and Vibrational Raman optical activity spectra of "large" molecules using DFT response (with **Oslo**, involving an YR): Implementation of the Static Exchange Approximation (STEX) in DIRAC, a fully relativistic quantum chemistry program. Application of STEX and related methods for investigation of relativistic effects on X-ray spectra (with **Stockholm** involving YR).

P7 U-Helsinki

A novel *ab initio* program package for calculations of optical properties of strain-induced quantum dots has been developed in collaboration with the **node in Odense**. This is the first *ab initio* program package for large-scale correlated calculations on strain-induced semiconductor quantum dots. The computational methods have been used for studying energy levels, photon relaxation rates, and photon recombination rates of excitons, biexcitons and triexcitons confined a InGaAs/GaAs strain-induced quantum dot. In a collaborative effort with the **Mainz node**, electron-correlated schemes have been implemented to compute current-densities with the gauge-including atomic orbital framework.

P8 U-Odense

Relativistic 4-component RPA has been derived and implemented for various non-linear properties. Relativistic 4-component large scale CI and MCSCF energy calculations, London orbitals for NMR shieldings,

Table 1: Essential collaboration between nodes during 3rd year

<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
Valencia		-	X	X	X			X	
Santiago		X	-			X		X	
Mainz		X		-		X	X	X	
Modena		X			-			X	X
Pisa	X		X	X		-			X
Helsinki				X			-	X	
Odense				X		X	X	-	X
Oslo	X				X	X		X	-

and ESR g-tensors for any spin state on the Hartree-Fock level have been implemented. Several applications of these methods have been carried out together with the **Helsinki and Pisa nodes**. A novel linear scaling algorithm replacing Fock matrix diagonalizations have been developed in collaboration with the **Oslo node**. Developments within the coupled cluster hierarchy of methods have been further carried out in collaboration with the **Mainz node**.

P9 U-Oslo

The following collaboration projects have been carried out: a) The Oslo node has finished the development of multipole methods in Dalton, including fully working, efficient implementations of the fast multipole method (FMM) (scales as N) and of the tree-code (scales as N logN). As a result, we are now in a position to calculate the Kohn-Sham matrix of large systems very efficiently, for systems containing more than thousand atoms. b) In collaboration with the **Stockholm and Pisa** nodes work has been carried out to implement and apply response theory in Dalton: c) In collaboration with the **Odense** node a coupled-cluster code for the calculation of molecular gradients at the CCSD(T) level has been developed: d) In collaboration with the **Modena** node, work is being carried out on the calculation of dipole hyperpolarizabilities in the Hellmann-Feynman theorem:

Final Report

A.1 Scientific Highlights - Final Report

We describe below the scientific highlights from each of the nodes, emphasizing the contracted work plan, the midterm milestones and the collaborative aspects. The latter are marked by boldfacing.

P1 - Stockholm

As constituting the coordinating node the Stockholm partners have tried to follow the scientific development within the network as closely as possible, and specialized on a few of these. On the development

side the foremost work of Stockholm has been associated to the first milestone, the 4th order toolbox, and in particular to the development of time-dependent density functional theory (DFT) and to the inclusion of DFT linear and nonlinear properties in the toolbox. In collaboration with the **Oslo** node the DFT theory and code is now developed to comprise properties generated by interactions with fields of various sources; electric, magnetic, time-independent, time-dependent, internal or external fields. The DFT code offers electron-correlated calculations of properties as different as linear and non-linear optical coefficients, multi-photon excitations, spin-dependent properties, magnetizabilities, magnetic resonance parameters (NMR, EPR, ODMR), and X-ray phenomena. This main objective has been fulfilled very well, in some parts well beyond the initial expectations and plans. Combined with the linear scaling technology developed by the Oslo partners we feel this to be a very significant result of the MOLRPOP network in terms of prospects for future simulations of molecular materials.

Several collaboration projects have been pursued with the MOLPROP partners. Thus with the **Pisa node** we have collaborated on X-ray spectra and properties (V. Carravetta, and Ulf Ekström (YR)), and on higher order response properties (A. Rizzo); with the **Valencia node** we have collaborated on properties of heavy metal compounds using approximate relativistic methods (A. Sanchez and B. Jansik (YR)), together with the **Mainz node** we have been involved in benchmarking CC-to-DFT calculations on hyperpolarizabilities (J. Gauss and D. Jonsson (YR)). The drug solubility problem was addressed in collaboration with the **Odense node** (K. Mikkelsen and L. Pettersson YR).

The Stockholm partners have taken a special responsibility for the high end - application - goals - of the network. In this research they have focussed much on optical limiting processes and materials. A goal has been to characterize all important optical excitation processes within a material and couple this information to a dynamic laser propagation program in order to simulate how the material - and an actual device - behaves for different characteristics of the laser light and of the sample itself (dimension, composition etc.) The research has led to increased understanding of the critical processes and factors for optical limiting in particular and for light control in general. A number of porphyrine and organo-platinum compounds have been predicted with outstanding properties in this respect. These are now synthesized in a couple of laboratories.

P2 U-Valencia

The main goal of Valencia node inside the MOLPROP project was to reduce the scaling of coupled cluster methods. This has been accomplished by means of Cholesky decomposition, although the program we have written still needs further improvements. The development in dressing techniques for CI wavefunctions resulted in an improved code for determination of molecular energy and first order properties.

Applications have focussed in electronic spectra (urea, TTF and TCNE among others) and magnetic properties (phosphoalkenes, pyrrolo-pyrroles and furano-furans among others). The work on van der Waals complexes has been conducted together with the the **Santiago node**. A new collaboration line was opened with the **Stockholm** YR (B. Janisk) using coupled cluster methods together with ECP and Douglas-Kroll relativistic methods for calculations of heavy metal compounds, studying also relativistic effects in these compounds. A joint project with the **Modena node** is started, focusing on coupled cluster studies of the polarizabilities and hyperpolarizabilities of benzene isomers. Also some magnetic properties of heteropentalenes have been being calculated in the frame of the CTODD formalism. In collaboration with the **Mainz node**, we determine the NMR spectra of HCP and CH₃CP at the coupled

cluster level.

P3 U-Santiago de Compostela

Regarding the code development, during the first 18 months of the network, we dealt with the development of gauge invariant coupled cluster theory. Using the time-dependent Lagrangian response approach, the orbital optimized coupled cluster model was reformulated using nonorthogonal orbital rotations. The gauge invariance and the simple pole structure of the coupled cluster response function are retained, while the dimension of the eigenvalue problem is reduced by a factor of 2. We started considering the reduction in the scaling for the SCF and correlated models as CCSD, using the Cholesky decomposition of the two-electron integrals. During the last year we programmed the the CCSD(T) using the Cholesky decomposition of the orbital energy denominators. This work was done together with the nodes i in **Valencia** and **Odense**.

As applications, we focused on the interaction properties of van der Waals complexes, studying on the one hand the (hyper)polarizabilities and the corresponding second virial coefficients of noble gases and on the other rovibrational and Raman spectra of complexes like the helium-, neon- and argon-cyclopropane, benzene-Ar, Ar-CO and benzene-N₂. In these applications we collaborated with the nodes in **Pisa**, **Valencia** and **Odense**.

P4 U-Mainz

The main achievement of the research at Mainz within the network can be summarized as follows:

- a) implementation of a coupled-cluster hierarchy for the computation of indirect spin-spin coupling constants with the first consideration of triple excitations together with extensive calibration for various small molecules (including BH, for which Full Configuration Interaction (FCI) results have been obtained (together with **Pisa**));
- b) formulation and implementation (almost completed) of analytic second derivatives for excited states treated within the coupled-cluster singles and doubles linear-response theory framework;
- c) computation of mixed electric-magnetic properties at highly accurate coupled-cluster level (e.g., shielding polarizabilities at CCSD(T) and electric-field gradient induced birefringence at CC3 level (together with **Pisa**));
- d) implementation of schemes for the electron-correlated calculations of current densities within the gauge-including atomic-orbital (GIAO) framework (together with **Helsinki**);
- e) benchmark calculations for molecular equilibrium geometries together with an exploration of the use of computed vibrational corrections to extract (empirical) equilibrium geometries from experimentally determined rotational constants (together with **Odense** and **Oslo**);
- f) benchmark coupled-cluster calculations for frequency-dependent electrical properties for para-nitro aniline (together with **Oslo** and **Stockholm**);
- f) calculation of the NMR spectra of HCP and its derivatives using coupled-cluster methods (together with **Valencia**).

P5 U-Modena

Methodologies were developed for rationalizing molecular response to external electromagnetic fields and intramolecular perturbations via property density functions representable in 3-space: (1) The analytic procedure of continuous transformation of the origin of the current density-diamagnetic term to zero (CTOCD-DZ) for the calculation of magnetic susceptibility and nuclear magnetic shielding has been implemented within the DALTON code, together with the **Valencia and Odense** nodes. Extended numerical tests have been carried out on a series of small molecules at the coupled Hartree-Fock level of accuracy and including electronic correlation within second-order polarization-propagator approach and MCSCF. Analytical CTOCD-DZ coupled cluster techniques have been developed, together with the **Oslo node**: (2) Efficient graphical codes have been implemented for representing streamlines and modulus of the current density induced by a magnetic field in the electrons of a molecule and for representing nuclear magnetic shielding density and nuclear spin-spin coupling density functions: (3) Codes for the calculation of nuclear electric shieldings and hypershieldings have been implemented in DALTON.

P6 CNR-Pisa

Studies of electric and magnetic optical properties in molecules, in particular:

Linear birefringences (magnetic induction field induced - Cotton-Mouton effect; electric field gradient induced - Buckingham's effect; electric field induced - Kerr effect) and axial birefringences (magnetochirality). The emphasis has been both in benchmark-type studies for small reference systems and on larger systems, studied at the Hartree-Fock level. The motivation has always been the comparison with experiment, or the prediction of observables within reach of experimentalists. In some cases the predictions contradict the experimental evidence, and rise doubts on the interpretation of recent very sophisticated experiments (magnetochirality). In others they shed light on disagreements existing between different theories which interpret the experiment (Buckingham's effect). The study of solvent effects on the birefringence has also been undertaken. This study involves several nodes and both the YR.

Natural optical activity, Raman scattering, (Vibrational) Raman optical activity, a field in rapid expansion; the studies have been both on small molecules (Raman scattering, where the effect of basis set, electron correlation within the Coupled Cluster hierarchy and DFT and of relativity have been analyzed) and on larger systems (ROA, VROA, where also the effect of correlation and basis set quality have been analyzed in some detail). Collaboration with the **Oslo** node. Interaction induced frequency dependent electric and mixed electric and magnetic properties, in rare gas van der Waals complexes, which allow to determine the influence of density (pressure) on the optical properties, both with a semiclassical and a fully quantum mechanical approach. The study has involved also the determination of the density dependence of the chemical shift of Helium. Collaboration with the nodes of **Santiago de Compostela** and **Odense**.

Electric field dependence of chemical shifts and electric field gradient at the nuclei, which are essential for simulation of the effect of intra and intermolecular interactions on the observed spectra. The studies have been carried out exploiting the new DFT response codes, and have involved in some cases also the analysis of relativistic effects. Collaboration with the **Oslo** and **Stockholm** nodes.

Theoretical analysis and numerical simulations aimed at correlating spectral features and electronic structure in connection with experimental techniques for synchrotron radiation spectroscopies; Direct

SCF-direct Static Exchange Approximation (STEX) developed for the numerical simulation of different spectroscopies using synchrotron radiation: absorption and emission of X-ray, photoemission by UV and X-ray absorption, Auger decay, natural circular dichroism in the X-ray region. Original computer codes developed and interfaced to a modified version of DALTON were applied for the interpretation of spectra for molecules of medium-large (50- 200 electrons) size in gas phase, polymers (approximated by oligomers), small molecules adsorbed on surfaces (approximated by clusters). This is in collaboration with the **Stockholm** node.

P7 U-Helsinki

A novel *ab initio* program package for calculation of optical properties of strain-induced quantum dots has been developed. This is the first *ab initio* program package for large-scale correlated calculations on strain-induced semiconductor quantum dots. The computer program package allows full configuration interaction (FCI) studies of the energy levels and photoluminescence spectra of semiconductor quantum dots containing 1-4 excitons. To treat larger multiexciton systems, we have developed and implemented computational approaches based on truncated configuration interaction (CI) and coupled-cluster (CC) expansions.

The computational methods have been used for studying energy levels, photon relaxation rates, and photon recombination rates of excitons, biexcitons and triexcitons confined a InGaAs/GaAs strain-induced quantum dot. The obtained energy level spacings, the phonon relaxation, and the photon dynamics are used for the interpretation of the observed photoluminescence spectra of the quantum dot system. The calculations show that the electron-hole correlation effects increase the radiative recombination rates and they significantly affect the recombination trends as a function of the dot size. The calculated stabilization energies suggest the formation of multi-exciton complexes. The stability of multi-charged multi-exciton complexes have also been studied at the CI level. The main results of these studies have been published in international scientific journals.

Since Bi(Ph)₅ was synthesized in 1952, scientists have been puzzled by its violet colour. To understand the structure and colour of the Bi(V) compounds, we have performed extensive relativistic studies on BiH₅, Bi(CH₃)₅, Bi(CCH)₅, and Bi(Ph)₅. The UV-Vis spectra of these compounds were calculated at the Dirac-Fock level using the Dirac program package developed in the **Odense** node. The results look promising and we will soon be able to give an explanation for the observed colour.

Disaturated thiocyanate anions have recently synthesized but their structures could not be experimentally characterized. The aim of our studies were to computationally characterize these molecules. Molecular structure calculations and calculation of vibrational frequencies including anharmonic corrections show that for molecules with neutral ligands (L = H₃P or Me₃P), the connectivity of the synthesized complexes is [LAu-SCN-AuL]⁺ rather than the expected [μ_2 -(LAu)₂SCN]⁺.

Together with the **Mainz** node we have implemented schemes for the electron-correlated calculations of current densities within the gauge-including atomic-orbital (GIAO) framework.

P8 U-Odense

Developments within the coupled cluster hierarchy of methods have been carried out in collaboration with the **Mainz** node. Calculations show that the CC3 model is a good compromise between cost and

accuracy for the prediction of excitation energies and many response properties. Reduced scaling coupled cluster algorithms have also been developed, e.g. for frequency dependent polarizabilities at the CC3 level. A novel linear scaling algorithm replacing Fock matrix diagonalizations have been developed in collaboration with the **Oslo node**. This collaboration has also involved the development of a molecular gradient code for the calculation of CCSD(T) gradients, and a code for coupled-cluster calculations of gauge-origin independent magneto-optical activity. Together with Oslo a large number of very accurate calculations have been carried out for a range of molecular properties, including atomization energies, reaction enthalpies, molecular structure, vibrational frequencies and other spectroscopic constants.

Relativistic 4-component RPA has been derived and implemented, both for frequency dependent properties and for excitation energies and transition moments as well as for quadratic response. Relativistic 4-component large scale CI and MCSCF energy calculations, London orbitals for NMR shieldings, and ESR g-tensors for any spin state on the Hartree-Fock level have been implemented and applied. Some applications of these methods have also been carried out together with the **Helsinki node**. Many applications on higher order properties have been carried out together with the **Pisa node**.

A more correct description of the anomalous g-factor in e.g. ESR has been developed and implemented. Hybrid QC/MM methods at the Hartree-Fock, MCSCF, and Coupled Cluster levels for response properties up to third order as well as heterogeneous solvation models at the Hartree-Fock and MCSCF levels for properties up to fourth order have been developed and implemented. Theory and implementation for MCSCF calculations of near-resonant absorption which account for finite lifetimes has been finished.

P9 U-Oslo

a) The main work carried out in Oslo is the development of a code for the efficient calculation of Coulomb and exchange-correlation interactions in a linear-scaling manner. A fully working, efficient implementations of the fast multipole method (FMM) (scales as N) and of the tree-code (scales as $N \log N$) are now in place. In addition, new linear-scaling implementations of the DFT contribution to the Kohn-Sham matrix and of the nonclassical Coulomb contribution (as distinct from the classical Coulomb contribution treated by multipole methods) have been coded. This work has been carried out by the YRs Mark Watson (multipole methods for classical Coulomb interactions), Peter Macak (nonclassical Coulomb interactions), and Pawel Salek (linear-scaling DFT code).

As a result, we are now in a position to calculate the Kohn-Sham matrix of large systems very efficiently, for systems containing more than thousand atoms. Indeed, we have now reached a situation where our main concern is no longer the construction of the Kohn-Sham matrix, but rather the optimization of the density itself. This is currently achieved by a standard self-consistent scheme, with a diagonalization of the Kohn-Sham matrix that scales as the cubic power of N . In the future, work will be directed towards eliminating this bottleneck and also to improve convergence of the optimization scheme.

The linear-scaling code has been applied to the calculation of energies and molecular properties at the LDA and GGA levels of DFT - in particular, for the calculation of singlet and triplet excitation energies, static and frequency-dependent polarizabilities, and NMR spin-spin coupling constants. Several publications are being planned and prepared.

b) In collaboration with the **Stockholm node**, much work has been carried out on the implementation of response theory in Dalton. Dalton now has full functionality up to cubic response. Several applications

Table 2: Essential collaboration between nodes - full period

<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	X
Valencia	X	-	X	X	X			X	
Santiago		X	-			X		X	
Mainz		X		-		X	X	X	X
Modena		X			-			X	X
Pisa	X		X	X		-		X	X
Helsinki	X			X			-	X	X
Odense	X	X	X	X	X	X	X	-	X
Oslo	X			X	X	X	X	X	-

have already been carried out.

c) In collaboration with the **Odense** node, a large number of very accurate calculations have been carried out for a range of molecular properties, including atomization energies, reaction enthalpies, molecular structure, vibrational frequencies and other spectroscopic constants. These calculations serve a double purpose: to provide benchmark results for less accurate methods; to provide accurate molecular data, independent of experimental measurements.

In addition, much development work has been carried out in collaboration with the **Odense** node - in particular, the development of molecular gradient code for the calculation of CCSD(T) gradients, and a code for coupled-cluster calculations of gauge-origin independent magneto-optical activity. Both codes are ready and have been applied to problems of chemical interest. Also, we have recently developed a code for the calculation of all two-electron integrals that contribute to first-order in relativistic corrections - in particular, a first implementation of orbit-orbit integrals.

Finally, in collaboration with the **Odense** node, the Oslo node has worked on methods for the optimization of Hartree-Fock/DFT without diagonalization. Our method, which is based on an exponential parametrization of the AO density matrix, now works in a model implementation. True linear scaling will be reached as soon as sparse matrix routines (for addition and multiplications) are implemented in Dalton. This work complements the work on the development of linear-scaling Coulomb and exchange-correlation codes, recently finished.

d) With the **Pisa** node, work has been carried out on the calculation of molecular properties at the DFT level - one paper on EFG and Sternheimer shieldings, many papers on spin-spin coupling constants.

d) In collaboration with the **Modena** node, work is being carried out on the calculation of polarizabilities in different gauges, and on the calculation of dipole hyperpolarizabilities in the Hellmann-Feynman theorem (paper submitted).

3rd Year Report

A.2 Joint Publications - 3rd Year Report

The following list contains publications involving node collaboration and publications involving hired Young Researchers. The latter are presented in boldface.

1. **P1, P7 Z. Rinkevicius**, J. Vaara, L. Telyatnyk and O. Vahtras, Calculations of nuclear magnetic shielding in paramagnetic molecules, *J. Chem. Phys.*, 2550, 118 (2003).
2. **P1, P9 Z. Rinkevicius**, I. Tunell, **P. Salek**, O. Vahtras and H. Ågren, Restricted density functional theory of linear time-dependent properties in open-shell molecules, *J. Chem. Phys.* 00, 000 (2003).
3. **P1, P7 L. Telyatnyk**, J. Vaara, **Z. Rinkevicius** and O. Vahtras, The influence of hydrogen bonding in the paramagnetic NMR shieldings of nitronyl nitroxide derivative molecules, *J. Phys. Chem. B* (submitted)
4. **P1, P9 Z. Rinkevicius**, L. Telyatnyk, **P. Salek**, O. Vahtras and H. Ågren, Restricted density functional linear response theory: application to electronic g-tensor calculations, in preparation.
5. **P1. B. Jansik**, B. Schimmelpfennig, P. Norman, P. Macak, H. Ågren and K. Ohta, Relativistic effects on linear and nonlinear polarizabilities of the furan homologues, *Mol. Phys.* 00, 000 (2003).
6. **P1 B. Jansik**, B. Schimmelpfennig, and H. Ågren, Relativistic study of VUV radiation properties from KrXe gas mixtures, *Phys. Rev. A*, 67, 042501 (2003)
7. **P1, P9 O. Rubio-Pons**, B. Minaev, O. Loboda and H. Ågren, Ab initio Calculations of Vibronic Activity in Phosphorescence Microwave Double Resonance Spectra of para-Dichlorobenzene Submitted to THEOR CHIMICA ACC (2003)
8. **P1, P9 O. Rubio-Pons**, O. Loboda, B. Minaev, B. Schimmelpfennig, O. Vahtras and H. Ågren, CASSCF calculations of triplet-state properties. Applications to benzene derivatives, *Mol. Phys.* 00, 000 (2003)
9. **P1, P9 S. Kashtanov**, **O. Rubio-Pons**, Y. Luo, H. Ågren, S. Stafström, and S. Csillag, Characterization of aza-fullerene C₅₈N₂ by X-ray spectroscopy, *Chem. Phys. Lett.*, 371, 98 (2003).
10. **P1 A. Baev**, F. Gel'mukhanov, **O. Rubio-Pons**, P. Cronstrand, and H. Ågren, Upconverted lasing based on many-photon absorption: An all dynamic description, Submitted to *J. Opt. Soc. Am. B* (2003)
11. **P1, P9 J.-D. Guo**, Y. Luo, P. Salek, O. Vahtras, T. Helgaker, and H. Ågren, Calculations of two-photon absorption cross sections by means of density functional theory, *Chem. Phys. Lett.*, 00, 000 (2003).
12. **P2, P8 I. Garcia Cuesta**, A.M. Sanchez de Meras and H. Koch Coupled cluster calculations of the vertical excitation energies of tetracyanoethylene, *J. Chem. Phys.* 118, 8216 (2003).
13. **P2, P8 H. Koch**, A.M. Sanchez de Meras and **T.B. Pedersen**, Reduced scaling in electronic structure calculations using Cholesky decompositions, *J. Chem. Phys.* 118 9481 (2003).

14. **P3,P5 R. Soriano Jartin**, I. Garcia Cuesta, A.M. Sanchez de Meras and P. Lazzeretti, Can aromaticity be connected with molecular polarizability? A theoretical study of benzene isomers and five-membered heterocyclic molecules, *J. Comput. Meth. Sci. Engin.* (in press)
15. **P2,P5 I. Garcia Cuesta, R. Soriano Jartin**, A.M. Sanchez de Meras and P. Lazzeretti Current Density Maps, Magnetizability and Nuclear Magnetic Shielding Tensors of Bis-Heteropentalenes. I. Pyrrolo[2,3-b]pyrrole, Pyrrolo[3,2-b]pyrrole, Pyrrolo[3,4-b]pyrrole and Pyrrolo[3,4-c]pyrrole *J. Chem. Phys.* (submitted)
16. **P3,P6,P8 A. Rizzo, C. Haettig, B. Fernandez, H. Koch**, The effect of intermolecular interactions on the electric properties of helium and argon. III. Quantum statistical calculations of the dielectric second virial coefficients. *J. Chem Phys.*, 117, 2609, 2002.
17. **P3,P6,P8 A. Rizzo, S. Coriani, B. Fernandez, O. Christiansen**, A coupled cluster response study of the electric dipole polarizability, first and second hyperpolarizabilities of HCl. *Phys. Chem. Chem. Phys.*, 4, 2884, 2002.
18. **P3,P8 T.B. Pedersen**, J. Lopez Cacheiro, B. Fernandez, H. Koch, Rovibrational structure of the Ar-CO complex based on a novel three-dimensional ab initio potential. *J. Chem Phys.*, 117, 6562, 2002.
19. **P3, P6 J. Lopez Cacheiro, B. Fernandez, D. Marchesan, S. Coriani, C. Hättig and A. Rizzo**, Ab initio calculations for sextuple zeta potentials and quadruple zeta property curves for the mixed dimmers HeNe, HeAr and NeAr. submitted to *J. Chem. Phys.*
20. **P4, P6 A.A. Auer, J.Gauss, and M.Pecul**, Full Configuration-Interaction and Coupled-Cluster Calculations of the Indirect Spin-Spin Coupling Constant of BH, *Chem. Phys. Letters* 368, 172 (2003)
21. **P4, P6 S. Coriani, A. Halkier, D. Jonsson, J. Gauss, A. Rizzo, and O. Christiansen**, On the Electric-Field-Gradient-Induced Birefringence and Electric Quadrupole Moment of CO, N₂O, and OCS, *J. Chem. Phys.* 118 7329 (2003).
22. **P4,P7 J. Juselius, D. Sundholm, and J. Gauss**, Current Densities Calculated Using Gauge-Including Atomic Orbitals *J. Chem. Phys.*, to be published.
23. **P4,P8 R. Wugt Larsen, F. Pawlowski, F. Hegelund, P. Jørgensen, J. Gauss, and B. Nelander**, The Empirical Equilibrium Structure of trans-Glyoxal from Experimental Rotational Constants and Calculated Vibration-Rotation Interaction Constants. *J. Chem. Phys.*, to be published
24. **P5,P9 A. Soncini, P. Lazzeretti, V. Bakken, T. Helgaker**, Calculation of electric dipole hyper-shieldings at the nuclei in the Hellmann-Feynman approximation, *J. Chem. Phys.* submitted, (2003).
25. **P6 M. Pecul and S. Coriani** The effect of triple excitations in coupled cluster calculation of Raman scattering cross sections. *Chem. Phys. Lett.*, 355 (2001), 327-338.
26. **P6 M. Pecul and A. Rizzo**, Relativistic effects on the electric polarizabilities and their geometric derivatives for hydrogen halides and dihalogens. A Dirac-Hartree-Fock study. *Chem. Phys. Lett.*, 370, (2003), 578-588

27. **P6 M. Pecul** and A. Rizzo Raman Optical Activity spectra: basis set and electron correlation effects. In press, Mol. Phys.
28. **P6 C. Cappelli, U. Ekström, A. Rizzo and S. Coriani**, The molecular electric quadrupole moment and electric-field-gradient induced birefringence (Buckingham effect) of Cl₂. Submitted, J. Comp. Meth. Sci. Eng. (JCMSE).
29. **P6, P9 M. Pecul**, T. Saue, K. Ruud and A. Rizzo, Electric field effects on the shielding constants of noble gases as calculated at Dirac-Hartree-Fock level. submitted to Chem. Phys. Lett.
30. **P6, P9 M. Pecul**, K. Ruud, A. Rizzo, T. Helgaker, Computational study of conformational effects on optical rotation in proline and alanine, to be submitted, Chem. Phys. Lett.
31. **P7, P8 S. Corni**, J. Olsen, M. Braskén, M. Lindberg, D. Sundholm, Electron-Hole Recombination Density Matrices Obtained from Large Configuration-Interaction Expansions, Phys. Rev. B 67, (2003) 085314.
32. **P7, P8 S. Corni**, J. Olsen, M. Braskén, M. Lindberg, D. Sundholm, Size Dependence of the Electron-Hole Recombination Rates in Semiconductor Quantum Dots, Phys. Rev. B 67 (2003) 045313; Virtual J. Nanoscale Sci. & Tech. January 27, 2003.
33. **P7, P8 S. Corni**, M. Braskén, M. Lindberg, J. Olsen, D. Sundholm, Stabilization Energies of Charged Multiexciton Complexes Calculated at Configuration Interaction Level, Physica E, in press.
34. **P7, P4 J. Jusélius**, D. Sundholm, J. Gauss, Current Densities Calculated Using Gauge-Including Atomic Orbitals, (manuscript in preparation).
35. **P7, P8 M. Patzschke**, H. J. Aa. Jensen, J. Pedersen, P. Pyykkö, D. Sundholm, Excitation Energies of Bi(V) compounds, manuscript in preparation.
36. **P1, P9 P. Salek**, O. Vahtras, T. Helgaker, and H. Ågren, Density-functional theory of linear and nonlinear time-dependent molecular properties, J. Chem. Phys. 117, 9630-9645 (2002)
37. **P8, P9 F. Pawłowski**, A. Halkier, P. Jørgensen, K. L. Bak, T. Helgaker, and W. Klopper, Accuracy of spectroscopic constants of diatomic molecules from ab initio calculations, J. Chem. Phys. 118, 2539-2549 (2003).
38. **P8, P9 K. Hald**, A. Halkier, P. Jørgensen, S. Coriani, C. Hättig, and T. Helgaker, A Lagrangian, integral-density direct formulation and implementation of the analytic CCSD and CCSD(T) gradients, J. Chem. Phys. 118, 2985-2998 (2003)
39. **P6, P9 M. Pecul** and T. Helgaker The spin-spin coupling constants in ethane, methanol and methylamine: a comparison of DFT, MCSCF, and CCSD results, Int. J. Mol. Sci. 4, 143-157 (2003)
40. **P1, P6, P9 A. Rizzo**, K. Ruud, T. Helgaker, **P. Salek** H. Ågren, and O. Vahtras, Sternheimer shieldings and EFG polarizabilities: a density-functional theory study, Chem. Phys. Lett., 372, 377-385 (2003)
41. **P8, P9 T. A. Ruden**, T. Helgaker, P. Jørgensen, and J. Olsen, Coupled-cluster connected-quadruples corrections to atomization energies, Chem. Phys. Lett. 371, 62-67 (2003)

42. **P6, P9 M. Pecul**, J. Sadlej, and T. Helgaker, Calculations of hydrogen-bond-transmitted indirect nuclear spin-spin couplings: comparison of density-functional and ab initio methods Chem. Phys. Lett. 372, 476-484 (2003)

Final Report

A.2 Joint Publications - Final Report

The following list contains publications involving node collaboration and publications involving hired Young Researchers. The latter are presented in boldface.

1. **P1, P6. P. Sałek**, V. Carravetta, H. Ågren, Dynamical suppression of atomic peaks in resonant dissociative photoemission, Chem. Phys. Lett. 343, 342 (2001).
2. **P1, P6, P9.** O. Plashkevych, T. Privalov, H. Ågren, V. Carravetta, and K. Ruud, On the validity of the equivalent cores approximation for computing X-ray photoemission and photoabsorption spectral bands, Chemical Physics, 260, 11 (2000).
3. **P1, P4, P6, P9. D. Jonsson**, P. Norman, H. Ågren, A. Rizzo, S. Coriani, and K. Ruud, The Cotton–Mouton effect of gaseous CO₂, N₂O, OCS and CS₂. A Cubic Response MCSCF study, J. Chem. Phys. 114, 8372 (2001).
4. **P2, P8.** H. Koch and A. Sanchez de Meras, Size-intensive decomposition of orbital energy denominators, J. Chem. Phys., 113(2) 508 (2000).
5. **P3, P8 T. B. Pedersen**, B. Fernandez and H. Koch, Comment on 'The importance of higher-order correlation effects for the CO-CO interaction potential', Chem. Phys. Lett., 334, 419-423 (2001).
6. **P4, P8, P9** K. L. Bak, P. Jørgensen, J. Olsen, T. Helgaker and J. Gauss, Coupled-cluster singles, doubles and triples (CCSDT) calculations of atomization energies, Chem. Phys. Lett. 317, 116-122 (2000).
7. **P7, P8** M. Braskén, M. Lindberg, D. Sundholm, J. Olsen, Full Configuration Interaction Calculations of Electron-hole Correlation Effects in Strain-induced Quantum Dots, Phys. Rev. B 61 (2000) 7652.
8. **P7, P8** M. Braskén, M. Lindberg, D. Sundholm, J. Olsen, Carrier-Carrier Correlations in Strain-Induced Quantum Dots, Phys. Stat. Sol. (b) 221 (2000) 37.
9. **P7, P8** M. Braskén, M. Lindberg, D. Sundholm, J. Olsen, Full Configuration Interaction Calculations of Electron-hole Correlation Effects in Strain-induced Quantum Dots, Phys. Stat. Sol. (b) 224 (2001) 775.
10. **P4, P8** A. Halkier, T. Helgaker, W. Klopper, and J. Olsen, Basis-set convergence of the two-electron Darwin term, Chem. Phys. Lett. 319, 287-295 (2000).

11. **P4, P8** K. L. Bak, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, Accuracy of atomization energies and reaction enthalpies in standard and extrapolated electronic wave function/basis set calculations, *J. Chem. Phys.* 112, 9229-9242 (2000).
12. **P4, P8** T. Helgaker, H. Larsen, J. Olsen, and P. Jørgensen, Direct optimization of the AO density matrix in Hartree-Fock and Kohn-Sham theories, *Chem. Phys. Lett.* 327, 397-403 (2000).
13. **P4, P8** S. Coriani, C. Hättig, P. Jørgensen, and T. Helgaker, Gauge-origin independent magneto-optical activity within coupled cluster response theory, *J. Chem. Phys.* 113, 3561-3572 (2000).
14. **P4, P8** H. Larsen, P. Jørgensen, J. Olsen, and T. Helgaker, Hartree-Fock and Kohn-Sham atomic-orbital based time-dependent response theory, *J. Chem. Phys.* 113, 8908-8917 (2000).
15. **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).
16. **P1, P6** V. Carravetta and H. Ågren, An ab initio method for computing multi-atom resonant photoemission, *Chem. Phys. Lett.* 354, 100 (2002).
17. **P1, P6** K. Kaznatcheyev, A. Osanna, C. Jacobsen, O. Plashkevitch, O. Vahtras, H. Ågren, V. Carravetta, and A.P. Hitchcock, Inner-shell absorption spectroscopy of amino acids. *J. Chem. Phys.*, 106, 3153 (2002).
18. **P3, P1** **B. Jansik**, A. Sanchez de Meras, B. Schimmelpfennig and H. Ågren. A coupled cluster study of the structures of the lanthanum trihalides LaF₃ and La Cl₃, *J. Chem. Soc. Dalton Transactions*, 24, 4603 (2002).
19. **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.
20. **P1** **B. Jansik**, B. Schimmelpfennig, P. Norman, Y. Mochizuki, Y. Luo and H. Ågren, Size, order and dimensional relations for silicon cluster polarizabilities, *J. Phys. Chem. A*, 106, 395, 2002
21. **P3, P8** **T.B. Pedersen**, B. Fernandez, H. Koch, Gauge Coupled Cluster response theory using optimized nonorthogonal orbitals', *J. Chem. Phys.* 114, 6983 (2001).
22. **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).
23. **P4, P6** A. Rizzo and J. Gauss, CCSD(T) Shielding Polarizabilities, *J. Chem. Phys.* 116, 869 (2002).
24. **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).
25. **P6, P4** **M. Pecul** and A. Rizzo Linear response coupled cluster calculation of Raman scattering cross sections. *J. Chem. Phys.*, 116 (2002), 1259.
26. **P6, P4** **M. Pecul** and A. Rizzo A Full Configuration Interaction calculation of the density dependence of the ³He shielding constant, *Mol. Phys.*, 100 (2002), 447.

27. **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.
28. **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.
29. **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).
30. **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)
31. **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).
32. **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).
33. **P1, P7** **Z. Rinkevicius**, J. Vaara, L. Telyatnyk and O. Vahtras, Calculations of nuclear magnetic shielding in paramagnetic molecules, *J. Chem. Phys.*, 2550, 118 (2003).
34. **P1,P9** **Z. Rinkevicius**, I. Tunell, **P. Sałek**, O. Vahtras and H. Ågren, Restricted density functional theory of linear time-dependent properties in open-shell molecules, *J. Chem. Phys.* 00, 000 (2003).
35. **P1, P7** L. Telyatnyk, J. Vaara, **Z. Rinkevicius** and O. Vahtras, The influence of hydrogen bonding in the paramagnetic NMR shieldings of nitronyl nitroxide derivative molecules, *J. Phys. Chem. B* (submitted)
36. **P1, P9** **Z. Rinkevicius**, L. Telyatnyk, **P. Sałek**, O. Vahtras and H. Ågren, Restricted density functional linear response theory: application to electronic g-tensor calculations, in preparation.
37. **P1.** **B. Jansik**, B. Schimmelpfennig, P. Norman, P. Macak, H. Ågren and K. Ohta, Relativistic effects on linear and nonlinear polarizabilities of the furan homologues, *Mol. Phys.* 00, 000 (2003).
38. **P1** **B. Jansik**, B. Schimmelpfennig, and H. Ågren, Relativistic study of VUV radiation properties from KrXe gas mixtures, *Phys. Rev. A*, 67, 042501 (2003)
39. **P1,P9** **O. Rubio-Pons**, B. Minaev, O. Loboda and H. Ågren, Ab initio Calculations of Vibronic Activity in Phosphorescence Microwave Double Resonance Spectra of para-Dichlorobenzene Submitted to *THEOR CHIMICA ACC* (2003)
40. **P1,P9** **O. Rubio-Pons**, O. Loboda, B. Minaev, B. Schimmelpfennig, O. Vahtras and H. Ågren, CASSCF calculations of triplet-state properties. Applications to benzene derivatives, *Mol. Phys.* 00, 000 (2003)

41. **P1,P9** S. Kashtanov, **O. Rubio-Pons**, Y. Luo, H. Ågren, S. Stafström, and S. Csillag, Characterization of aza-fullerene C₅₈N₂ by X-ray spectroscopy, *Chem. Phys. Lett.*, 371, 98 (2003).
42. **P1** A. Baev, F. Gel'mukhanov, **O. Rubio-Pons**, P. Cronstrand, and H. Ågren, Upconverted lasing based on many-photon absorption: An all dynamic description, Submitted to *J. Opt. Soc. Am. B* (2003)
43. **P1,P9** J.-D. Guo, Y. Luo, P. Salek, O. Vahtras, T. Helgaker, and H. Ågren, Calculations of two-photon absorption cross sections by means of density functional theory, *Chem. Phys. Lett.*, 00, 000 (2003).
44. **P2,P8** I. Garcia Cuesta, A.M. Sanchez de Meras and H. Koch Coupled cluster calculations of the vertical excitation energies of tetracyanoethylene, *J. Chem. Phys.* 118, 8216 (2003).
45. **P2,P8** H. Koch, A.M. Sanchez de Meras and **T.B. Pedersen**, Reduced scaling in electronic structure calculations using Cholesky decompositions, *J. Chem. Phys.* 118 9481 (2003).
46. **P3,P5** **R. Soriano Jartin**, I. Garcia Cuesta, A.M. Sanchez de Meras and P. Lazzeretti, Can aromaticity be connected with molecular polarizability? A theoretical study of benzene isomers and five-membered heterocyclic molecules, *J. Comput. Meth. Sci. Engin.* (in press)
47. **P2,P5** I. Garcia Cuesta, **R. Soriano Jartin**, A.M. Sanchez de Meras and P. Lazzeretti Current Density Maps, Magnetizability and Nuclear Magnetic Shielding Tensors of Bis-Heteropentalenes. I. Pyrrolo[2,3-b]pyrrole, Pyrrolo[3,2-b]pyrrole, Pyrrolo[3,4-b]pyrrole and Pyrrolo[3,4-c]pyrrole *J. Chem. Phys.* (submitted)
48. **P3,P6,P8** A. Rizzo, C. Haettig, B. Fernandez, H. Koch, The effect of intermolecular interactions on the electric properties of helium and argon. III. Quantum statistical calculations of the dielectric second virial coefficients. *J. Chem Phys.*, 117, 2609, 2002.
49. **P3,P6,P8** A. Rizzo, S. Coriani, B. Fernandez, O. Christiansen, A coupled cluster response study of the electric dipole polarizability, first and second hyperpolarizabilities of HCl. *Phys. Chem. Chem. Phys.*, 4, 2884, 2002.
50. **P3,P8** **T.B. Pedersen**, J. Lopez Cacheiro, B. Fernandez, H. Koch, Rovibrational structure of the Ar-CO complex based on a novel three-dimensional ab initio potential. *J. Chem Phys.*, 117, 6562, 2002.
51. **P3, P6** J. Lopez Cacheiro, B. Fernandez, D. Marchesan, S. Coriani, C. Hättig and A. Rizzo, Ab initio calculations for sextuple zeta potentials and quadruple zeta property curves for the mixed dimmers HeNe, HeAr and NeAr. submitted to *J. Chem. Phys.*
52. **P4, P6** A.A. Auer, J.Gauss, and **M.Pecul**, Full Configuration-Interaction and Coupled-Cluster Calculations of the Indirect Spin-Spin Coupling Constant of BH, *Chem. Phys. Letters* 368, 172 (2003)
53. **P4, P6** S.Coriani, A.Halkier, **D.Jonsson**, J.Gauss, A.Rizzo, and O.Christiansen, On the Electric-Field-Gradient-Induced Birefringence and Electric Quadrupole Moment of CO, N₂O, and OCS, *J. Chem. Phys.* 118 7329 (2003).

54. **P4,P7** J.Juselius, D.Sundholm, and J.Gauss, Current Densities Calculated Using Gauge-Including Atomic Orbitals *J. Chem. Phys.*, to be published.
55. **P4,P8** R. Wugt Larsen, **F.Pawlowski**, F. Hegelund, P. Jørgensen, J. Gauss, and B. Nelander, The Empirical Equilibrium Structure of trans-Glyoxal from Experimental Rotational Constants and Calculated Vibration-Rotation Interaction Constants. *J. Chem. Phys.*, to be published
56. **P5,P9** A. Soncini, P. Lazzaretti, V. Bakken, T. Helgaker, Calculation of electric dipole hyper-shieldings at the nuclei in the Hellmann-Feynman approximation, *J. Chem. Phys.* submitted, (2003).
57. **P6 M. Pecul** and S. Coriani The effect of triple excitations in coupled cluster calculation of Raman scattering cross sections. *Chem. Phys. Lett.*, 355 (2001), 327-338.
58. **P6 M. Pecul** and A. Rizzo, Relativistic effects on the electric polarizabilities and their geometric derivatives for hydrogen halides and dihalogens. A Dirac-Hartree-Fock study. *Chem. Phys. Lett.*, 370, (2003), 578-588
59. **P6 M. Pecul** and A. Rizzo Raman Optical Activity spectra: basis set and electron correlation effects. In press, *Mol. Phys.*
60. **P6** C. Cappelli, **U. Ekström**, A. Rizzo and S. Coriani, The molecular electric quadrupole moment and electric-field-gradient induced birefringence (Buckingham effect) of Cl₂. Submitted, *J. Comp. Meth. Sci. Eng. (JCMSE)*.
61. **P6, P9 M. Pecul**, T. Saue, K. Ruud and A. Rizzo, Electric field effects on the shielding constants of noble gases as calculated at Dirac-Hartree-Fock level. submitted to *Chem. Phys. Lett.*
62. **P6, P9 M. Pecul**, K. Ruud, A. Rizzo, T. Helgaker, Computational study of conformational effects on optical rotation in proline and alanine, to be submitted, *Chem. Phys. Lett.*
63. **P7, P8 S. Corni**, J. Olsen, M. Braskén, M. Lindberg, D. Sundholm, Electron-Hole Recombination Density Matrices Obtained from Large Configuration-Interaction Expansions, *Phys. Rev. B* 67, (2003) 085314.
64. **P7, P8 S. Corni**, J. Olsen, M. Braskén, M. Lindberg, D. Sundholm, Size Dependence of the Electron-Hole Recombination Rates in Semiconductor Quantum Dots, *Phys. Rev. B* 67 (2003) 045313; *Virtual J. Nanoscale Sci. & Tech.* January 27, 2003.
65. **P7, P8 S. Corni**, M. Braskén, M. Lindberg, J. Olsen, D. Sundholm, Stabilization Energies of Charged Multiexciton Complexes Calculated at Configuration Interaction Level, *Physica E*, in press.
66. **P7, P4** J. Jusélius, D. Sundholm, J. Gauss, Current Densities Calculated Using Gauge-Including Atomic Orbitals, (manuscript in preparation).
67. **P7, P8 M. Patzschke**, H. J. Aa. Jensen, J. Pedersen, P.Pyykkö, D.Sundholm, Excitation Energies of Bi(V) compounds, manuscript in preparation.
68. **P1, P9 P. Salek**, O. Vahtras, T. Helgaker, and H. gren, Density-functional theory of linear and nonlinear time-dependent molecular properties, *J. Chem. Phys.* 117, 9630-9645 (2002)

69. **P8, P9 F. Pawlowski**, A. Halkier, P. Jrgensen, K. L. Bak, T. Helgaker, and W. Klopper, Accuracy of spectroscopic constants of diatomic molecules from ab initio calculations, *J. Chem. Phys.* 118, 2539-2549 (2003).
70. **P8, P9 K. Hald**, A. Halkier, P. Jrgensen, S. Coriani, C. Httig, and T. Helgaker, A Lagrangian, integral-density direct formulation and implementation of the analytic CCSD and CCSD(T) gradients, *J. Chem. Phys.* 118, 2985-2998 (2003)
71. **P6, P9 M. Pecul** and T. Helgaker The spin-spin coupling constants in ethane, methanol and methylamine: a comparison of DFT, MCSCF, and CCSD results, *Int. J. Mol. Sci.* 4, 143-157 (2003)
72. **P1, P6, P9 A. Rizzo**, K. Ruud, T. Helgaker, **P. Salek H. Ågren**, and O. Vahtras, Sternheimer shieldings and EFG polarizabilities: a density-functional theory study, *Chem. Phys. Lett.*, 372, 377-385 (2003)
73. **P8, P9 T. A. Ruden**, T. Helgaker, P. Jrgensen, and J. Olsen, Coupled-cluster connected-quadruples corrections to atomization energies, *Chem. Phys. Lett.* 371, 62-67 (2003)
74. **P6, P9 M. Pecul**, J. Sadlej, and T. Helgaker, Calculations of hydrogen-bond-transmitted indirect nuclear spin-spin couplings: comparison of density-functional and ab initio methods *Chem. Phys. Lett.* 372, 476-484 (2003)

Part B

Comparison with the joint program of work

3rd Year Report

B.1 Research Objectives - 3rd year Report

As during the two first years of the MOLPROP network, the research objectives - both the low and the high end objectives - were maintained during the third year. Theoretical work referring to basic science as well as applications of the theory has thus 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 were continuously developed and applied in a variety of contexts.

As the coupled cluster theory now has reached a very significant level of both accuracy and sophistication, much owing to the efforts in this network, more and more of our attention has turned to density functional

theory (DFT), and properties computed with this theory: We have during the year completed a DFT theory for linear and nonlinear response functions using an explicit exponential parametrization of the density operator -up to cubic response. 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. We have already made applications of properties like two-photon absorption and phosphorescence and excited state polarizabilities. Furthermore, spin-restricted DFT for (high-spin) open-shell molecules has been derived and implemented and has been already used in some applications on polarizabilities, spectroscopy and magnetic resonance parameters. This development has thus now fulfilled the goal to complete the 4th order property toolbox for density functional theory, something that makes it possible to treat technologically interesting compounds, and something that makes an excellent connection to the high-end goals of the network.

The reduced scaling goal is largely fulfilled through the third year development. Efficient calculations of Coulomb and exchange-correlation interactions are thus now feasible with linear-scaling. A fully working, efficient implementation of the fast multipole method (FMM) (scales as N) and of the tree-code (scales as $N \log N$) are now in place. In addition, new linear-scaling implementations of the DFT contribution to the Kohn-Sham matrix and of the nonclassical Coulomb contribution have been coded. As a result, we are now in a position to calculate the Kohn-Sham matrix of large systems very efficiently, for systems containing more than thousand atoms. Indeed, we have now reached a situation where our main concern is no longer the construction of the Kohn-Sham matrix, but rather the optimization of the density itself. The linear-scaling code has been applied to the calculation of energies and molecular properties at the LDA and GGA levels of DFT - in particular, for the calculation of singlet and triplet excitation energies, static and frequency-dependent polarizabilities, and NMR spin-spin coupling constants. Several publications are being planned and prepared.

Correlated techniques have been developed within the coupled cluster methodologies, including new CC3 models and Cholesky decomposition to reduce scaling. 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 the network research is the integration between relativistic theory and DFT techniques.

As during first and second years new hyperfine coupling modules have been implemented for applications of magnetic resonance phenomena (NMR, EPR and ODMR spectroscopies), in order to produce diagnostics and structure-property relations of molecular compounds. We emphasize two new elements during the third year work: the derivation and implementation of shielding constants for paramagnetic NMR, thus for open shell systems with radical character. The theory for paramagnetic systems contains new and complex ingredients compared to the usual diamagnetic theory, but which still are possible to master computationally as we demonstrated during the 3rd year. The application of NMR on paramagnetic species provides a rich field of applications on radicals in general, and particularly on bioradicals that play vital roles in the catalytic activity of enzymes. The usefulness of this spectroscopy derives from the facts that the interaction between unpaired electrons and a resonating nucleus causes hyperfine shifts in the NMR spectra that can be used for diagnostics. The sign and magnitude of the electron spin

density can then be evaluated from the contact shifts without further approximations and only moderate magnetic fields are required in order to obtain spectra with resolved hyperfine structure. These intrinsic properties make paramagnetic NMR an attractive alternative to e.g. EPR for studying radicals. The second line of development of magnetic resonance parameters during the 3rd year concerned so-called zero-field splitting parameters, thereby completing calculations of the full spin Hamiltonian. In particular, the so-called D-tensor is now coded at ab initio and DFT levels of theory. Apart from these new 3rd year developments we emphasize the continuing work on the g-tensor where we now have produced a working code for DFT spin restricted calculations and obtained new and very promising results. As for paramagnetic NMR, the EPR g-tensor is very useful for diagnostics of bio-radicals. As in the first and second years there has been a considerable development also of relativistic treatments of the magnetic resonance parameters, in particular for the g-tensor.

The computation and the viewing of current densities have progressed as planned. Electron-correlated schemes up to the full coupled-cluster singles, doubles, triples levels have been implemented to compute current-densities with the gauge-including atomic orbital framework and ring-current models based on computed current densities have been developed. The graphical codes implemented in the first and second years of i network activity have now reached a stage where they can be routinely applied; thus streamlines and modulus of the current density induced by a magnetic field in the electrons of molecules as complex as 2- and 4-pyrones, 1-2 dithiin and its derivatives, have now been studied in detail. The aromaticity of these systems has in this context been discussed in relation to their magnetic properties.

As for the applicative side of the network project we emphasize the work during the third year concerning computations of quantum dot properties, and multi-photon effects for optical limiting and control. 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. The ab initio program package for calculation of optical properties of strain-induced quantum dots developed during the network period is now in operation: The computer program package allows full configuration interaction studies of the energy levels and photoluminescence spectra of semiconductor quantum dots containing several excitons. To treat larger multiexciton systems, approaches based on truncated configuration interaction and coupled-cluster expansions have been developed and implemented. Calculations have predicted energy level spacings, phonon relaxation, and photon dynamics and the results have been used for interpretation of the observed photoluminescence spectra of various quantum dot systems.

The research concerning optical limiting has, as already reported last year, arrived at new compounds that have been suggested for synthesis, in particular metallo-porphyrines and Platinum oligomer compounds. These are predicted to show optical limiting capability in the whole visible range of the electromagnetic spectrum. Research on second harmonic generation has also been pushed forward. Extended systems have also been studied through the development and applications of solvent models, in particular heterogeneous solvation models implemented at the Hartree-Fock, MCSCF and DFT levels; these models enabled calculations of properties up to fourth order. This includes the so-called polarized continuum model as well as a QMMM[®] (Quantum mechanics - molecular mechanics) methodology. As a special ingredient in the third year work in this field we emphasize the development of a theory and computer program for dynamical laser pulse propagation in linear and non-linear media. In combination with the quantum computations of microscopic properties like excitation energies and cross sections, this provides a very powerful means to simulate the macroscopic behaviour of a materials for various characteristics of the laser beam and sample. In fact, this provides the possibility to simulate the behaviour of the

molecular material as it is used in the actual device.

B.2 Research Method - 3rd year Report

One aim with the MOLPROP research is to develop its own research tools. In this sense there were continuous changes of the research method, or methods, employed. These methods fall under the broad context of first principle “ab initio” methods for molecular modeling. They have during the passed 3 years 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.

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 almost completely our ab initio toolbox. 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. In parallel much efforts were devoted coupled cluster methodology which is central to the network involving 5 nodes.

During the third year a strong focus was maintained on 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 and perturbational wave functions and to density functional theory. Among them we can also mention the magnetic resonance parameters for which we produced new algorithms and codes.

B.3 Work Plan - 3rd year Report

B.3.1 Breakdown of tasks - 3rd year Report

In Table 4 we specify the degree of fulfillment of the schedule outlined concerning months 25-36 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. 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

During the third year the focus in this project was on 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 has reached a working level and was applied to a wide set of problems. Simplifying relativistic models were further implemented and applied.

B.3.1.3 Linear scaling and density functional theory

New linear-scaling implementations of the DFT contribution to the Kohn-Sham matrix and of the nonclassical Coulomb contribution have been coded. Efficient calculations of Coulomb and exchange-correlation interactions are thus now feasible with linear-scaling. A fully working, efficient implementation of the fast multipole method (FMM) (scales as N) and of the tree-code (scales as $N \log N$) are now in place. Solvent models have been implemented, "PCM", "QCMM" and "semiclassical" models.

B.3.1.4 Response theory in the time domain

We have developed a formulation of resonant X-ray scattering in the whole time domain based on a reduction of the Keldysh-Dyson equations for the Green's function to a set of linear algebraic equations. Applications led to increased understanding of time-scales and relaxation in the formation of various X-ray spectra of molecules and solids.

B.3.1.5 Direct dynamics

Lagrangian techniques have been derived and implemented for computing excited state gradients, which are the underlying quantities for performing direct dynamics. Time-dependent wave packet techniques for nuclear dynamics were utilized to analyze femto-second spectroscopy in the X-ray region, in particular for X-ray Raman scattering spectroscopy.

B.3.1.6 Nuclear magnetic spin resonance

Theory and code for paramagnetic NMR shieldings have been derived and utilized for a set of molecular crystals characterized as "molecular magnets". Much work has been accomplished within the coupled cluster and the density functional technologies.

B.3.1.7 Electron spin resonance

Fully relativistic calculations of g-tensors have been carried out. The full spin Hamiltonian is now available including A- and g-tensors, and zero-field parameters (D-tensor). Open shell response functions have been derived in Hartree-Fock and DFT. The so-called PCM model has been implemented for the magnetic resonance parameters.

B.3.1.8 Non-uniform fields

Electron-correlated schemes up to the full coupled-cluster singles, doubles, triples levels have been implemented to compute current-densities with the gauge-including atomic orbital framework and ring-current models based on computed current densities have been developed. The graphical codes implemented in the year one and two 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 molecules.

B.3.1.9 Chirality and dichroism

The new efficient coupled Hartree-Fock computational schemes for parity-violating energy differences in enantiomeric molecules have been applied. Natural or field induced dichroic properties have been studied by the response theory techniques.

Table 3: Tasks attended by each team 3rd year

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

B.3.2 Schedule and Milestones - 3rd year Report

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

Table 4: Schedule and fulfillment of tasks during months 25-36. Marks 0-5 are given, where 5 denotes a perfect fulfillment of the plan.

<i>Months</i>	<i>Projects</i>	<i>Comment</i>
1- Fourth order Toolbox		
25-36	Resonant and transition state properties	Complex PP program - 5
Relativistic Formulations		
25-36	Relativ. Coupled Cluster program	Prototype in DIRAC - 4
25-36	Optical properties of actinide and lanthanide complexes	Some results - 4
25-36	Structure and properties of oligomer-metal interfaces	Organometallic molecules only - 2
Reduced Scaling correlated methods		
25-36	Photonic Applications	Working, some results - 4
25-36	Applications to quantum dots	Rich results - 5
Direct Dynamics		
25-36	Local expansions of split wave packets	Not started - 1
Nuclear Magnetic Resonance		
25-36	Visualization of NMR through current densities	Program working - 5
Non-uniform fields modeling		
25-36	Chemical shift variation in intense magnetic fields	Rich results - 3
Chirality and Dichroism		
25-36	Chiral Multi-photon Absorption	Paper out - 4

B.3.2.1 Fourth order property toolbox

The toolbox is basically completed for ab initio wave functions. Density functional electric and non-London magnetic field properties have been completed up to 4th order. Relativistic properties (linear and nonlinear) are implemented at the Dirac-Fock level.

B.3.2.2 Non-linear optical properties and materials

The midterm milestone for optical limiting has been completed, and much results have been obtained for second harmonic generation. The method development and coding has been completed. Much work after mid-term has focused on applications.

B.3.2.3 Relativistic formulations

Full one-electron implementation for 4-component theory has been fulfilled and included in the toolbox. 4-component energy, wave function and many properties are implemented for explicitly correlated methods and at the density functional theory level.

Reduced scaling in correlated methods

Implementation of the N-scaling fast multipole method completed. Linear-scaling implementations of the DFT contribution to the Kohn-Sham matrix and of the nonclassical Coulomb contribution have been coded. New low-scaling algorithms for iterative density matrix optimization. Reduction has been achieved for coupled cluster models through the Cholesky decomposition scheme.

B.3.3 Research effort of the participants - 3rd year Report

Table 5: Professional research effort on the network project (man-months) during 02-05-15 to 03-05-15

<i>Participant</i>	<i>YR Months delivered</i>	<i>From other sources</i>	<i>Total individuals</i>
1	40.5	34	8
2	12	20	5
3	12	18	3
4	9.5	23	3
5	12	12	3
6	12	18	3
7	15.5	15	2
8	32	54	12
9	18	33	6
Totals	163.5	227	43

Final Report

B.1 Research Achievements - Final Report

B.1.1 Research Objectives - Final Report

The main objective with MOLPROP network has been to develop method and theory for linear and nonlinear properties of molecules and molecular materials. The objective was to produce a mathematically consistent and theoretically versatile toolbox for applications on molecular properties up to and including fourth order in the matter-field interaction. This includes properties generated by interactions with fields of various sources; electric and magnetic, time-independent or time-dependent, internal or external, uniform or non-uniform, fields. The methodology should be applicable for general states; ground, excited or scattering states, equilibrium or transitions states. A special goal was to include gauge-invariant electron-correlated calculations of linear and non-linear optical properties, multi-photon excitations, spin-dependent properties, magnetizabilitites, magnetic resonance parameters, and X-ray phenomena. This main objective has been fulfilled very well, in some parts well beyond the initial expectations and plans.

The objective of the network and the original scientific originality of the project can be traced to the mid 80ies with the derivation of molecular models completely within the realm of second quantization using analytic gradient and response theory. This was a path to generalize the first dimension of quantum chemistry for computations of the total energy to second and third dimensions for computing the gradient and properties, respectively. This gave way for a mathematical machinery where key formula manipulations are transferred from the wave function to the operators, making the property calculations independent of the particular parametrisations of the wave function. This means that an “analytical transferability” between the wave function and its properties was obtained and a common formalism—and, to a large

extent, also a common code—that handles all kinds of perturbations and its associated properties could be derived. This in turn brought about a hierarchical set of methods that can be converged on a controlled manner and that so makes possible a meaningful interpretation of experimental data. In essence the MOLPROP project can be viewed as the full and final realization of this endeavour.

The methodology and the associated computer softwares have matured within MOLPROP and have, in several aspects, become completed during the 3-year period of the network execution. The low-scaling implementations for extended species (linear scaling and Cholesky decomposition), and effective computational implementations (screening, parallelization) have made possible applications of molecular materials at the nano-scale. The applications of this methodological development has within the network followed several main lines, of which molecular photonics and quantum dot properties are the two major ones.

From the outset of having completed the fourth order non-relativistic ab initio state-of-the-art toolbox we envisaged a wealth of development, maintaining the dual line of basic research and applications. The latter activity has been greatly promoted with the fulfillment of the linear scaling capability of the toolbox. Work with relativistic wave functions and inclusion of these into the toolbox has also proceeded; properties for 1-,2-,4- component relativistic wave functions at the one-particle level have been accounted for within MOLPROP.

We have for some time been working with time-dependent density functional theory and have accomplished the goal to include fourth order properties with DFT. A main objective for the present proposal was the inclusion of a linearly scaled DFT response theory in the fourth order toolbox, including all properties as treated hitherto. After some agony we decided to play along in the DFT ballpark. The fact that we are latecomers in this area is compensated by having at hand the full power of the property toolbox and the long experience with propagator theory and general response property and analytical gradient calculations. One should remind oneself that the enormous success of DFT for gradients, Hessians and structures after the introduction of the gradient corrected functional in 1988, actually followed a corresponding development of these quantities on the ab initio side earlier in the 80'ies. We are thus convinced that the corresponding scenario will take place, or even be enhanced, for general property calculations, and that the full implementation of the DFT propagator toolbox in in MOLPROP, with applications to systems with ten thousand atoms, will have wide ramifications.

Having pure ab initio results available at the highly correlated low end (small systems) and also with the well-denied HF/RPA at the high-end (large systems and scaling linearly as DFT), we have the possibility to fend off, and to some extent control, principal problems that already are known to exist or that may come up in DFT calculations of properties. This project has rested heavily on the linear scaling techniques now developed, and to some extent also by further development of the solvent techniques using so-called PCM and QMMM. This, as we plan, will lead to the versatile "real" toolbox applications on polymers, surface adsorbates, solutions, protein segments, functional centers in enzymes etc. Thus it will be possible not only to follow the energetics and conformation but also the general (electromagnetic) properties and responses of these systems as they evolve, including spin-dependent and relativistic effects, and so to learn more about their functionality. With this as basis we can press the quantum description of any microscopic system towards the end and so perhaps short cut the way to describe global properties of materials and living matter.

Finally a main objective was to transfer knowledge through the computer programs, which offer excellent

vehicles for that purpose. We have thereby succeeded extremely well, for instance the 4th order toolbox containing up-to-date ab initio reference wave functions and DFT in the DALTON software system, which currently holds over 1000 user licenses and over 100 site licenses over the world. DALTON is documented and free of charge. Thus all progress within MOLPROP is immediately conveyed to hundreds of European young researchers who are regular users of this program.

B.1.2 Research Method - Final Report

As already discussed above, one aim with the MOLPROP research is to develop its own research tools, and we have therefore faced a continuous change in the research method, or methods, employed. We summarize the development of research methodology within MOLPROP as follows:

B.1.2.1 Development of high-level correlation methods

Due to its computational simplicity, the main thrust of the development of quantum methods nowadays takes place within the realm of DFT. Nevertheless, since modern DFT is somewhat semi-empirical in nature, it was and is essential that a similar development is also undertaken for the **hierarchical ab initio methods**. These methods are not only important in themselves, in that they enable rigorous calculations of molecular properties to chemical accuracy, they are also important in that they provide capabilities for benchmarking and tests of DFT. Such benchmarking have been actively pursued in the MOLPROP project. We have within MOLPROP therefore put considerable effort into the development of ab initio theory, in particular **coupled-cluster theory**, including the use of **Cholesky decomposition** methods. The methods include considerations not only the evaluation of the energy but also the calculation of linear and nonlinear molecular properties at the coupled-cluster level of theory using nonvariational response theory. In addition, new cost-efficient techniques with explicit inclusion of the interelectronic distances within the framework of coupled-cluster theory have been developed for both closed and open-shell systems. Such methods are essential for the achievement of chemical accuracy for any but the smallest systems.

B.1.2.2 Relativistic methods

Apart from extending the scale and scope of the applicability range of current electronic-structure techniques, it has remained essential to study and develop the basic aspects of electronic-structure theory as such. In particular, we have focused on the relativistic, in particular 4-component, theory at ab initio and DFT levels and aimed to make such approaches applicable for general property calculations. The aims to develop such methodology has in general been successful within MOLPROP; the DIRAC program now contains a large set of options for property calculations covering a wide range in the electromagnetic spectrum. This goes for properties as different as molecular g-tensors, NMR shieldings, and X-ray spectra. In particular, we emphasize here the recent development in relativistic DFT calculations, which now almost matches the one in the corresponding non-relativistic limit. In the non-DFT case we can mention the development of multi-configurational reference expansions for 4-component calculations that has taken place within the network. With this development one covers most of the periodic table by one and the same approach.

B.1.2.3 Linear Scaling methods

An essential objective of the network was to transfer the scale of quantum modelling from the atomic domain into the nano domain. Indeed, its fulfillment is very essential for the other objectives of applicability of materials properties and of modelling materials of technological interest. A primary target of the network was therefore to develop **linear-scaling techniques**, i.e., techniques with a cost proportional to the system size, extending the applicability range into the nano regime, beyond 1000 atoms. This could not be achieved merely by utilizing high-performance computing technology, it also depended critically on the development and adaptation of new computational schemes.

This project has been very successful: For example, we have now the technology necessary for calculating the potential generated by thousands of atoms in density-functional theory, and we have derived and made tests on an algorithm that efficiently solves the self-consistent field equations that these potentials give rise to. Thus to eliminate the diagonalization bottleneck in self-consistent field theories such as Kohn–Sham (KS) DFT and Hartree–Fock (HF) theory, we optimize the one-electron density matrix directly, invoking an exponential ansatz for the atomic-orbital density matrix. Moreover, although the routine energy optimization for several thousand atoms was essential to our development of a scale-extensive technology, its potential can only be fully realized by the development of a companion technology for properties such as forces, excitation energies, frequency-dependent polarizabilities, and magnetic-resonance parameters. This goal has now also been fulfilled to a significant extent.

A different route to the treatment of large systems is based on the strategy of onion models, whereby techniques of variable accuracy and efficiency are hierarchically interconnected. We here aimed to develop methods that enable a mixed classical/quantum-mechanical description of the processes in homogeneous and heterogeneous solution by combining the **quantum-mechanics/molecular-mechanics (QM/MM)** model with models of **heterogeneous and homogeneous solvation**, thereby enabling the study of nonlinear processes of molecular systems solvated or attached to metal surfaces and nanoparticles. In these calculations, the electronic structure of the solvated compound is rigorously described by ab initio or DFT electronic-structure theory, with the polarization of the surrounding medium included in the quantum-mechanical equations. We have during the course of the network reached new steps in order to fulfill this goal.

B.1.2.4 Methods for modelling of characterizing technologies

Although being part of the general methodologies for property calculations briefly described in the three subsections above we can distinguish methods (or "sub-methods") that are applicable for close analysis of experimental results - i.e. for modelling of characterizing technologies. One can distinguish between those which concern the interaction with **external** electromagnetic fields discussed above, and those that concern the interaction of the electrons with **internal** molecular fields such as those generated by spinning nuclei and electrons. The latter, although exceedingly weak, provide numerous possibilities for **diagnostics of materials by spectroscopy**. For example, our methods for simulations of the magnetic resonance parameters generate indispensable information about materials such as their conformational structure and chemical bonding. We have in this context focused on the modelling of various magnetic resonance processes—namely, nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and optically detected magnetic resonance (ODMR). We have also pursued development of modelling for

spectroscopic processes in other regions of the electromagnetic spectrum, we can here mention; vibrational Raman optical activity in the infrared region, natural and magnetically induced circular dichroism in the optical region, and Raman scattering in the X-ray region. The MOLPROP network combined world expertise in the simulation in all of these characterizing spectroscopic techniques.

B.1.3 Breakdown of tasks - Final Report

In Table 7 we specify the degree of fulfillment of the Task Schedule outlined in section 3.2 of the technical Annex. In the rightmost column of the Table a comment is given and a digit 0-5, where 5 denotes what we regard as a perfect fulfillment of the plan. In the following we briefly summarize the execution of the work plan.

B.1.3.1 Gauge-invariant fourth order property toolbox

We accomplished an excellent fulfillment of research plans in this area: Through the common MOLPROP effort a wide range of 1st, 2nd, 3rd and 4th order properties are now available for the general community of computational chemists in Europe. The goal to derive a new *time-dependent density functional code* has successfully been fulfilled and incorporated into the 4th order toolbox.

B.1.3.2 Relativistic formulations

The full Dirac-Fock -4-component implementation of the 4th order toolbox has been accomplished. Several simplifying relativistic models have been implemented and applied. Moreover, multi-configurational self-consistent field as well as density functional theory 4-component codes are incorporated in the DIRAC program. Calculations using relativistic theory are already executed in a routine fashion in several past and ongoing research projects. This was a very successful subproject within MOLPROP.

B.1.3.3 Linear scaling and density functional theory

Also here the success is complete, in this case actually far beyond the expectation at the start of the project. New *linear scaling* scaling algorithms have thus been derived and coded for the Coulomb integral part, both classical and non-classical contributions. Applications on +1000 atom systems have been carried out on our PCs using this code. An algorithm for iterative density optimization has been derived and tested. Its full implementation will give way for +10.000 atom calculations. Solvent models have been implemented, "PCM", "QMMM" and "semiclassical" models.

B.1.3.4 Response theory in the time domain

Of the nine subprojects this was the least successful. Most of the results were obtained in the X-ray region where we developed a formulation of resonant X-ray scattering in the whole time domain based on a reduction of the Keldysh-Dyson equations for the Green's function to a set of linear algebraic

equations. Applications led to increased understanding of time-scales and relaxation in the formation of various X-ray spectra of molecules and solids.

B.1.3.5 Direct dynamics

We have derived time-dependent wave packet techniques for nuclear dynamics and implemented these for computations in connection with femtosecond spectroscopy. Applications for X-ray Raman scattering have been used to interpret pulsed synchrotron radiation experiments. The excited state EOM-CC method has produced gradients and Hessians for excited states using a new Lagrangian technique. An efficient code for RPA excited state gradients have been derived and implemented for ab initio wave functions and for DFT. The basic quantities for performing direct dynamics also of excited states are there. In many respects a successful project, although the final goal of an automatized excited state dynamics have not been reached yet.

B.1.3.6 Nuclear magnetic spin resonance

A successful subproject, even beyond the expectations at the start of the project. Theory and code for paramagnetic NMR shieldings have been derived and can already be applied in a routine fashion, in connection, of for instance, enzyme radical characterization. Implementations of shieldings and spin-spin coupling constants are now available in coupled cluster, MCSCF, fully relativistic 4-component Dirac-Fock and in DFT with all common density functionals.

B.1.3.7 Electron spin resonance

A very successful subproject, well beyond the expectations at the start of the project. The full spin Hamiltonian is now available including A-, g- and D-tensors, something unique in the area. Open shell response functions have been derived in Hartree-Fock and DFT and used for the A-,g- and D-tensors and for hyperfine interaction parameters in general. The open-shell DFT rests on our formulation and implementation of a spin-restricted approach. A fully relativistic, 4-component, implementation of g-tensors are now also available.

B.1.3.8 Non-uniform fields

The graphical codes implemented in the beginning of the network period have been used for representing streamlines and modulus of the current density induced by a magnetic field in the electron clouds of a series molecules. These codes give qualitative interpretations of paths whereby the spin and density information passes through the molecules, and have been used in a routine fashion for complex molecules during the latter part of the network. The subproject has been very successful.

B.1.3.9 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. Chirality and dichroism have been analyzed in the IR, optical and X-ray regions. Definitely a successful subproject.

Table 6: Tasks attended by each team - full period

<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.1.4 Schedule and Milestones - Final Report

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

B.1.4.1 Fourth order property toolbox

Fully completed. Ab initio highly correlated wave functions, Dirac-Fock and density functional theory for all common types of exchange-correlation functions.

B.1.4.2 Non-linear optical properties and materials

The midterm milestone for optical limiting has been fully completed, and much results have been obtained for second harmonic generation. The method development and coding has been completed, and many applications have been carried out. The quantum toolbox has here been used together with a dynamical density matrix program for laser pulse propagation in nonlinear media, derived by the partners.

B.1.4.3 Relativistic formulations

Full one-electron implementation for 4-component theory has been accomplished. Explicitly correlated (MCSCF, CC) as well as density functional theory implementations of 4-component theory have reached

Table 7: Schedule and fulfillment of tasks during months 1-36. Marks 0-5 are give, where 5 denotes a perfect fulfillment of the plan.

<i>Months</i>	<i>Projects</i>	<i>Comment</i>
1- Fourth order Toolbox		
1-12	MCSCF and CC third and fourth order properties	Gone well - 5
1-12	CC applications of excited state properties	New algorithms derived - 5
13-24	EOM-CC second derivative program	Fully implemented - 5
25-36	Resonant and transition state properties	Complex PP program - 5
Relativistic Formulations		
1-18	Relativ. RPA - including applications	To the point - 5
6-24	Relativ. 4-component 2nd order MCSCF - CI	Formulation + code - 4
25-36	Relativ. Coupled Cluster program	Prototype in DIRAC - 4
25-36	Optical properties of actinide and lanthanide complexes	Some results - 4
25-36	Structure and properties of oligomer-metal interfaces	Organometallic molecules only - 2
Reduced Scaling correlated methods		
1-12	TD-DFT spectra and properties	Formulated, implemented - 5
1-18	Reduced Scaling in CC	Cholesky method working - 5
13-24	Linear Scaling in response properties	Linear properties OK - 4
25-36	Photonic Applications	Working, some results - 4
25-36	Applications to quantum dots	Rich results - 5
NLO properties and materials		
1-12	Multi-photon and optical limiting	Rich results - 5
1-12	SHG and Kerr materials	Some results - 3
13-24	2D charge-transfer systems	Compounds predicted - 4
13-24	Optical smart windows	Started but delayed - 2
Direct Dynamics		
1-12	Interface to EOM-CC	The EOM-CC part developed - 5
13-24	Use of evolution operator techniques	X-ray problems - 4
25-36	Local expansions of split wave packets	Not started - 1
Nuclear Magnetic Resonance		
1-12	CC hierarchy for spin-spin couplings	Well met - 5
13-24	Relativistic approaches	With perturbation theory - 4
25-36	Visualization of NMR through current densities	Program working - 5
Electron Spin Resonance		
1-12	Benchmarking	Much development - 5
13-24	London orbital implementation	Not yet - 1
13-24	CC implementation	Some results - 3
Non-uniform fields modeling		
1-12	Topological features of current densities	Working - 5
13-24	NM dipole induced current densities	New results - 5
25-36	chemical shift variation in intense magnetic fields	results - 3
Chirality and Dichroism		
1-12	MCD and Magnetic Optical Dichroism	Several Papers - 5
13-24	EF induced Chiral Absorption	Paper out - 5
25-36	Chiral Multi-photon Absorption	Results out - 4

quite far. Many, if not most, of the toolbox properties can now be analyzed fully relativistically through Dirac-Fock theory.

B.1.4.4 Reduced scaling in correlated methods

Linear scaling density functional and Hartree-Fock based methods have been derived, implemented and applied for +1000 atom systems. New low-scaling algorithms for iterative density matrix optimization have been derived and tested. Considerable scaling reduction has been achieved for coupled cluster models through the Cholesky decomposition scheme.

B.1.5 Research effort of the participants - Final Report

Table 8: Professional research effort on the network project (man-months) during 00-05-15 to 03-05-15

<i>Participant</i>	<i>YR Months delivered</i>	<i>From other sources</i>	<i>Total individuals</i>
1	72	108	8
2	23	70	5
3	24	52	3
4	24	55	3
5	21	39	3
6	22.5	55	3
7	28.5	45	2
8	51.5	186	12
9	37.5	102	6
Totals	304	712	43

3rd Year Report

B.4 Organization and Management - 3rd Year Report

B.4.1 Network organization - 3rd Year Report

The 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 was 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.4.2 Network meetings - 3rd Year Report

B.4.2.1 2002-06-24 - 2002-07-06 SOSTRUP Summer School in Molecular Properties in Aarhus

Time : June 24 - July 6, 2002.

Place: Sostrup, Denmark

Title: 7th SOSTRUP Summer School in Molecular Properties.

Lectures: 56 hours of lectures and exercises

52 PARTICIPANTS: Including all MOLPROP hired YRs. All lecturers belong to MOLPROP

The full program, participant lists and description of the summer school content can be found at: <http://www.chem.au.dk/teo/>

As an integral part of the training/mobility program in MOLPROP the SOSTRUP summer school on Molecular Properties was held during two weeks 2002-06-24 to 2002-07-06. SOSTRUP is a biannual school for graduate and postgraduate students. The school, organized and staffed by members of the network (Oslo and Odense), started in 1990 and was arranged for the 7th time in 2002. During two weeks of intense training, through lectures and exercises, the students are brought up to the research level in the field. 52 students attended the summer school 2002 including all hired MOLPROP YRs. As for the previous schools, about fifty percent of the students were from Scandinavia and forty percent were from other European countries.

At the summer school, the following topics were discussed: 1) Second quantization. 2) HF, CI, MCSCF, CC, MP, DFT, and explicitly correlated methods. Each method is described in depth, including its computational scaling and performance in comparison with other methods. 3) Time-independent response theory: geometrical derivatives and force constants, vibrational frequencies and intensities, electric and magnetic susceptibilities, NMR shielding constants and spin-spin coupling constant. 4) Time-dependent response theory: dynamic polarizabilities and hyperpolarizabilities, one- and two-photon transition moments and electronic excitation energies. 5) Atomic orbitals, molecular basis sets, and molecular integral evaluation. 6) Convergence in N- and one-electron spaces, calibration and benchmarking. 7) The molecular electronic Hamiltonian: external electromagnetic fields, electron spin, relativistic corrections, and gauge transformations.

B.4.2.2 2002-10-04 - 2002-10-05 MOLPROP meeting in Valencia

Time : 4-5 October, 2002.

Place: Valencia

Title: 4th MOLPROP scientific and organizational meeting

Lectures: 16 lectures plus poster presentations

36 PARTICIPANTS: Including all MOLPROP hired YRs

The full program can be found at: <http://www.theochem.kth.se/molprop/valencia-meeting/PROGRAM>

The full participant list can be found at: <http://www.theochem.kth.se/molprop/valencia-meeting/PARTICIPANTS>

The meeting was held at "Colegio Mayor Rector Peset", an old palace from XVI century. The meeting consisted of scientific dissertations from the various nodes in the network on 4/10 and discussion of organizational issues on 5/10, including future perspectives. The status and updates of the various codes related to the network were also discussed. 10 of the scientific talks were present by MOLPROP hired YRs.

B.4.2.3 2002-09-12 - 2002-12-12 Winter School in Theoretical Chemistry in Helsinki

Time : 9-12 December, 2002.

Place: Helsinki

Title: Condensed Phase Dynamics Lectures: 20 hours of lectures plus poster presentations

75 PARTICIPANTS: Including all (17) MOLPROP hired YRs. 1 lecturer belong to MOLPROP

The full program can be found at: <http://www.chem.helsinki.fi/Info/WinterSchool/ws2002.html>

The full participant list can be found at: <http://www.chem.helsinki.fi/Info/WinterSchool/part2002.html>

This was the third 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 the broad scope: Condensed Phase Dynamics.

B.4.2.4 2003-04-23 - 2003-04-25 MOLPROP meeting on Density Functional Theory in Stockholm

Time : 23-25 April, 2003.

Place: Stockholm

Title: WORKSHOP ON DENSITY FUNCTIONAL THEORY: PRESENT AND FUTURE CHALLENGES (5th MOLPROP scientific and organizational meeting). Lectures: 20 lectures plus poster presentations

49 PARTICIPANTS (36 international): Including all MOLPROP hired YRs and node leaders

The full program can be found at: http://www.theochem.kth.se/molprop/final_meeting/

The full participant list can be found at: http://www.theochem.kth.se/molprop/final_meeting/list.html

The meeting was held at the new ALBANOVA campus shared by the Royal Institute of Technology and Stockholm University in Stockholm. The topic of the conference focused on Density Functional Theory which also is a central topic in MOLPROP research and training. Apart from MOLPROP researchers and students, special invitations were sent to **36 of the DeMon network of experts** representing another "branch" of density functional theory. The presentations by the two groups and the common discussions of present and future challenges were considered as being most fruitful and spurred the initiation for a series of meetings of the kind. The MOLPROP researchers and students were given the chance to disseminate much of their results to this general audience. The participation of MOLPROP YRs in the discussions was considerable. 3 of the 20 plenary talks were given by MOLPROP YRs.

B.4.2.5 2003-04-26 - 2003-04-26 MOLPROP Final Meeting in Stockholm

Time : 26 April, 2003.

Place: Stockholm

Title: MOLPROP Final Meeting Lectures: 1 Day of organizational discussion.

9 PARTICIPANTS : All MOLPROP Node Leaders

The full program can be found at: http://www.theochem.kth.se/molprop/final_meeting/

The meeting agenda contained the following issues:

Resolution of Scientific and Training Issues

Resolution of Organisational and Financial Issues

Outlook and Closing of Network

An informal and intense discussion of different aspects of the network was brought up among the node leaders. The final financial issues were settled, and preparations for the final report were made. A large part of the discussion was focused on the way to proceed in order to capitalize on the great achievements of the MOLRPOP network in terms of training, research and organization. It was agreed that the structuring effect of the network was very strong, something that was considered to be very useful for future activities. A continuation in some form in the European FP6 program was therefore highly recommended.

B.4.3 MOLPROP visits - 3rd year Report

MOLPROP visits were executed according to the following:

1. Kenneth Ruud, (Oslo node) visited Stockholm on two periods 12-22/1 2003, and 20-24/3 2003 for merging the DFT open-shell codes.
2. Olav Vahtras, (Stockholm node) visited Oslo two periods 3-11/9 2002 and 8-15/5 2003 for work with DFT and for merging the direct AO g-tensor code.
3. Antonio Rizzo (Pisa) visited Stockholm to work on Sternheimer shielding calculations, 20-27/4 2003.

Table 9: MOLPORP visits during 3rd year

<i>From/To</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					
Santiago		X	-			X			
Mainz				-		X		X	
Modena		X			-				X
Pisa	X		X	X		-		X	X
Helsinki	X			X			-	X	X
Odense	X			X		X	X	-	X
Oslo	X			X		X	X	X	-

4. Antonio Rizzo (Pisa) visited Santiago node to work on virial coefficients in noble atom gases, 10-27/3 2003.
5. Antonio Rizzo (Pisa) visited Oslo node to work on optical rotation, 10-18/4 2003.
6. Mark Watson, (hired YR, Oslo node), visited Stockholm on two occasions, 5-15/12 2002 and 18-29/4 2003 to work on linear scaling code.
7. Trygve Helgaker, Oslo node, visited Stockholm 20-24/3 2003 to work on linear scaling code.
8. Vincenzo Carravetta (Pisa) visited Stockholm to work on the DALTON STEX code 12-22/5 2003.
9. Ulf Ekström (hired YR, Pisa) visited Stockholm to work on the DALTON STEX code 12-22/5 2003.
10. Javier Lopez Cacheiro visited Valencia node 3 times: Development of the CCSD(T) code with the Cholesky decomposition.
11. Jonas Juselius (Helsinki node) visited Mainz on two occasions, 4-11 to 22-11-2002, 16-3 to 4-4-2003, to work on electron correlated calculation of current densities using gauge-including atomic orbitals and on development of new ring current models.
12. Antonio Rizzo (Pisa node) visited Mainz node on 6-4 to 16-4 2003, to work on coupled-cluster calculations including triple excitations for the Cotton-Mouton-effect.
13. Inmaculada Garcia Cuesta (Valencia) visited Modena from 03-2003 to 04-2003
14. Jeppe Olsen (Odense node) visited Helsinki and worked on the quantum dot project on two occasions: 4.2.2003-9.2.2003 and 3.6.2002-6.6.2002.
15. Trygve Helgaker (Oslo node) visited Odense 15.08.02 - 21.08.02 to work on DIRC code.
16. Magda Pecul (YR, Pisa noed) visited Oslo 26.08.02 - 13.09.02 to work on spin-spin coupling constants.

B.4.3.1 Summer Schools, Meetings

All hired YRs in MOLRPOP participated in the SOSTRUP summer school, the Helsinki Winter school, the Valencia meeting and the Stockholm DFT meeting. All MOLPROP node leaders participated in the Valencia meeting and the two Stockholm meetings (DFT + Final).

Final Report

B.2 Organization and Management - Final Report

B.2.1 Network organization - Final Report

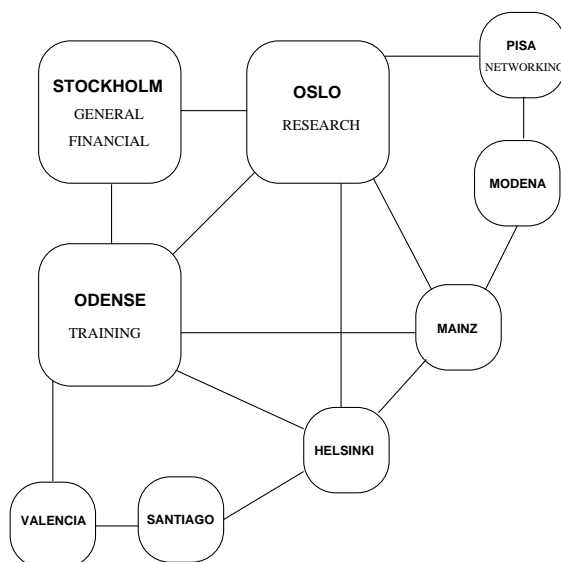
Management structure and techniques. The organization has been structured into three tiers: coordinator node, core nodes, network nodes. The 20-year collaboration between the Scandinavian partners has guaranteed a **tight, seamless management of the network by the core**, without this management being burdensome. The coordinator had full financial responsibility, and additionally the overall responsibility for all network activities: training, science and administration, but consultation and decision-making has been shared with the core. The harmonious relationships among the pre-MOLPROP partners and the new nodes further legitimized this decision-making process, and it has certainly been one of the winning features of MOLPROP. A high level of integration of the network ensured that the coordination technique essentially remained **informal as concerned matters for the seniors**, while coordination remained **structured concerning YR matters**.

Among the core nodes the Odense node had special responsibility for training coordination and the Oslo node for the record of research. This division of affairs is quite obvious from the outlay of the network activities. Furthermore, the Pisa partner, who is very well integrated into the network collaboration, took special care of the program for networking activities, like the meeting and twinning programs. Finally, since high performance computing was an essential ingredient in both the training and the research activities of the network, we have exploited the long-term experience of some partners (Mainz, Oslo, Odense) to organize computing issues of common relevance for the network. The management chart below indicates the nodes with main responsibilities in the network.

B.2.2 Communication Strategy - Final Report

An ubiquitous technology utilized by the network is the world-wide web. A local home page was created for special and detailed network information; home page <http://www.theochem.kth.se/molprop/>. It has a link from the main CORDIS home page. It has been frequently used by the participants as a working array. It contains three areas:

- Network Data: Vacancies, Partners, Objectives, Applications, Collaboration, Publications, Training, Results and Achievements.



Management of the MOLPROP network

- Network Events: Employments, Organized meetings, Attendance of Meetings and Schools, Visits, Twinning.
- Financial information: For the node leaders, and sealed with a password.

The home page provides links to the individual URL pages of the nodes, and was constantly updated by the partners, but with the coordinator having the overall responsibility.

We have also used the existing page/ mailing list for the DALTON program system, which is a main common software system of the network. Much of the actual scientific activity, correspondence, result presentations, benchmarking, program discussions, dissemination and updates, took place in connection with the DALTON program and through the use of its home page <http://www.kjemi.uio.no/software/dalton/dalton.html>

Intranet reporting also took place through the special network events, in particular meetings and other visits among senior and junior researchers, which were very frequent in the network.

Financial Management. The financial management followed the same theme throughout the network period. Thus the advanced payment was immediately distributed to the nodes in proportion to the contracted amount. The yearly payments then regulated the financing of the nodes according to the most

pressing criterion, namely the **delivery of man-months in the hiring**, though with the sideconditions that the training was fulfilled to the point, and that an essential participation of other network activities had taken place. If these criteria were fulfilled the yearly payments to a node directly followed its share of the contracted amount. Before the start of the network this principle was made clear and it was also stated that the coordinator does not withhold any funding except the particular management part reserved for him. In this way the **financial situation for the nodes became well-defined** and the incitement for the node to maintain its most important mission, namely the hiring schedule, was strong. We announced the principle: If a node faces problem with hiring in such a way that it is clear that it will not produce the contracted amount, the responsibility, and the appropriate financing for that, will be shifted to another node. This actually happened on two occasions. The situation was extra highlighted at midterm and at the end of the second year. Contributions for **management related expenses** were kept a minimum, however a small sum was reserved for the coordinator for general network auditing, as well as for secretarial and other management costs.

B.2.3 Dissemination of results - Final Report

Dissemination of results took place using the following channels:

- **Normal academic channels:** Through publications, conferences and smaller meetings. Network partners are frequently invited to international conferences where they took the opportunity to display network results.
- **Home pages:** The MOLPROP home page contains messages in bullet form of scientific activity (see "Visits"). A summary of results is also given at the (linked) Cordis home page. The DALTON home page was used for more technical results concerning software development.
- **Direct contact** with potential end-users of results: experimentalists, companies, computer centers have been undertaken.
- **Network conference invitation.** In the final MOLPROP conference in Stockholm an invitation to 40 international scientists was made in order to spread network results (see 3rd year report).

Intellectual property rights. The partners have been free to publish their results in international journals according to normal academic procedures.

B.2.3.1 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-Jurgen 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/lazzaretti.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.2.4 Network Meetings and Schools - Final Report

B.2.4.1 2000-05-28 - 2000-05-29: First MOLPROP network meeting

Time : 28-29 May, 2000.

Lectures: 15 lectures plus 2 Discussion sessions

The meeting comprised 43 participants representing all 9 nodes of the Network.

This first MOLPROP network meeting took place in Stockholm, more precisely on the island of Lidingö, which is a suburb located half an hour from Stockholm city. The meeting was run in series with the EU COST/D9 meeting in "Molecules in mixed condensed media", at the Royal Institute of Technology, Stockholm, 26-27 May.

During the meeting talks with recent results were presented on subjects that overlapped with the contracted scientific goals of the network. The final afternoon of the meeting was devoted to discussion and planning of the network, especially on the training content and hiring of Young Researchers.

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

The full (signed) participant list can be found at: <http://www.theochem.kth.se/molprop/arch/list1.pdf>.

B.2.4.2 2000-12-11 - 2000-12-15 Winter School in Theoretical Chemistry 2000

Time : 11-15 December, 2000.

Title: MAGNETIC PROPERTIES OF MOLECULES

Lectures: 24 lectures plus poster presentations

65 PARTICIPANTS: 35 of them belonging to MOLPROP

11 LECTURERS: 10 of them belonging to MOLPROP

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

The full (signed) participant list can be found at: <http://www.theochem.kth.se/molprop/arch/list2.pdf>.

This was the first of the yearly Winter Schools organized by partner 7, and with lecturers and participations from the MOLPROP network. It focuses each year on a subject that is central to the network goals and with strong participation of the MOLPROP YRs. The YRs even contribute as lecturers (4 of them this time, see program above).

B.2.4.3 2000-01-25 - 2000-01-27 First MOLPROP Workshop Meeting in Santiago de Compostela

Time : 25-27 January, 2001.

Lectures: 21 lectures plus 3 Discussion/ Group work sessions

42 Participants.

In this workshop the first new results from the network were presented and discussed. YR presentations were also made. Much of the time was devoted to 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 the possibilities to fill the remaining holes for the YR employments, for which there was consensus to help each other out.

Full program can be found at: http://www.theochem.kth.se/molprop/extras/program_Santiago2.html

The full (signed) participant list can be found at: <http://www.theochem.kth.se/molprop/arch/list3.pdf>.

B.2.4.4 2001-12-10 - 2001-12-13 Winter School in Theoretical Chemistry in Helsinki

Time : 10-13 December, 2001.

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.2.4.5 2002-01-24 - 2002-05-25 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.2.4.6 2002-01-25 - 2002-01-26 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.2.4.7 2002-06-24 - 2002-07-06 SOSTRUP Summer School in Molecular Properties in Aarhus

Time : June 24 - July 6, 2002.

Place: Sostrup, Denmark

Title: 7th SOSTRUP Summer School in Molecular Properties.

Lectures: 56 hours of lectures and exercises.

52 PARTICIPANTS: Including all MOLPROP hired YRs.

All lecturers belong to MOLPROP:

The full program, participant lists and description of the summer school content can be found at: <http://www.chem.au.dk/teo/>

As an integral part of the training/mobility program in MOLPROP the SOSTRUP summer school on Molecular Properties was held during two weeks 2002-06-24 to 2002-07-06. SOSTRUP is a biannual school for graduate and postgraduate students. The school, organized and staffed by members of the network (Oslo and Odense), started in 1990 and was arranged for the 7th time in 2002. During two weeks of intense training, through lectures and exercises, the students are brought up to the research level in the field. 52 students attended the summer school 2002 including all hired MOLPROP YRs. As for the previous schools, about fifty percent of the students were from Scandinavia and forty percent were from other European countries.

At the summer school, the following topics were discussed: 1) Second quantization. 2) HF, CI, MCSCF, CC, MP, DFT, and explicitly correlated methods. Each method is described in depth, including its computational scaling and performance in comparison with other methods. 3) Time-independent response theory: geometrical derivatives and force constants, vibrational frequencies and intensities, electric and magnetic susceptibilities, NMR shielding constants and spin-spin coupling constants. 4) Time-dependent response theory: dynamic polarizabilities and hyperpolarizabilities, one- and two-photon transition moments and electronic excitation energies. 5) Atomic orbitals, molecular basis sets, and molecular integral evaluation. 6) Convergence in N- and one-electron spaces, calibration and benchmarking. 7) The molecular electronic Hamiltonian: external electromagnetic fields, electron spin, relativistic corrections, and gauge transformations.

B.2.4.8 2002-10-04 - 2002-10-05 MOLPROP meeting in Valencia

Time : 4-5 October, 2002.

Place: Valencia

Title: 4th MOLPROP scientific and organizational meeting

Lectures: 16 lectures plus poster presentations

36 PARTICIPANTS: Including all MOLPROP hired YRs

The full program can be found at: <http://www.theochem.kth.se/molprop/valencia-meeting/PROGRAM>

The full participant list can be found at: <http://www.theochem.kth.se/molprop/valencia-meeting/PARTICIPANTS>

The meeting was held at "Colegio Mayor Rector Peset", an old palace from XVI century. The meeting consisted of scientific dissertations from the various nodes in the network on 4/10 and discussion of organizational issues on 5/10, including future perspectives. The status and updates of the various codes related to the network were also discussed. 10 of the scientific talks were present by MOLPROP hired YRs.

B.2.4.9 2002-12-9 - 2002-12-12 Winter School in Theoretical Chemistry in Helsinki

Time : 9-12 December, 2002.

Place: Helsinki

Title: Condensed Phase Dynamics

Lectures: 20 hours of lectures plus poster presentations

75 PARTICIPANTS: Including all (17) MOLPROP hired YRs.

The full program can be found at: <http://www.chem.helsinki.fi/Info/WinterSchool/ws2002.html>

The full participant list can be found at: <http://www.chem.helsinki.fi/Info/WinterSchool/part2002.html>

This was the third 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 the broad scope: Condensed Phase Dynamics.

B.2.4.10 2003-04-23 - 2003-04-25 MOLPROP meeting on Density Functional Theory in Stockholm

Time : 23-25 April, 2003.

Place: Stockholm

Title: WORKSHOP ON DENSITY FUNCTIONAL THEORY: PRESENT AND FUTURE CHALLENGES (5th MOLPROP scientific and organizational meeting).

Lectures: 20 lectures plus poster presentations

49 PARTICIPANTS (36 internationals): Including all MOLPROP hired YRs and node leaders

The full program can be found at: http://www.theochem.kth.se/molprop/final_meeting/

The full participant list can be found at: http://www.theochem.kth.se/molprop/final_meeting/list.html

The meeting was held at the new ALBANOVA campus shared by the Royal Institute of Technology and Stockholm University in Stockholm. The topic of the conference focused on Density Functional Theory which also is a central topic in MOLPROP research and training. Apart from MOLPROP researchers and students, special invitations were sent to 36 of the DeMon network of researchers representing another "branch" of density functional theory. The presentations by the two groups and the common discussions of present and future challenges were considered as being most fruitful and spurred the initiation for a series of meetings of the kind. The MOLPROP researchers and students were given the chance to disseminate much of their results to this general audience. The participation of MOLPROP YRs in the discussions was considerable. 3 of the 20 plenary talks were given by MOLPROP YRs.

B.2.4.11 2003-04-26 - 2003-04-26 MOLPROP Final Meeting in Stockholm

Time : 26 April, 2003.

Place: Stockholm

Title: MOLPROP Final Meeting

Lectures: 1 day of organizational discussion.

9 PARTICIPANTS : All MOLPROP Node Leaders

The full program can be found at: http://www.theochem.kth.se/molprop/final_meeting/

The meeting agenda contained the following issues:

Resolution of Scientific and Training Issues

Resolution of Organisational and Financial Issues

Outlook and Closing of Network

An informal and intense discussion of different aspects of the network was brought up among the node leaders. The final financial issues were settled, and preparations for the final report were made. A large part of the discussion was focused on the way to proceed in order to capitalize on the great achievements of the MOLRPOP network in terms of training, research and organization. It was agreed that the structuring effect of the network was very strong, something that was considered to be very useful for future activities. A continuation in some form in the European FP6 program was therefore highly recommended.

B.2.5 Networking Activities - Final Report

The networking activities are summarized in the following list of node-to-node visits. For more details on the meetings, attendances, visits, twinning and other network issues we refer to the home page <http://www.theochem.kth.se/molprop/>

B.2.5.1 Node-to-node visits

1. 2000-11-20: Vincenzo Carravetta (Pisa) visited Stockholm node during 22/9 to 6/10 2000 to work on theory and code for multi-atom resonant photoemission.
2. 2000-07-10: Dr. Henrik Koch (Odense) visited Valencia during three weeks for developing Cholesky decomposition of two-electron
3. 2000-12-02: 2-7/12 Jeppe Olsen visited the Helsinki node for work on quantum dots.
4. 2001-06-07: Visit of Dan Jonsson (YR, Mainz) to Oslo from 2001-03-29 to to work on the implementation of integral direct response theory for high-spin restricted open-shell HF within the Dalton program package travel.
5. 2001-05-29: Visit of J. Gauss (Mainz) to Pisa (5/5/2001-9/5/2001) to collaborate with A. Rizzo on coupled-cluster calculations of mixed electric-magnetic properties.
6. 2001-01-08: Dage Sundholm (Helsinki) visited Mainz 16-23.10.2000
7. 2001-01-28: 28/1 - 11/2. Visit by Antonio Rizzo to Santiago de Compostela, Spain for a total of thirteen days.
8. 2001-05-22: 22-28/5 Hans Ågren (Stockholm) visit to Pisa, in collaboration with the V. Carravetta and A. Rizzo.
9. 2001-05-27: 27/5-3/6 Helena Larsen (YR, Odense) visited the Oslo node to work with Trygve Helgaker.
10. 2001-01-02: Visit of Christof Hättig (YR) to Oslo 12.11.00-24.11.00
11. 2001-01-02: Visit of Mark Watson (YR) to Oslo 10.10.00 - 24.10.00
12. 2001-01-02: Visit of Sonia Coriani(YR, Odense) to Oslo 12.11.00-24.11.00

13. 2001-01-02: Mark Watson (YR): Visit to Oslo 08.12.00-21.12.00
14. 2001-02-28: Visit of Torgeir Ruden (YR, Oslo) to Aarhus, Denmark 05.02.01 - 17.02.01
15. 2001-04-30: Jeppe Olsen (Odense) visited Helsinki 3.12.2000-7.12.2000.
16. 2001-01-16: 16-21/1 Kenneth Ruud (YR, Oslo), visited Stockholm to work on electron spin spin coupling integrals.
17. 2001-02-19: 19/2 -3/3 Oscar Rubio (YR, Valencia) visited Stockholm to do response calculations on some naphthalene species.
18. 2001-04-26: 26/4-5/5 Kenneth Ruud (YR, Oslo), visited Stockholm to work on Douglas-Kroll implementation in Dalton.
19. Kenneth Ruud, (YR) Oslo node visited Stockholm 21-29/11 2001 for merging the HSROHF and the spin-spin coupling codes.
20. Vincenzo Carravetta (Pisa) visited Stockholm to work on the DALTON STEX code, and coorganize a Swedish-Italian workshop in Stockholm including MOLPROP students.
21. 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.
22. 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).
23. 2001-12-01: Dr. Henrik Koch (Odense) visited Valencia, following up on the implementation of the Cholesky decomposition code.
24. Visit of Alfredo Sanchez (Valencia) to Modena (17-21/10 2002) to start joint applications in the field of high order properties
25. Visit of Alfredo Sanchez (Valencia) to Mainz (29/6 - 4/7 2001) to work on applications of CCSD response to calculate NMR parameters
26. Berta Fernandez from Santiago de Compostela visits the node in Valencia 2002-06-08.
27. Visit of Berta Fernandez, Santiago de Compostela, to Pisa, 8th-15th of April 2002. Collaboration of interaction electric and optical properties of Neon.
28. 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
29. 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.
30. Visit of Jurgen Gauss (Mainz) to Aarhus (19/3 -22/4 2002) to work on a benchmark study on vibrational frequencies
31. 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.
32. 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.
33. 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.
34. Jeppe Olsen (Odense) visited Helsinki 3.6.2002-6.6.2002. Development of the quantum dot program
35. Jeppe Olsen (Odense) visited Helsinki 12.9.2001-18.9.2001. Development of the quantum dot program.
36. Dage Sundholm (Helsinki) visited the Odense (Arhus) node for work on quantum dots (20.01.2002-24.01.2002).
37. Helena Larsen (Odense, YR) visited the Oslo node 27/5-3/6 2001 to work with Trygve Helgaker.
38. Visit of Trygve Helgaker (Oslo) to Aarhus 02.02.02 - 08.02.02, work on benchmarking with P. Jorgensen and J. Olsen.
39. Visit of Trygve Helgaker (Oslo) to Odense 25.08.01 - 26.08.01, to work on the DIRAC program with with H.J.Jensen.
40. Visit of Trygve Helgaker (Oslo) to Cambridge 12.06.01 - 15.06.01 to work with Mark Watson.

Table 10: MOLPROP research visits during full period.

<i>From/To</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	X	X
Valencia	X	-	X	X	X	X		X	
Santiago	X	X	-			X		X	
Mainz	X			-	X	X	X	X	X
Modena	X	X		X	-	X			X
Pisa	X	X	X	X	X	-	X	X	X
Helsinki	X			X		X	-	X	X
Odense	X			X		X	X	-	X
Oslo	X			X	X	X	X	X	-

41. Visit of Trygve Helgaker (Oslo) to Aarhus 07.09.01 - 12.09.01. Work on frequencies with Filip Pawlowski.
42. Kenneth Ruud, (Oslo node) visited Stockholm on two periods 12-22/1 2003, and 20-24/3 2003 for merging the DFT open-shell codes.
43. Olav Vahtras, (Stockholm node) visited Oslo two periods 3-11/9 2002 and 8-15/5 2003 for work with DFT and for merging the direct AO g-tensor code.
44. Antonio Rizzo (Pisa) visited Stockholm to work on Sternheimer shielding calculations, 20-27/4 2003.
45. Antonio Rizzo (Pisa) visited Santiago node to work on virial coefficients in noble atom gases, 10-27/3 2003.
46. Antonio Rizzo (Pisa) visited Oslo node to work on optical rotation, 10-18/4 2003.
47. Mark Watson, (hired YR, Oslo node), visited Stockholm on two occasions, 5-15/12 2002 and 18-29/4 2003 to work on linear scaling code.
48. Trygve Helgaker, Oslo node, visited Stockholm 20-24/3 2003 to work on linear scaling code.
49. Vincenzo Carravetta (Pisa) visited Stockholm to work on the DALTON STEX code 12-22/5 2003.
50. Ulf Ekström (hired YR, Pisa) visited Stockholm to work on the DALTON STEX code 12-22/5 2003.
51. Javier Lopez Cacheiro visited Valencia node 3 times: Development of the CCSD(T) code with the Cholesky decomposition.
52. Jonas Juselius (Helsinki node) visited Mainz on two occasions, 4-11 to 22-11-2002, 16-3 to 4-4-2003, to work on electron correlated calculation of current densities using gauge-including atomic orbitals and on development of new ring current models
53. Antonio Rizzo (Pisa node) visited Mainz node on 6-4 to 16-4 2003, to work on coupled-cluster calculations including triple excitations for the Cotton-Mouton-effect.
54. Inmaculada Garcia Cuesta (Valencia) visited Modena from 03-2003 to 04-2003
55. Jeppe Olsen (Odense node) visited Helsinki and worked on the quantum dot project on two occasions: 4.2.2003-9.2.2003 and 3.6.2002-6.6.2002.
56. Trygve Helgaker (Oslo node) visited Odense 15.08.02 - 21.08.02 to work on DIRAC code.
57. Magda Pecul (YR, Pisa node) visited Oslo 26.08.02 - 13.09.02 to work on spin-spin coupling constants.

3rd Year Report

Table 11: MOLPROP site visits (research, conferences, schools, twinning) during full period.

<i>From/To</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	X	X	X	X
Valencia	X	-	X	X	X	X	X	X	
Santiago	X	X	-			X	X	X	
Mainz	X	X	X	-	X	X	X	X	X
Modena	X	X	X	X	-	X	X	X	X
Pisa	X	X	X	X	X	-	X	X	X
Helsinki	X	X	X	X		X	-	X	X
Odense	X	X	X	X		X	X	-	X
Oslo	X	X	X	X	X	X	X	X	-

B.5 Training - 3rd Year Report

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 - 3rd Year Report

Table 12: Recruitment of Young Researchers in MOLPROP network

Participant	Young Researchers financed by the contract (person-months)*			Contract deliverable of Young Researchers to be financed by the contract (person-months)		
	Pre-doc (a)	Post-doc (b)	Total (a+b)	Pre-doc (c)	Post-doc (d)	Total (c+d)
P1-Stockholm	72 (40.5)		72 (40.5)	24		24
P2-Valencia		23 (12)	23 (12)		24	24
P3-Santiago	12 (12)	12	24 (12)		24	24
P4-Mainz		24 (9.5)	24 (9.5)		24	24
P5-Modena	21 (12)		21 (12)		24	24
P6-Pisa	10 (10)	12.5	22.5 (10)	24		24
P7-Helsinki	25.5 (12.5)	3(3)	28.5 (15.5)		24	24
P8-Odense	39.5 (21.5)	12 (10.5)	51.5 (32)	36	12	48
P9-Oslo	13.5 (4.5)	24 (13.5)	37.5 (18)	36		36
Total	193.5	110.5	304	120	132	252

* Hiring during the third year is given in parenthesis

The hiring is commented in the final report below.

B.5.3 Integration of YRs - 3rd Year Report

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. All hired YRs thus participated in the three network meetings and in the two schools during the 3rd year. As in previous periods, there was also an extensive participation of other YRs, not hired by MOLPROP, in the network meetings and schools; in the meetings between 20-30, in the schools about 50. Many publications have been produced involving the YRs; 17 such publications have been obtained during the 3rd year, most of them in node-to-node collaboration, see A.2.

B.5.4 Special measures - 3rd Year Report

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. 20 oral presentations were made by YRs in the MOLRPOP network meetings alone. All this has 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 the 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.5.5 Equal opportunities - 3rd Year Report

We 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.5.6 Multidisciplinarity - 3rd Year Report

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.5.7 Industrial connections - 3rd Year Report

Laban Pettersson (Odense YR) has received support from the BioVitrum AB pharmaceutical company and he intends to continue in this company after completion of his PhD studies in "Modelling of Drug Solubility".

B.6 Difficulties - 3rd Year Report

The network has been running very smoothly and effectively during the third year. The delay in back-payments from the commission produced initially a problem in that some universities were reluctant to pre-pay student salaries to the amount and for the time period that was necessary. These problems were finally resolved and the hiring could proceed as planned.

B.7 Adjustments to costs previously reported - 3rd Year Report

In this section we explain the "adjustments to costs previously reported" that have been made in the cost statement summary.

- P2 - University of Valencia

In the 2nd year report there were claimed personnel costs for Dr. T. Bondo Pedersen, duration of appointment 09/07/01 - 08/07/02. The period of appointment was not complete within the reporting period 15/05/01 - 14/05/02. All costs allocated to the period 15/05/02 - 08/07/02 has now been claimed in the present cost statement, and the costs for the previous period adjusted accordingly.

- P4 - Universitat, Mainz, Germany

In the 2nd year report there were claimed personnel costs for Dr. Dan Jonsson, duration of appointment 01/05/01 - 30/04/02. The period of appointment was not full within the reporting period 15/05/01 - 14/05/02. Therefore, 2,710,19 EURO (half of a monthly salary plus 20% cost category "adjustments to costs previously reported" in this years report.

- P5 - University of Modena, Italy

In the 2nd year report there were claimed personnel costs for Mr. Rafael Soriano Jartin, duration of appointment 09//01 - 05/02. The period of appointment was not complete within the reporting period 15/05/01 - 14/05/02. This is adjusted for now.

- P7 - University of Helsinki, Finland

In the 2nd year report there were claimed personnel costs for Mr. Stefano Corni, duration of appointment 05/01 - 06/01 and 10/01. The period of appointment was not full within the reporting period 15/05/01 - 14/05/02. Therefore, 1,972.88 EURO (half of a monthly salary plus 20 % overhead) is claimed under cost category "adjustments to costs previously reported" in this years report.

- P9 - University of Oslo, Norway

In the 2nd year report the wrong exchange rate was used; 8.25 instead of 7,4340. This is now adjusted for in the present report.

Final Report

B.3 Training Overview - Final Report

B.3.1 Training Activities - Final Report

A central aim with the MOLPROP proposal was to make it possible to train young researchers to acquire skills, to promote their scientific and personal abilities in a research environment, and to make them work well both independently and in collaboration. The aim was thus divided between the special and the general; **to educate specialists within the scientific field defined by the MOLPROP project, and to train general skills in theory, modelling and in scientific computing.** The activities carried out within the project required a background in quantum theory and experience in scientific computing and programming. The training in MOLPROP proceeded along several lines with a total of 181.5 man-months allocated for training of predocs, and 110 Postdocs. The recruited persons have been given employment contracts or, fixed-amount stipends augmented by insurances that secure the required social benefits. Career development plans have been considered for each trainee with special responsibility of the node leader and general responsibility of the coordinator to secure for its implementation.

B.3.1.1 Training instruments

The network has provided training through instruments divided in 5 categories:

Summer Schools

Meeting and visit program

Twinning program

Internet tutorials - Coherent training

Use of softwares as platforms for training and transfer of knowledge. Other Measures

B.3.1.2 Summer Schools

Since a great deal of the research within the project took the character of basic theory and method development, much emphasis of the training was put on pure theory, that is quantum theory, algebra and mathematical algorithms. An important part of the training program therefore took place through attending summer schools in theory.

- A1. **SOSTRUP Summer School on Molecular Properties** is a biannual school with on average 50 graduate and postgraduate students. The school, organized and staffed by members of the network (Odense and Oslo nodes), provides two weeks of intense training, through lectures and exercises, which bring the students up to the research level in the field.
- A2. **The European Summer School in Quantum Chemistry** runs also biannually but every odd year, organized by our colleagues in Lund, Sweden. This school runs two weeks with on average 80 - 100 students. It complements the SOSTRUP school excellently in a scheme where the students first attend ESQC and then SOSTRUP.

- A3. **The Finnish Winter school in Theoretical Chemistry**, organized by the Helsinki partner, is focused around a set of invited research talks on a current topic in theoretical chemistry. About 50 students participated in the school, where they also get the opportunity to present their own work. This school thus ran all three years of the network.

B.3.1.3 Twinning Program

The mobility among the YRs has been high, and was further encouraged with the opportunity given to work and train at more than one node. In order to ensure this we assumed a **twinning program** i.e. **a program in which each trainee project is carried out at two nodes**. The experience is that such a geographic flexibility promotes the total project as such and also the scientific and personal profits for the young researchers; it became in fact very popular among the YRs. The twinning program as carried out is summarized 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 Pederson 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 Arhus (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.3.1.4 Workshop and Visit program.

The YRs received important training through the meeting and visit program in MOLPROP, reported on in section B.2. We pursued the strong mobility within the MOLPROP project, by setting up **7 major meetings**, about **60 node-to-node visits**, and which resulted in **74 internod publications** out of which **43 involved young researchers**. The meeting program is given in section B.2.4.

B.3.1.5 Tutorials over the net - Coherent training

A set of 15 training exercises - tutorials - for molecular and material properties was made available to the YRs. Each exercise contains theory, explanations and problem solving using the network software. See "Booklet.pdf" given in <http://www.theochem.kth.se/courses/masterscourse.html> The documentation of the DALTON program system, including more than one hundred run examples in the training set were available for the YRs.

We regard the training offered as "coherent", in the sense several parts were assembled in a systematic fashion. This means training through: **Basic textbooks** written by partners: (e.g. T. Helgaker et al., "Molecular Electronic Structure Theory", 906 pages) – through **Summer schools** staffed by partners (SOSTRUP/ESQC summer schools, see above) – through **Computer Software** developed by partners, T. Helgaker et al., DALTON - A molecular property program, including full manual, and training set with over 100 run examples) – and through **Tutorials** provided by the partners, see above. The ambition was to provide a "bottom-up" approach in the training and to run it through from the very basic aspects given through textbook reading and summer school teaching over to the applied, project-oriented, aspects, through training in the use of the underlying software and the tutorials.

B.3.1.6 Use of softwares as platforms for training and transfer of knowledge.

We especially emphasize the role of the software development and the use of **the softwares as platforms for transfer of knowledge**. The network supported the program systems, DALTON, DIRAC, ACES II, which are three of the world's leading software systems for accurate molecular modelling. Through these program systems the network produced new, documented, algorithms and new coding free of charge for users. This is, however, not only a research deliverable by the network, but also its most important training and transfer of knowledge deliverable. Of these programs, DALTON is perhaps the most important one for the various projects in this network (the network collects most of its authors), but all three have their roles to play. The code is documented, available on a so-called CVS server, and with a mailing-list. The documentation, and the more than one hundred run examples in the training set are available free

of charge. This constitutes a very strong training and transfer-of-knowledge resource both within the network and outside. We emphasize that 52 % of the more than one thousand license holders of the DALTON program are Europeans, and the great majority are young researcher. 12 % of the licences are site licences, which in turn implies special collective training opportunities. **Thus all measures in the network for method and program development have been directly conveyed to the training of hundreds of young European researchers.**

B.3.1.7 Other Measures

Communication skills were promoted by encouraging YRs to give talks at the network meetings and other relevant meetings. One **”Young Researcher Workshop”** was held (Valencia) during the 2nd year focusing entirely on their achievements in the network (presentation of projects and early results).

The gender aspects were scrutinized at the time for the hiring as well as in the training. As we are in a field in which females are notoriously poorly represented this is a delicate aspect. Some funding was reserved for a coordinated effort in the announcement with a stated priority of gender. Still the actions were moderately successful. Only one female student was recruited (one node leader is female).

Multidisciplinarity. The fields covered by the network projects are versatile with objectives covering basic science as well as applications; mathematics, numerical analysis, quantum mechanics, scientific computing and materials science. In addition to skills in the particular fields many of the YRs acquired skills in general simulations techniques, in computing and programming as well.

B.3.2 Final result for hiring of young researchers - Final Report

The final hiring results are summarized in Table 13 below:

We can compare with the table in Annex I of the contract: We have provided training for 21 Young Researchers: We have provided 62 more man-months than the contract: We have provided 73.5 pre-doc months more and 21.5 post-doc months less than the contract. If we scale the surplus of pre-doc months by the Marie-Curie ratio of post- to pre-doc costs = 1.41 we end up with a total surplus of 31 Post-doc months. The change in balance between post-docs and pre-docs did not alter the scientific outcome or the work plan of the project as a whole to any significant extent, but added a quite considerable training value. The reason for the change can be traced to the hiring situation at the beginning of the network period.

B.3.3 What happened with the YRs after appointment ? - Final Report

We discuss this node by node:

- Stockholm: B. Jansik will go for PostDoc to Norway.
O. Rubio-Pons is still enrolled as PhD student in Stockholm.
Z. Rinkevicius is still enrolled as PhD student in Stockholm.

Table 13: Hiring Scheme

<i>Node</i>	<i>PhD/Post – Doc</i>	<i>Period</i>	<i>NrMonths</i>
Stockholm	PhD	1/11 2000 - 15/5 2003	30.5
Stockholm	PhD	1/9 2001 - 15/5 2003	20.5
Stockholm	PhD	1/1 2002 - 15/5 2003	16.5
Stockholm	PhD	1/1 2003 - 15/5 2003	4.5
Valencia	Post-Doc	15/7 2001 - 15/5 2003	23
Santiago	Post-Doc	1/7 2000 - 30/6 2001	12
Santiago	PhD	18/8 2002 - 15/5 2003	9
Santiago	PhD	12/2 2003 - 15/5 2003	3
Mainz	Post-Doc	1/3 2001 - 28/2 2003	24
Modena	PhD	15/9 2001 - 15/5 2003	21
Pisa	Post-Doc	1/4 2001 - 30/3 2002	12.5
Pisa	PhD	15/7 2002 - 15/5 2003	10
Helsinki	PhD	1/9 2001 - 15/5 2003	20.5
Helsinki	PhD	15/1 2002 - 15/6 2002	5
Helsinki	Post-Doc	1/10 2002 - 31/12 2002	3
Odense	PhD	1/2 2001 - 15/5 2003	27.5
Odense	Post-Doc	1/4 2002 - 31/3 2003	12
Odense	PhD	1/3 2002 - 28/2 2003	12
Olso	Post-Doc	1/7 2001 - 30/6 2002	12
Olso	PhD	15/8 2001 - 14/8 2002	13.5
Olso	Post-Doc	1/5 2002 - 30/4 2003	12
Total	PhD		193.5
Total	Post-Doc		110.5
Grand-total			304

Ivaylo Minkov continues his PhD studies at the Royal Institute of Technology in Stockholm. The MOLPROP network made it possible for him to start his research career there.

- Valencia: T. Bondo-Pedersen received a research position at the University of Copenhagen. The research experience obtained within the network was very beneficial for his appointment.
- Santiago: T. Bondo-Pedersen went to Valencia and from there to a position in Copenhagen (see above).
Cristian Munteanu remains PhD student in Santiago.
Domenico Marchesan went to Trieste University to continue his PhD there.
- Mainz: Dan Jonsson received a "forskarassistent" (assistant professor) position at the Department of Physics at Stockholm University. The research experience obtained within the network (training as well as the pursued research) was beneficial for his appointment.
- Modena: Rafael Soriano Jartin will stay in Modena after appointment in MOLPROP in order to complete his PhD studies there.
- Pisa: Dr. Magdalena Pecul received a permanent staff position at the Dept. of Chem., Univ. of Warsaw (assistant professor), and will now be on leave at the Dept. of Chemistry of the University of Tromsø, Norway. The experience obtained within the network was very beneficial for her appointment.

Table 14: Hiring-Months of Young Researchers in MOLPROP network

Participant	Young Researchers financed by the contract (person-months)			Contract deliverable of Young Researchers to be financed by the contract (person-months)		
	Pre-doc (a)	Post-doc (b)	Total (a+b)	Pre-doc (c)	Post-doc (d)	Total (c+d)
P1-Stockholm	72		72	24		24
P2-Valencia		23	23		24	24
P3-Santiago	12	12	24		24	24
P4-Mainz		24	24		24	24
P5-Modena	21		21		24	24
P6-Pisa	10	12.5	22.5	24		24
P7-Helsinki	25.5	3	28.5		24	24
P8-Odense	39.5	12	51.5	36	12	48
P9-Oslo	13.5	24	37.5	36		36
Total	193.5	110.5	304	120	132	252

Ulf Ekström will continue his PhD studies in Linköping, Sweden, but will remain in close collaboration with the IPCF/CNR of Pisa.

- Helsinki: Stefano Corni is now Post-doc researcher in the quantum-dot research group at the University of Modena. His opinion is that the network appointment was very beneficial for him.

Michael Patzschke continues his Ph.D. studies in Helsinki under supervision of Dage Sundholm.

Raphael Berger is now employed as post-doc researcher within another project in Helsinki.

- Odense: Filip Pawlovski will continue with Post-Doctoral work at University of Karlsruhe. His opinion is that the network appointment was very beneficial for him.

Miroslav Ilias has obtained a research position in Bratislava, Slovak republic. He will continue with research initiated at his MOLPROP stay in Odense.

Laban Pettersson has received support from a pharmaceutical company in Stockholm (BioVitrum AB), and will continue his PhD studies in Stockholm (at the Royal Institute of Technology). His MOLPROP studies in Denmark gave a flying start of his career in theoretical modelling in the pharmaceutical industry.

- Oslo: Pawel Salek Received a "forskarassistent" (assistant professor) position at the laboratory of theoretical chemistry at KTH, Stockholm. The research experience and scientific results that he obtained within the network were very crucial for his appointment.

Peter Macak obtained a Post-Doc scholarship at the Department of Physics at Stockholm University (Quantum Chemistry group). The research experience obtained within the network (training as well as research) was very beneficial for his appointment.

Mark Watson went back to Cambridge to complete his PhD exam there. He intends to continue in Academia.

B.3.4 Importance of MOLPROP training for YR careers

We end this report on training by a general comment about the long-term career opportunities of the MOLPROP trainees. It rests on the fact that we are now witnessing a development all over the world of **materials research that explicitly joins experimental laboratory work with computer simulations**. Such joint approaches develop to encompass almost all aspects of research and production of the new materials. One foresees the use of global simulations in assembly lines, which, when used in combination with experimental techniques, synthesis and characterization, can assist in the completion of new products at costs that are orders of magnitude smaller than traditional research and development costs. It follows from this thesis that the **role of advanced computer simulations is increasingly recognized in the industrial world**, as reflected already in the huge investments in development of computer hardware and software in the EU, USA and elsewhere. The basic philosophy is thus to replace expensive laboratory tests by inexpensive computer simulations that implement basic principles.

These ideas on the role of computer simulations are not new, but they have recently been brought to the fore by the rapid pace in the development of current theoretical modelling, with increased accuracy, applicability and versatility with respect to materials processes and properties. The MOLPROP project is an example of just that. These advances are complemented by the ubiquity of massive broadband digital transmission to every lab and home, with its consequent catalyzing of computational grid concepts: developments that have **revolutionized the access to simulations**.

It follows that expanding our knowledge in materials phenomena through modelling at basic levels and that **training of skills and know-how in materials simulations will be of utmost importance for the competitiveness of research into new materials** at any level, including the European level. It is therefore of great strategic importance to train young researchers in materials simulations and modelling, giving them the know-how of current modelling techniques and computer programs and in skills in tailoring simulations to given research problems. We believe that the importance of the training in molecular and materials simulations provided by MOLPROP should be viewed in this perspective, and we believe that training in this network will greatly help the YRs in their future careers in industrial companies that involve materials research of any kind.

B.4 Industry connections - Final Report

Since most of the trainees are pre-docs the majority of them remain right now in Academia. As explained in the previous subsection, there is a great potential to exploit the MOLPROP training in industry active in materials research. At this moment Laban Pettersson (Odense YR) has received support from the BioVitrum AB pharmaceutical company in Stockholm, and he intends to continue in this company after completion of his PhD studies. The theme for his studies "Modelling of Drug Solubility" will form the platform for his work in BioVitrum AB also later on.

B.5 Recommendations - Final Report

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, we feel, is not surprising since it owes to the close connections between most of the nodes that already were established, in some cases since a long time. This fact has also greatly alleviated the coordination of the network. We have great confidence that we in the future can capitalize much on the training and research achievements and the structuring of collaboration that MOLPROP has brought about.

We have only two general points that in retrospect could have simplified the coordination; i) One is the commencement date. With the payment rules it is very essential that all nodes are prepared with their hiring in order not to lose momentum; ii) Connected to the aforesaid, the delay in back-payments from the commission produces a strong risk of nodes not being able to fulfill their hiring quota. Some universities are utterly reluctant to pre-pay student salaries to the amount and for the time period that is necessary. In MOLPROP, for instance, we had to run the third year with a 33 % deficit. Here the delayed payment could act as a self-fulfilling prophecy. In MOLPROP we did finally manage the situation. Other than that we can quote a few comments from the participants:

"The twinning program was an excellent idea. However, more money should be allocated to networking cost if one really wants to have mobility of YRs within the Network."

"Annual network meetings are not always necessary. By combining them with Network workshops, they become more attractive. However, I would prefer to spend the money on exchange of YRs, twinning, winter and summer schools, and research visits of SRs.

"My student moved from Berlin and began his doctoral studies almost 2 years ago, which means that he will continue his Ph.D studies for about another 2 years. He was employed by MOLPROP, and if an eventual continuation of the Network is successful I am not allowed to employ him again as he has been in our group for more than 2 years. These rules could have exception for this small group of Ph.D. students."