

Mid-TERM Review Report Report on the HPRN-Network:

Molecular Properties and Molecular Materials: MOLPROP

Network Data:

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Part A

Research Results

A.1 Scientific Highlights

A.1.1 Node contributions

We describe below first the scientific highlights from each of the nodes, emphasizing the contracted work plan and the midterm milestones. The collaborative aspects of the work is reviewed in the second part of the section. In the last part we comment on the advancement to the international state-of-the art of the different projects.

P1 KTH-Stockholm

The Stockholm partner has focused on development and application of response methodology for non-linear optical properties. Much of the research efforts have been devoted to various *optical limiting* processes, with the ultimate goal to derive useful materials for laser protection. This research, which adheres mostly to the second milestone of the mid-term review, has produced predictions of promising materials with multi-dimensional and multi-branched structures, for instance a series of cummulene derived compounds has been proposed for synthesis. We have realized that metallo-organic compounds have outstanding properties for optical limiting and multi-photon absorption, and we have taken interest in the use of approximate relativistic methods for optical properties of such compounds, and obtained some first results in this respect. The main collaborators in this work are the Oslo, Odense, Pisa and Valencia nodes.

P2 U.Valencia

The goal of enlarging the applicability of coupled cluster methods is being accomplished through the use of techniques based on the Cholesky decomposition of positive definite matrices. First they were applied to the decomposition of the energy denominators appearing in the CCSD(T) formulas. Secondly, a similar technique has been used to Cholesky decompose two-electron integrals taking then profit of their sparsity when considered as a regular matrix with compound indices. This allows for storing the integrals even when using more than 1200 basis functions, avoiding direct methods and eventually diminishing one more order the scaling. This part of the project has been developed in collaboration with the Odense node and with Thomas Pedersen as the main responsible during his postdoc stay in Valencia from July 1st. We are also involved in studies of NMR spectra of HCP and derivatives in collaboration with the Mainz node.

P3 U.Santiago de Compostela We work with development of gauge invariant coupled cluster theory. This work is carried out in collaboration with the nodes in Odense and Valencia. Applications of the coupled cluster theory has also been made for studying van der Waals complexes. We started considering the reduction in the scaling for the SCF and correlated models like the CCSD, using the Cholesky decomposition of the two-electron integrals. During the first 18 months of the project we have been dealing with the development of a model based on Coupled Cluster response theory. In this way, 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 CC linear response function are retained, while the dimension of the eigenvalue problem is reduced by a factor of 2.

P4 U.Mainz

The node at Mainz investigated the performance of a coupled-cluster (CC) hierarchy consisting of CC2, CCSD, CC3, and CCSDT for the calculation of indirect spin-spin coupling constants. It is concluded that the CC3 model with orbital relaxation excluded is well suited for the accurate prediction of spin-spin coupling constants based on coupled-cluster methods with an approximate inclusion of triple excitation effects. At Mainz, the theory for calculating second-order properties (harmonic force constants, polarizabilities, etc) for excited states has been worked out within the CCSD response theory/EOM-CCSD framework. The derived equations are currently implemented in the ACES II program package. Parallel to this methodological development, anharmonic force fields (so far based on analytic gradients) have been calculated for the S1 state of benzene in order to obtain vibrational corrections to rotational constants. Combination of these corrections with experimentally determined rotational constants allowed the determination of an "experimental" equilibrium geometry.

P6 U.Modena

The Modena group got involved in four main research activities: (i) resolution of molecular response properties into atomic contributions (ii) analysis of contributions to electronic energy of chiral molecules arising from parity-violating weak neutral currents (iii) graphical representation of the current density vector field induced in a molecule by an external magnetic field (iv) methodological developments. Another paper investigates the partition of optical rotatory power into atomic contributions within the torque formalism. As regards (i), allowing for the dipole acceleration formalism, and studying small size alkanes, we obtained a series of atomic polarizabilities that can be adopted to obtain molecular polarizabilities of higher members in the same homolog series. As regards (iii) we have obtained interesting results on aromatic molecules, for instance we discovered a "leap-frog effect" in ring currents, which cause sensible deviations from a pure London diamagnetic regime.

P6 CNR.Pisa We have studied electric, magnetic and optical properties in molecules, in collaboration with other nodes. We have studied the non-additive two and three body contribution to dispersion energies and electric properties in rare gases, and in small molecules with CC response techniques (collaboration with the Odense node). We have determined the first virial coefficients for magnetizability, chemical shielding, electric dipole polarizability and Cotton-Mouton birefringence (collaboration with the Oslo node and first results obtained in the training of the YR in Pisa) and studied the effect of static electric fields on the chemical shift of some two- and three-atomic systems. Study of the magnetizability and electric dipole polarizability anisotropies of CO₂, CS₂, OCS and N₂O, and of their hypermagnetizability anisotropies.

P7 U.Helsinki

A new computational approach and the corresponding *ab initio* program package for calculation of the optical properties of strain-induced quantum dots is being developed. This is the first *ab initio* program package for large-scale correlated calculations on strain-induced quantum dots. The new program package allows full configuration interaction studies of the energy levels and photoluminescence spectra of quantum dots containing 1-4 excitons. To treat larger systems, truncated configuration interaction expansions can be used. The methods have been used for studying the energy levels, photon relaxation

rates, and photon recombination rates of excitons, biexcitons and triexcitons confined a InGaAs/GaAs strain-induced quantum dot.

P8 U.Odense The research has focused on the development of methods for molecular property calculations using highly correlated coupled cluster theory, quantum relativistic theory and heterogeneous solvent models. The performance of the coupled cluster hierarchy CC2, CCSD, CC3 and CCSDT has been tested for the calculation of triplet excitation energies. It is concluded that CC3 constitutes a good compromise between cost and accuracy for calculation of excitation energies. QM/MM methods have been developed and implemented at the Hartree-Fock, MCSCF and Coupled Cluster levels. These methods enable calculations of properties up to third order. Heterogeneous solvation models have been developed and implemented at the Hartree-Fock and MCSCF level and these methods enable calculations of properties up to fourth order. A more correct description of the anomalous g-factor in e.g. ESR has been developed and implemented. New reduced scaling methods have been developed for 4-component relativistic calculations, which means the scaling is approaching non-relativistic calculations.

P9 U.Oslo

The Oslo node has been involved with three main MOLPROP projects: the development and implementation of the fast multipole method (FMM), the accurate calculation and calibration of quantum-chemical methods, and the development and implementation of linear and quadratic response methods for density-functional theory (DFT). The FMM has now been implemented in Dalton for the optimization of non-hybrid density functionals of DFT, although not yet in a form that scales linearly with system size. The preliminary work on atomic-orbital (AO) based optimization has been concluded, and medium-sized systems have been optimized entirely in the AO-basis with large basis sets, bypassing the diagonalization of the Fock matrix. AO-based calculations of second-order properties have also been carried out. We have also worked on the calibration of quantum-chemical methods with respect to the calculation of atomization energies, molecular structure and vibrational frequencies. Finally, the DFT development work on linear and quadratic response theory is now in its final debugging stage, and we expect soon to be able to carry out the first calculations in early 2002.

A.1.2 Essential collaboration between nodes

Stockholm - Valencia

Twinning program in which relativistic and non-relativistic effective core potentials are used in conjunction with the coupled cluster response program to compute linear and non-linear properties of organometallic compounds.

Stockholm - Odense

Implementation of the Douglas-Kroll algorithm for relativistic calculations of properties. Comparison with full 4-component Dirac-Fock results.

Stockholm - Pisa - Oslo

Studies of the magnetizability and electric dipole polarizability anisotropies of small molecules and of their hypermagnetizability anisotropies, both with fully ab-initio and semiempirical approaches, using, respectively, analytic and mixed analytic-numerical algorithms.

Stockholm - Oslo

DFT development on linear and quadratic response theory is carried out in collaboration with the Oslo node. Coding is now in its final debugging stage, and we expect to be able to carry out the first calculations in early 2002. With the Oslo node, we have also been involved in the development of Hartree-Fock and DFT methods for the calculation of excited-state properties (in particular gradients) by means of response theory.

Valencia - Santiago-de-Compostela - Odense

Collaboration regarding the reduction of the computational scaling using Cholesky decomposition. An implementation of the Cholesky algorithm of two-electron integrals is already done. Test calculations at the MP2 level have given encouraging results, making it worthwhile to program a more sophisticated algorithm.

Valencia - Mainz

Application of the developed CC schemes in the calculation of NMR spectra are currently carried out for several examples in collaboration with the node at Mainz. First results for the HCP molecule, for example, point to some discrepancies between high-level calculations and experiment. In addition schemes for the routine treatment of vibrational and temperature corrections in the calculation of NMR properties have been incorporated in the used quantum chemical programs and are used in the on-going calculations.

Valencia - Modena

With the aim of choosing a suitable basis set to investigate high-order electronic properties of indazene, a hierarchy of coupled cluster, as well as non-correlated, methods is being used to carry out a basis set study of the electronic polarizability and hyperpolarizability of benzene, molecular system for which experimental data are available.

Valencia - Odense

Theoretical determination of electronic spectra. Using coupled cluster methods, we have determined the electronic vertical spectrum of some medium-sized organic molecules. The spectrum of urea is already published. At present, we are nearly finishing the study of the spectrum of tetrathiofulvalene.

Santiago-de-Compostela - Pisa

Collaboration with the Pisa node for benchmark type study of the (hyper)polarizabilities of HCl, at CC3 level and including an in depth analysis of the effects of valence and core electron correlation, basis set limitation, molecular vibrations.

Santiago-de-Compostela - Odense

Theoretical studies of intermolecular interactions in van der Waals complexes, running applications on the helium-, neon-, and argon-cyclopropane and the CO-CO complexes. We used correlation consistent polarized basis sets and the Coupled Cluster singles and doubles including connected triples method to evaluate the interaction energies for different intermolecular configurations. After fitting these energies to a potential function, we studied the intermolecular dynamics. The results were satisfactory in all cases.

Mainz - Pisa

The nodes at Mainz and Pisa developed schemes for CC calculations of mixed electric and magnetic

properties using response theory techniques. Results for shielding polarizabilities demonstrate the high accuracy which can be obtained for such properties at the CCSD(T) level when employing gauge-including atomic orbitals together with sufficiently large basis sets. This work is currently extended to other mixed electric and magnetic properties such as, for example, electric-field gradient induced birefringence.

Mainz - Helsinki

Work in collaboration with the node at Helsinki currently focuses on the use of current densities for the characterization of ring current effects in aromatic molecules.

Mainz - Odense - Oslo

Together with the nodes at Odense (Aarhus) and Oslo, benchmark calculations have been carried out with the coupled cluster methodology for various properties, like vibration-rotation interaction constants. These calculations again testify the high accuracy which can be obtained in high-level calculations are currently extended to the prediction of fundamental frequencies, zero-point energies, as well as atomization energies.

Pisa - Odense

Studies of the non-additive two and three body contribution to dispersion energies and electric properties in rare gases and small molecules with CC response techniques. Studies of axial anisotropy induced in a chiral system by a magnetic field parallel to the direction of propagation of the radiation.

Pisa - Oslo

Determination of the first virial coefficients for magnetizability, chemical shielding, electric dipole polarizability and Cotton-Mouton birefringence.

Helsinki - Odense

Studies of energy level spacings, phonon relaxation, and photon dynamics of strained quantum dot systems. Results are used for the interpretation of the observed photoluminescence spectra of these quantum dot system. We have shown that quantum chemical methods originally developed for studying atomic and molecular systems can be successfully applied to the study of few-body electron-hole systems in semiconductor nano-structures.

Odense - Oslo

In a cooperation between the Oslo and Odense nodes, the preliminary work on atomic-orbital (AO) based optimization has now been concluded, and medium-sized systems have been optimized entirely in the AO-basis with large basis sets, bypassing the diagonalization of the Fock matrix. AO-based calculations of second-order properties have also been carried out. The Oslo and Odense nodes have also cooperated closely on the calibration of quantum-chemical methods, in particular with respect to the calculation of atomization energies, molecular structure and vibrational frequencies.

A.1.3 International state-of-the-art

The methodologies and the associated computer softwares for modeling of molecular properties developed by the applicants, now constitute the contemporary state-of-the art for such modeling, be it adiabatic or non-adiabatic properties arising from electric or magnetic, time-independent or time-dependent,

Table 1: Essential collaboration between nodes

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

linear or non-linear, internal or external, uniform or non-uniform field perturbations. A special edge is given by gauge-invariant electron-correlated calculations of magnetic properties, magnetizabilities and nuclear magnetic shielding and by solvent modeling of such properties. The previous strong position by the applicants have been further consolidated by the network support and the network collaboration.

A.2 Joint Publications

The partner collaboration is listed. Young Researchers are presented in boldface. Young Researchers hired by the network are presented in italic.

1. P1, P6. **P. Salek**, V. Carravetta, H. Ågren, F. Gel'mukhanov, Dynamical suppression of atomic peaks in resonant dissociative photoemission, *Chem. Phys. Lett.* 343, 332 (2001).
2. 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).
3. P1, P6, P8. V. Carravetta, H. Ågren, O. Vahtras, and H.J.Aa. Jensen, Ab initio calculations of molecular resonant photoemission spectra, *J. Chem. Phys.* 113, 7790 (2001).
4. P1, P8, P9. **P. Norman**, B. Schimmelpfennig, **K. Ruud**, H.J.Aa. Jensen, and H. Ågren, Relativistic effects on linear and non-linear polarizabilities studied by Douglas-Kroll and Dirac-Fock response theory calculations, *J. Chem. Phys.* 00, 000 (2002).
5. P2, P8. H. Koch and A. Sanchez de Meras, Size-intensive decomposition of orbital energy denominators, *J. Chem. Phys.*, 113(2) 508 (2000).
6. P2, P8. A.M.J. Sanchez de Meras, I. Garcia Cuesta and H. Koch, A coupled cluster calculation of the spectrum of urea, *Chem. Phys. Lett* 348 (2001) 469-476
7. 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 (2001).

8. P3, P8 **J.K. Pedersen**, H. Koch and B. Fernandez, Basis set convergence of three-body interactions in He₃, Ne₃ and Ar₃, *Theor. Chem. Acta*, in press.
9. P3,P6,P8 A. Rizzo, **S. Coriani** and B. Fernandez and O. Christiansen A coupled cluster response study of the electric dipole polarizability, first and second hyperpolarizabilities of HCl. Submitted, *Phys. Chem. Chem. Phys.*
10. P4, P6 A. Rizzo and J. Gauss, CCSD(T) Shielding Polarizabilities *J. Chem. Phys.*, in press
11. 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).
12. P4, P8, P9 *F. Pawłowski*, P. Jørgensen, J. Olsen, **F. Hegelund**, T. Helgaker, J. Gauss, K.L. Bak, J.F. Stanton Molecular equilibrium structures from experimental rotational constants and calculated vibration-rotation interaction constants *J. Chem. Phys.* submitted
13. P4, P8, P9 K. L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker, and J. F. Stanton, The accurate determination of molecular equilibrium structures, *J. Chem. Phys.* 114, 6548 (2001)
14. P4, P8, P9 **H. Larsen**, J. Olsen, P. Jørgensen and J. Gauss. Comparison of full-configuration interaction and coupled-cluster harmonic and fundamental frequencies for BH and HF. *Chem. Phys. Letters* 342, 200-206 (2001).
15. P6, P8 A. Rizzo, **K. Ruud**, D. M. Bishop, Intermolecular interactions and the Cotton-Mouton effect (CME) for helium, *Mol. Phys.*, in print.
16. P6, P8 M. Jaszunski, A. Rizzo, P. Jørgensen, Coupled Cluster calculation of dispersion contributions to interaction energies and polarizabilities, *Theor. Chem. Acc.*, 116, (2001), 251-258.
17. P6, P8 *M. Pecul*, **S. Coriani**, A. Rizzo, P. Jørgensen and M. Jaszunski Ab initio study of magnetochiral birefringence. In preparation, *J. Chem. Phys.*
18. P6, P8 *M. Pecul*, A. Rizzo, J. Leszczynski The Raman Optical Activity of glyceraldehyde, lactic acid and lactic acid anion: Random Phase Approximation approach. In preparation, *Chem. Phys. Lett.*
19. 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.
20. 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.
21. 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.
22. P7, P8 **M. Braskén**, **M. Lindberg**, D. Sundholm, J. Olsen, "Spatial Carrier-Carrier Correlations in Strain-Induced Quantum Dots", *Phys. Rev. B* 64 (2001) 035312(1-9).

23. P7, P8 **M. Braskén**, *S. Corni*, **M. Lindberg**, J. Olsen, D. Sundholm, "Full Configuration Interaction Studies of Phonon and Photon Transition Rates in Semiconductor Quantum Dots", *Mol. Phys.* (in press, January 2002).
24. P8, P9 **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).
25. P8, P9 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).
26. P8, P9 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).
27. P8, P9 **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).
28. P8, P9 **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).
29. P8, P9 **H. Larsen**, J. Olsen, P. Jørgensen and T. Helgaker. Direct optimization of the atomic-orbital density matrix using the conjugate-gradient method with a multilevel preconditioner, *J. Chem. Phys.* 115, 9685-9697 (2001)
30. P8, P9 **H. Larsen**, T. Helgaker, J. Olsen, and P. Jørgensen, Geometrical derivatives and magnetic properties in atomic-orbital density-based Hartree-Fock theory", *J. Chem. Phys.* 115, 10344 (2001)
31. P8, P9 T. Helgaker, W. Klopper, **A. Halkier**, K. L. Bak, P. Jørgensen, and J. Olsen, Highly Accurate Ab Initio Computation of Thermochemical Data", In "Understanding Chemical Reactivity", 22: "Quantum-Mechanical Prediction of Thermochemical Data", J. Cioslowski, ed. (Kluwer, Dordrecht, 2001), p. 1 - 30.
32. P8, P9 3. K. L. Bak, **A. Halkier**, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, Chemical accuracy from Coulomb-hole extrapolated molecular quantum-mechanical calculations", *J. Mol. Structure*, 567, 375 (2001)

Part B

Comparison with the joint program of work

B.1 Research Objectives

The research objectives - both the low- and the high-end objectives as defined by Annex I of the contract have been maintained without any significant changes. Thus theoretical work referring to basic science as well as applications of the theory have progressed. This holds for all the milestone items, like coupled cluster theory (milestone 4) and relativistic theory (milestone 3). Many of the remaining "holes" in

the 4th order property toolbox (milestone 1) have also been filled in. This refers especially to magnetic and magnetic resonance properties. Several new interaction phenomena have thus been derived and implemented in the response theory framework; magnetic g-tensors and new spin-spin coupling modules, to mention two examples. We can here also stress the implementation of relativistic 4-component calculations of ESR parameters as a particularly rewarding example. The computation and the viewing of current densities have progressed along the planned lines of research.

The correlated techniques have been broadened especially concerning the coupled cluster methodologies. This methodology has been advanced to a point where the calculations supersede the accuracy given by experiment for many properties. The reduced scaling demand has also been met to some extent by means of new algorithms (c.f. milestone 4). The reduced scaling will here also benefit from the so-called density matrix algorithms that now have been derived, and which will have particularly rewarding consequences for density functional applications within the network.

During the time which has elapsed since the commencement date we have also witnessed an interesting development of *time-dependent* density functional theory and implementations within the network, as was actually envisaged but yet not proven at the time of the contract negotiation. Many novel applications have followed and will follow from this development, and which are important for the high-end goals of the network.

We emphasize also the development with the relativistic methodologies (milestone 2). The advanced four-component Dirac method now also encompasses multi-configurational self-consistent field wave functions, something truly unique in its kind. Several simplifying relativistic schemes, e.g. the Douglas-Kroll technique, have been tried out in conjunction with property calculations, with the purpose to gain efficiency without losing too much accuracy. Although this research focuses on basic matters, the goal of efficiency and applicability evidently holds also for the relativistic methodologies.

Concerning milestone 2, focusing on actual materials applications, we have also advanced our front line. This goes especially for optical limiting applications with the toolbox, as well as with the newly developed methodology for quantum dot systems. In the case of optical limiting, the research has already arrived at some new compounds that have been suggested for synthesis. Much collaborative work is still needed emphasizing also new basic issues in this research. With respect to the milestone point on second harmonic generation we have reached some preliminary results, but a lot of work in this area still lies ahead.

Concerning properties of extended systems and materials the efforts for modeling environmental (solvent) effects should also be stressed, since these give clear possibilities for future large scale applications using the property toolbox. The so-called polarized continuum model has thus been incorporated as well as a new "QM-MM" (Quantum mechanics - molecular mechanics) methodology to describe heterogeneous solvation. We anticipate many useful applications of both these lines of methodological development.

B.2 Methodological Approach and Work Plan

Breakdown of tasks

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

B.2.1 Task 1. Gauge-invariant fourth order property toolbox

Several new properties have been coded, both for variational and perturbational wave functions. We emphasize new results with magnetic, hyperfine and excited state properties.

B.2.2 Task 2. Relativistic formulations

The planned line of research is followed, and has even advanced beyond the plan. For example, the Dirac-Fock implementation of non-linear electric properties is now working. Also several simplifying relativistic models have been implemented and applied.

B.2.3 Task 3. Reduced scaling in correlated methods

New *linear scaling* scaling algorithms have been derived basing on density matrix optimization and tested in model calculations. The goal to derive a new *time-dependent density functional code* has already been fulfilled to a significant extent. Solvent models have been implemented, "PCM", "QCMM" and "semiclassical" models.

B.2.4 Task 4. Non-linear properties and materials

Several new molecular materials with rewarding non-linear optical properties have been predicted, especially two-photon materials that can be used for optical limiting. The solvent models derived within the network has then been very helpful.

B.2.5 Task 5. Direct dynamics

We have derived time-dependent techniques for nuclear dynamics and implemented these for computations in connection with X-ray and femto-second spectroscopy. The excited state EOM-CC method has benefitted from new algorithms for excited state gradients and Hessians.

B.2.6 Task 6. Nuclear magnetic spin resonance

We have during the first half of the network published several papers for magnetic resonance parameters both within coupled cluster and density functional technologies, the latter represent a development that is new within the network.

B.2.7 Task 7. Electron spin resonance

Also ESR theory and codes have been developed to a quite large extent during the first period. This goes for g-tensors, spin-spin coupling strengths and zero-field parameters. The diagnostic capability of ESR has been exploited also for bio-radicals as simulated using these new routines. A fully relativistic implementation for g-tensors has also been accomplished.

B.2.8 Task 8. Non-uniform fields

Development within this area has taken place as planned for visualization of magnetic field induced current densities. This has been made possible by a production of new graphical codes showing how spin and density information passes through the molecules.

B.2.9 Task 9. Chirality and dichroism

Dichroic properties -either natural or field induced- have been studied by the proposed response theory techniques. The study of natural dichroism in the X-ray region has also been carried out, with applications performed for the common amino acids.

B.2.10 Joint program of work

Table 2: Professional effort of each team

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

B.3 Schedule and Milestones

In Table 1 we specify the degree of fulfillment of the Schedule outlined concerning months 1-18 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.

For the node involvement in the various tasks we refer to Table 2 given above.

Table 3: Schedule and fulfillment of tasks during months 1-18

<i>Months*</i>	<i>Tasks**</i>	<i>Comment</i>
1- Fourth order Toolbox		
1-12	MCSCF and CC third and fourth order properties	Well implemented- 5
1-12	CC applications of excited state properties	First Results - 4
13-24	EOM-CC second derivative program	New algorithms derived - 3
Relativistic Formulations		
1-18	Relativistic RPA - including applications	Done to the point - 5
6-24	Relativistic four-component, 2nd order MCSCF	Formulation + some results - 3
Reduced Scaling correlated methods		
1-12	TD-DFT spectra and properties	Formulated and implemented - 5
1-18	Reduced Scaling in CC	Some reduction obtained - 2
13-24	Linear scaling Response properties	Algorithms derived - 3
NLO properties and materials		
1-12	Multi-photon and optical limiting	Rich results - 5
1-12	SHG and Kerr materials	Some Results - 2
13-24	2-dimensional charge transfer systems	Systems predicted - 4
Direct Dynamics		
1-12	Interface to EOM-CC	The EOM-CC part developed - 3
13-24	Use of evolution operator techniques	Wave packet implementation -2
Nuclear Magnetic Resonance		
1-12	CC hierarchy for spin-spin couplings	Well met - 5
13-24	Relativistic approaches to shieldings and couplings	Promising first results - 4
Electron Spin Resonance		
1-12	Benchmarking	Much development - 5
13-24	London orbitals	Not yet started - 1
Non-uniform fields modeling		
1-12	Topological features of current densities	New program - 4
13-24	Nuclear magnetic dipole induced current densities	Some first results - 3
Chirality and Dichroism		
1-12	MCD and Magnetic Optical Dichroism	New methodology, several papers - 4
13-24	Electric field induced chiral absorption	First Implementation - 2

* "Months" refers to the scheduled plan in the Technical Annex.

** Tasks scheduled to start after 18 months are not commented.

B.3.1 Differences from work plan in the contract

No major changes in the work plan in the Contract have been made. The 4 milestones projects - tasks 1,2,3,4 above - are intact and progressed according to plan, or even advanced to points beyond those planned for midterm. There have been some minor changes in the other (non-milestone) tasks - 5,6,7,8,9: Among those we find a stronger focus on tasks 6 and 7 (Nuclear Magnetic resonance and Electron Spin resonance) than planned but a weaker focus on tasks 5 and 8.

Concerning the node involvement the major changes is that node 2 has been involved mostly in task 3 instead of 7, and that node 7 has been involved in tasks 2 and 4 (as scheduled) but not in task 7, while this task has been "taken over" by nodes 1 and 8. Likewise, node 6 has changed focus from task 4 to 3. In all, from the point of view of the output from the total network, these changes are minor.

B.3.2 Milestones

Table 4: Status of Milestones at Midterm

<i>Milestones</i>	<i>Percentage</i>	<i>Comment</i>
1- Fourth order Toolbox		
Completed for non-relativistic properties	100	Accomplished
2- Non-linear optical properties and materials		
Optical limiting materials	90	Rich results
SHG materials	50	Some Results
3- Relativistic Formulations		
1-component theory completely	100	Accomplished
Electric properties in 2-component theory	50	Ongoing work
Full 1-electron implementation for 4-component theory	100	Accomplished
4- Reduced Scaling correlated methods		
Reduced scaling in Coupled Cluster	50	Some reduction obtained
Linear scaling DFT properties	90	Algorithms and coding

B.4 Research effort of the participants

The research effort of the Research effort of the participants is given in Table 5 below. No significant deviation from the contract has taken place.

Table 5: Professional research effort on the network project (man-months)

<i>Participant</i>	<i>YR Months delivered</i>	<i>From other sources</i>	<i>Total individuals</i>
1	19	60	7
2	6	38	5
3	12	25	3
4	10	24	3
5	4	24	3
6	9	27	3
7	7	24	2
8	10	108	12
9	11	57	6
Totals	88	387	42

1. The Stockholm entry of the first year report should be correct by +3 months.

B.5 Cohesion with less favored regions

Two partners, representing the Valencia and Santiago-de-Compostela nodes (nodes 2 and 3, respectively), are from less favored regions of the community. They have been involved in several of the network projects, See Tables 2 and 3, and in the twinning program. We note that two out the three major network meetings took or take place at these nodes (Santiago-de-Compostela in January 2001, Valencia in June 2002).

B.6 Network Organization and Management

B.6.1 Home page utilization

The possibilities of the international telecommunications have been exploited as much as possible. A local home page has been created with the address

<http://www.theochem.kth.se/molprop/>

for special and detailed network information. It has a link from the main CORDIS home page. Our 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. The home page is thus constantly updated by the partners, but with the coordinator having the overall responsibility. The front page as it looks 16/12 is here enclosed.

As seen on this home page it contains information on

1) Network Data: Vacancies, Partners, Objectives, Applications, Collaboration, Training, Results and Achievements, Financial information (the latter reserved for the node leaders).

2) Network Events: Employments (12 items), Organized meetings (6 items), Attendance of Meetings and Schools (117 items), Visits (32 items), Twinning (13 items).

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, result 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.6.2 Special network events

The visits among senior and junior researchers have been very frequent. We have 18 longer research visits, node to node, reported, see list below.

B.6.3 Network meetings

2000-05-28/29: First MOLPROP network meeting

Time : 28-29 May, 2000 Stockholm, Sweden.

Lectures: 15 lectures plus 2 Discussion sessions

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

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>.

Purpose: During the meeting talks with recent results were presented on subjects that overlapped with the contracted scientific goals of the network.

2000-12-11/15 Winter School in Theoretical Chemistry 2000

Time : 11-15 December, 2000 Helsinki, Finland.

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 program : <http://www.chem.helsinki.fi/Info/WinterSchool/ws2000.html>

The participant list: <http://www.theochem.kth.se/molprop/arch/list2.pdf>

2001-01-25/27 First MOLPROP Workshop Meeting

Time : 25-27 January, 2001, Santiago de Compostela.

Lectures: 21 lectures plus 3 Discussion/ Group work sessions

42 Participants.

Full program : <http://www.theochem.kth.se/molprop/extras/program.Santiago2.html>

The participant list: <http://www.theochem.kth.se/molprop/arch/list3.pdf>

Purpose: The first results from the network were presented and discussed.

2001-12-10/13 Winter School in Theoretical Chemistry

Time : 10-13 December, 2001 Helsinki, Finland.

Title: Condensed Phase Dynamics

70 PARTICIPANTS: 12 of them belonging to MOLPROP (Hired YRs)

17 LECTURERS:

The program : <http://www.chem.helsinki.fi/Info/WinterSchool/ws2001.html>

The participant list: <http://www.theochem.kth.se/molprop/arch/list4.pdf>

2002-01-24/25 SCHEDULED Molprop Midterm Review Meeting

Time : 24-25 January, 2001 Copenhagen, Denmark

The meeting will comprise about 50 participants representing all 9 nodes of the Network.

A full program can be found at:

<http://www.theochem.kth.se/molprop/midterm/>

2002-01-25/26 SCHEDULED Molprop Second Network

Coordination Meeting Time : 25-26 January, 2001 Copenhagen, Denmark

The meeting will comprise about 50 participants representing all 9 nodes of the Network.

A full program can be found at:

<http://www.theochem.kth.se/molprop/midterm/>

B.7 Connections to Industry

No connections utilized so far.

Part C

Training

C.1 Employment of Young Researchers

Table 6: Hiring of Young Researchers (Months)

Participant	Young Researchers financed by the contract so far (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 ¹	19		19	24		24
P2-Valencia		6	6		24	24
P3-Santiago		12	12		24	24
P4-Mainz		10	10		24	24
P5-Modena	4		4		24	24
P6-Pisa		9	9	24		24
P7-Helsinki	7		7		24	24
P8-Odense	10		10	36	12	48
P9-Oslo	5	6	11	36		36
Total	45	43	88	120	132	252

1. The Stockholm entry of the first year report should be corrected by +3 months.

C.1.1 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 provided special possibilities to announce the positions.

C.2 Training Program

C.2.1 Twinning initiative

The mobility among the members of the nodes is quite high, and has been further encouraged as new young MOLPROP members have been joined in. We have offered them an opportunity to work and

Table 7: First YR twinning program

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

train at more than one node, both on short and long time scales, i.e. both by visits and by settling at another node for a period of time. In order to ensure this, the program for the young researchers was formulated as a *twinning* program, each Post- or Pre-Doctor has been allocated a second node for his studies and work. We believe that such a geographic flexibility also promotes the total project as such in addition to the the scientific and personal profits for the young researchers. The implementation of the original twinning program was aggravated by the irregular recruitments. With all positions filled we have therefore now changed the twinning schedule to two parts, one before midterm and one after. The first twinning program has thus been fulfilled as described on our home page: <http://www.theochem.kth.se/molprop/>. Table 7 shows the node constellations for this first YR twinning program.

C.2.2 Integration of YRs

As shown on the home page there has been a strong participation of YRs in the visit program (14 Young Researcher visits). The participation of the YRs (hired or associate) in the network meetings has amounted to about 20-35 each. Publications involving the hired YRs have already been produced. The number of these is about 15 at present.

C.2.3 Special measures

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

C.2.4 Equal opportunities

We have made special efforts to recruit female students, however, since the recruitment situation initially was problematic we were forced to lower our ambition in this respect. Node 6 has recruited a female

post-doctor.

C.2.5 Multidisciplinarity

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

C.3 Factual Information on the Young Researchers

Name:	Branislav Jansik
Nationality:	Slovak
Age (at the time of appointment):	27
Start- and likely end-date of appointment:	1.10.2000 - 30.09.2004
Category (Post- or Pre-doc):	Pre-Doc
Scientific speciality:	Quantum chemistry
Place of work:	KTH, Stockholm
Country of work:	Sweden
Whether the researcher had worked at another network partner:	No

Name:	Oscar Rubio Pons
Nationality:	Spanish
Age (at the time of appointment):	25
Start- and likely end-date of appointment:	1.09.2001 - 31.08.2005
Category (Post- or Pre-doc):	Pre-Doc
Scientific speciality:	Quantum chemistry
Place of work:	KTH, Stockholm
Country of work:	Sweden
Whether the researcher had worked at another network partner:	No

Name:	Thomas Bondo Pedersen
Nationality:	Danish
Age (at the time of appointment):	29
Start- and likely end-date of appointment:	1.07.2000 - 30.06.2001
Category (Post- or Pre-doc):	Post-doc
Scientific speciality:	Quantum chemistry
Place of work:	Santiago-de-Compostela
Country of work:	Spain
Whether the researcher had worked at another network partner:	With prof. Oddershede of the Odense node (before the network)

Name:	Thomas Bondo Pedersen
Nationality:	Danish
Age (at the time of appointment):	31
Start- and likely end-date of appointment:	9.07.2001 - 8.07.2002
Category (Post- or Pre-doc):	Post-doc
Scientific speciality:	Quantum chemistry (NOCC)
Place of work:	Departamento Quimica Fisica. Universidad de Valencia
Country of work:	Spain
Whether the researcher had worked at another network partner:	Yes, 1 year as post-doc in Santiago

Name:	Dan J. Jonsson
Nationality:	Swedish
Age (at the time of appointment):	32
Start- and likely end-date of appointment:	1.03.2001 - 28.02.2003
Category (Post- or Pre-doc):	Post-doc
Scientific speciality:	Quantum chemistry
Place of work:	Mainz
Country of work:	Germany
Whether the researcher had worked at another network partner:	Yes, Ph.D. with Prof. H. Agren, Linkoping

Name:	Rafael Soriano Jartin
Nationality:	Spanish
Age (at the time of appointment):	26
Start- and likely end-date of appointment:	13.09.2001 - 12.09.2005
Category (Post- or Pre-doc):	Pre-doc
Scientific speciality:	Theoretical chemistry
Place of work:	Modena
Country of work:	Italy
Whether the researcher had worked at another network partner:	No

Name:	Magdalena Zofia Pecul
Nationality:	Polish
Age (at the time of appointment):	27
Start- and likely end-date of appointment:	1.04.2001 - 31.03.2003
Category (Post- or Pre-doc):	Post-Doc
Scientific speciality:	Quantum Chemistry studies of optical properties
Place of work:	Pisa
Country of work:	Italy
Whether the researcher had worked at another network partner:	No

Name:	Stefano Corni
Nationality:	Italy
Age (at the time of appointment):	25
Start- and likely end-date of appointment:	1.4.2001
Category (Post- or Pre-doc):	Pre-doc
Scientific specialty:	Quantum dots and optical properties
Place of work:	Helsinki
Country of work:	Finland
Whether the researcher had worked at another network partner:	No

Name:	Michael Patzschke
Nationality:	German
Age (at the time of appointment):	28
Start- and likely end-date of appointment:	1.09.2001 - 31.08.2005
Category (Post- or Pre-doc):	Pre-doc
Scientific speciality:	Relativistic quantum chemistry
Place of work:	Helsinki
Country of work:	Finland
Whether the researcher had worked at another network partner:	No

Name:	Filip Pawlowski
Nationality:	Polish
Age (at the time of appointment):	26
Start- and likely end-date of appointment:	1.02.2001 - 31.01.2004
Category (Post- or Pre-doc):	Pre-doc
Scientific speciality:	Quantum chemistry
Place of work:	Aarhus
Country of work:	Denmark
Whether the researcher had worked at another network partner:	No

Name:	Mark A. Watson
Nationality:	British
Age (at the time of appointment):	23
Start- and likely end-date of appointment:	15.08.2001 - 14.08.2002
Category (Post- or Pre-doc):	Pre-doc
Scientific speciality:	Quantum chemistry, Electronic structure theory
Place of work:	Oslo
Country of work:	Norway
Whether the researcher had worked at another network partner:	No

Name:	Pawel Salek
Nationality:	Polish
Age (at the time of appointment):	27
Start- and likely end-date of appointment:	1.07.2001 - 30.06.2003
Category (Post- or Pre-doc):	Post-doc
Scientific speciality:	Quantum chemistry
Place of work:	Oslo
Country of work:	Norway
Whether the researcher had worked at another network partner:	Yes

Part D

Sketches of the young Researchers

Node 1 Stockholm YR 1

Branislav Jansik

I studied at the Comenius University in Bratislava / Slovakia and obtained a Masters Degree at the Faculty of Natural Sciences in the Department of Physical Chemistry under supervision of Prof. V. Kellö with a study on the dipole moments of transition metal compounds. Since October 2000, I am a PhD student at the Department of Theoretical Chemistry / Royal Institute of Technology with Prof. Ågren working on non-linear optical properties within the MOLPROP network.

Within this project, I was able to discuss not only with the people at my department, but also with the people from the other MOLPROP nodes. These discussions were very stimulating and gave me new insight and impact on my project. Additionally, the MOLPROP network also made visits to two winter-schools in Helsinki and one summerschool in Lund possible, which gave me the opportunity to broaden my scientific background and to exchange ideas with other students in the network. I benefitted a lot from the network initiative and consider it to be important for carrying out my PhD studies successfully.

Node 1 Stockholm YR 2

Oscar Rubio Pons

My research work in the Royal Institute of Technology has been a new experience for me, I started to study Quantum Chemistry in Valencia, always working in the spectroscopic area, which related to the electronic spectra and molecular properties. From my arrival here in September 2002, my research work has been put in forward in the same way to study the electronic spectra and molecular properties of several compounds.

Here at KTH, I have got the chance to learn more about the photophysics and photochemistry from the quantum chemical point of view. My work started under the supervision of the Professor Hans Agren, and Bernd Schimmelpfennig, working in the spin-orbit coupling, phosphorescence, relativistic effects.

In this work we have studied different systems of several interesting compounds, as a new materials design and biological compounds. I had the chance to work with the theoretical Chemistry group at KTH in Stockholm and to work with DALTON program, with the new parts of the code to run the phosphorescence calculations.

For the future, I am going to finish my studies phosphorescence and we have in mind to expand this study to the Photodynamic therapy and its applications in the medical area.

Node 2 Valencia

Thomas Bondo Pedersen

During the last 18 months in the network I have carried out research along two main lines, method development and applications to van der Waals complexes. The method development has resulted in a preliminary implementation of the so-called NOCC model, providing gauge invariance in the context of coupled cluster response theory, and in new MP2 and CCSD implementations employing Cholesky decomposition of the two-electron integrals. Coupled cluster theory, in its standard formulation, has been utilized to calculate intermolecular potential energy surfaces of the van der Waals complexes cyclopropane-Ar, -Ne, and -He, benzene-N₂, and CO-Ar. The cyclopropane-rare gas surfaces were used to calculate the intermolecular states. The benzene-N₂ calculations have assisted the assignment of experimental spectra. Finally, the CO-Ar surface is a benchmark study including all three internal nuclear degrees of freedom at an unprecedented level of theory. Recently, during a visit at the Mainz node, work has been carried out on rovibrational and thermal averaging of static molecular properties in the electronic ground state, notably the spin-spin coupling constants of NMR spectroscopy. The MOLPROP network has provided a lively forum for collaborations, although the bureaucracy, in my opinion, is somewhat out of phase with the reality of scientific work and progress.

Node 3 Santiago-de-Compostela

Thomas Bondo Pedersen

During the last 18 months in the network I have carried out research along two main lines, method development and applications to van der Waals complexes. The method development has resulted in a preliminary implementation of the so-called NOCC model, providing gauge invariance in the context of coupled cluster response theory, and in new MP2 and CCSD implementations employing Cholesky decomposition of the two-electron integrals. Coupled cluster theory, in its standard formulation, has been utilized to calculate intermolecular potential energy surfaces of the van der Waals complexes cyclopropane-Ar, -Ne, and -He, benzene-N₂, and CO-Ar. The cyclopropane-rare gas surfaces were

used to calculate the intermolecular states. The benzene-N₂ calculations have assisted the assignment of experimental spectra. Finally, the CO-Ar surface is a benchmark study including all three internal nuclear degrees of freedom at an unprecedented level of theory. Recently, during a visit at the Mainz node, work has been carried out on rovibrational and thermal averaging of static molecular properties in the electronic ground state, notably the spin-spin coupling constants of NMR spectroscopy. The MOLPROP network has provided a lively forum for collaborations, although the bureaucracy, in my opinion, is somewhat out of phase with the reality of scientific work and progress.

Node 4 Mainz

Dan J. Jonsson

I have a background in quantum chemistry. My Ph.D. thesis (Ph.D. in computational physics, Linköping (Sweden), March 1998, supervised by Prof. H. Agren) dealt with the development MCSCF of response theory methods for the calculation of higher-order electrical and magnetic properties. During his post-doctoral stay (University of California, San Diego, USA, with Prof. P.R. Taylor, March 1998 to February 2001), I was involved in the development of geminal methods for the electron correlation treatment.

My responsibility in the network is to formulate and implement second derivative methods for the calculation of excited state properties within the CCSD response theory/EOM-CCSD framework; and, furthermore, to keep contact with other nodes (in particular Pisa) for the calculation of mixed electric and magnetic properties.

My experience with the network is good in general and I appreciate the opportunity given by the network to learn new theory (by working at a specific node, by visits to other nodes, as well as through attendance of summer/winter schools), to establish new contacts, to have the chance to live in a foreign country with different culture and language, as well as the possibility to travel within the network (so far to Oslo and Pisa).

Node 5 Modena

Rafael Soriano Jartin

My scientific background is in Chemical Physics and Quantum Chemistry. I have gained experience in optimization of molecular geometries by GAUSSIAN and GAMESS codes at HF and correlated level of accuracy. Stepwise I have gained experience in programming (C and Fortran 77 languages), and have by now a very good experience as system-engineering on Linux operating systems. My job in the network is to implement auxiliary codes within the computer packages DALTON and SYSMO. The present field of research in Modena involves the study of conjugated cyclic molecules developing paramagnetic currents in the presence of external magnetic fields. I have so far a good experience with the network, although my period of employment has not been that long yet.

Node 6 Pisa

Magdalena Zofia Pecul

My scientific background before MOLPROP was focused on the calculations of static molecular properties (in particular NMR shielding constants and spin-spin coupling constants) and on intermolecular interactions, especially in the context of solvent effects. My PhD thesis, completed in 2000, has a title

"The influence of intermolecular interactions on the parameters of NMR spectra". During my stay at Istituto di Chimica Quantistica ed Energetica Molecolare del CNR in Pisa I got involved in projects including the calculations of dynamic properties, both first order (dynamic dipole-dipole, dipole-magnetic dipole and dipole-quadrupole polarizabilities and their geometric derivatives) and second order (magneto-chiral birefringence) ones. I have also continued to some extent to work on her former research subject, calculating the first virial coefficient of the shielding constant in helium. My experience of the MOLPROP network is on the whole favorable. I appreciate in particular the winter schools in Helsinki. My suggestion is that it would be a good idea to improve access to computational power, since the computer resources at the individual nodes are not always sufficient.

Node 7 Helsinki YR 1

Stefano Corni

I obtained the "Laurea" (a degree given at the end of a 5-year university course) in Chemistry at the University of Pisa in the 1999. My thesis was on the calculation of response properties of molecules near to a metal surface, and it was supervised by Prof. Jacopo Tomasi. In the same year, I got a Chemistry PhD position at the Scuola Normale Superiore di Pisa. I attended different schools, two of which are now introduced in the MOLPROP network: the European Summer School in Quantum Chemistry (Riolo, Italy, 2000) and the Winter School in Theoretical Chemistry (Helsinki, Finland, 2000). In the framework of the MOLPROP network, I work in the node of Helsinki to develop a program for the calculation of properties of Quantum Dots. I do both programming (creating for example an interface between the existing code and a new more flexible bi-particle integral code) and applications (calculations of the Quantum Dot size dependency of energy levels and radiative recombination rates of neutral and charged multiexcitons). A part of this work has been presented by myself at the Finnish Symposium of Quantum Chemistry (Kuusamo, Finland, June 2001). The period I spent in Finland has given me the possibility of working in the new and fascinating field of Quantum Dots, which I previously knew just at a textbook level, and to enrich my knowledge in the field of Computational Chemistry, mainly thanks to the competence of the people I worked with. Finally, from the human viewpoint, this experience has been strongly positive, allowing me to know better the culture and the customs of another European Country.

Node 7 Helsinki YR 2

Michael Patzschke

I studied chemistry at the Freie Universität Berlin. During my studies I attended special courses in different areas of theoretical chemistry. I did my 'Diploma-thesis' in the group of Prof. D. Haase at the before mentioned university. The title of my diploma-thesis is "Relativistic calculations on Bi(V) and Sb(V) compounds". In this work, I used different quantum chemistry computer programs but the main work was done using the DIRAC code.

Here in Helsinki I am working on my PhD-Thesis for that I am doing calculations on transition-metal/main-group-metal compounds including relativistic effects at different levels of theory including state of the art four-component relativistic calculations. I am also very interested in the properties of the calculated compounds. To calculate these, I am going to use the new DIRAC-linear-response code. My training in Odense will be very helpful for doing such calculations.

In the four month I have been here I learned quite a lot. The climate in the group is very good and the discussions with the other members very fruitful. The twinning training in Denmark is an important

opportunity to get experience of the research in other groups.

Node 8 Odense

Filip Pawlowski

In 1998-2000 I was taking part in the research, based on the Dirac-Fock method, which resulted, among others, in determination of the electronic structure of 3d-metals in solids as well as the changes in configuration of sulphur ions bombarding carbon foils. The results are published in 6 articles. I had many advanced courses on that time.

A knowledge I gained then has been constituting a valuable background for my PhD research at Aarhus University. The very first responsibility I had here was the detailed investigation of the accuracy that can be obtained of the equilibrium geometries based on the experimental rotational constants and the vibration-rotation interaction constants calculated at the various wave-function / basis-set levels. I derived the formulas establishing how the error in the calculated sum of the vibration-rotation interaction constants propagates into the error in geometry; it was quite exciting to see that these theoretical predictions are confirmed by the independent analysis of the wave-function / basis-set convergence. It turned out that the geometries obtained with the above approach are, in general, much more accurate than purely experimental or purely theoretical ones. The study has resulted in the paper which has already been accepted at JCP. Moreover, I included the results of this research in the short presentation I gave in September at a conference in Poland. I found this project a perfect introduction to the subsequent stages of my PhD studies.

At the moment I am involved in two other projects: (i) the study of the accuracy of calculation of harmonic frequencies and anharmonic constants (in collaboration with Oslo node), and (ii) the implementation of molecular response functions into the CC3 model. The last project is especially instructive and stimulating for me. I have also had some other duties such as teaching, and of calculating the specific spectral properties for some molecules to support the analysis of the spectra recorded at Aarhus University and Lund University, or designing a part of Chemistry Department web site.

Node 9 Oslo: YR 1

Mark A. Watson

I took my undergraduate BA and MSc courses in Natural Sciences (specializing in Chemistry) at the University of Cambridge (UK), finishing in June 2000. In October I went on to take a PhD place in the Chemistry Department under the supervision of Prof. N.C. Handy. I am now in the second year of my PhD studies and spending one year as a MOLPROP student in Oslo, working with Prof. T. Helgaker. The subject of my work is an investigation into Linear Scaling Methods for ab initio Quantum Chemistry. In particular, my responsibilities currently include the implementation into the program package Dalton of the Fast Multipole Method for evaluating Coulomb integrals with an amount of computational work that scales linearly with the system size.

My experiences to date of participating in the MOLPROP program have been very positive. Working in Oslo has been very refreshing; it has given me the opportunity to pursue new work with a different perspective, and has very much enriched my scientific outlook beyond what I had experienced in Cambridge. I have recently returned from visits to Stockholm and the Winter School in Helsinki. Both

were funded with MOLPROP money and again were very valuable experiences - not only for the formal teaching and learning that I was exposed to, but also, and perhaps more significantly, for the informal opportunity they gave me to meet and talk with many other researchers from around Europe.

Node 9 Oslo: YR 2

Pawel Salek

My scientific background is in wave packet modeling of gases interacting with X-rays. I have recently obtained my PhD degree in Theoretical Chemistry Laboratory in Stockholm, presenting a thesis on "Wave Packet Theory of Resonant X-ray Scattering". The work has been done in a close cooperation with other theoreticians as well as with experimentalists. I have gained also much experience in large numerical calculations from user's and programmer's sides.

After the dissertation, I have been employed in the framework of MOLPROP project by the Oslo node. I am involved here in two projects: implementation of quadratic response (QR) using a DFT reference and linear scaling methods. The goal of QR/DFT project is to develop a code that allows to compute properties of larger molecules using a wave function that explicitly includes correlation. I am responsible for the implementation and also partially responsible for the theory development. The goal of linear scaling project is to provide Coulomb and exchange integral evaluation methods that can evaluate all needed integrals of this kind in time T proportional to the number N of basis functions involved: $T=C*N$. My responsibility is implementation, in particular making sure constant C in the formula above is kept small.

My scientific experience after 5 months of my involvement is very positive. While I experienced some formal organizational problems due to move from one country to another, assistance of the MOLPROP members involved helped to resolve these issues in reasonable time.

Part E

Network Financing

The ratio between the expenditure to the date of this report and the total contracted amount, 33 %, follows quite closely the ratio between the amount of man-months of hired YRs to date and the contracted total amount of man-months (88 versus 252 or 35 %). Adding the 2 months of elapsed time between the data collection (1/12 2001) for this midterm review *report* and the midterm review *meeting* (24-25/1 2002) we note that the total amount of man-months spent will be 44 % of the contracted total, accounting for the three new hired YRs 1/1 2002. A corresponding increase in spending up to the time for the midterm review meeting can evidently be anticipated. The three new hired YRs are Miroslav Ileas from the Slovak republic (to node 8), Laban Pettersson, Sweden (to node 8) and Zilvinas Rincevcius from Lithuania (twinned between nodes 1 and 6).

Table 8: Allowable costs foreseen in the contract (in Euro)

<i>Node Number</i>	<i>Participant</i>	<i>Costs for young Res.</i>	<i>Networking Costs</i>	<i>Overheads</i>	<i>Totals</i>
1	P1-Stockholm	72,311	74,000	29,261	175,572
2	P2-Valencia	80,185	25,000	21,186	126,371
3	P3-Santiago	80,185	55,860	27,207	163,252
4	P4-Mainz	101,884	25,000	25,375	152,259
5	P5-Modena	91,830	25,000	23,366	140,196
6	P6-Pisa	74,226	27,000	20,245	121,471
7	P7-Helsinki	89,209	25,000	22,841	137,050
8	P8-Odense	181,751	46,000	45,550	273,301
9	P9-Oslo	109,273	37,000	29,254	175,527
Total		880,854	339,860	244,285	1,464,999

Table 9: Expenditure to date (01-12-01) of the network (in Euro)

<i>Node Number</i>	<i>Participant</i>	<i>Costs for young Res.</i>	<i>Networking Costs</i>	<i>Overheads</i>	<i>Totals</i>
1	P1-Stockholm	35,201	36,872	14,414	86,487
2	P2-Valencia	19,373	12,103	6,295	37,772
3	P3-Santiago	39,024	39,870	14,742	93,638
4	P4-Mainz	36,884	3,416	8,060	48,361
5	P5-Modena	15,600	6,100	2,500	24,200
6	P6-Pisa	28,528	11,225	2,818	42,571
7	P7-Helsinki	22,117	4,701	5,363	32,183
8	P8-Odense	32,440	10,650	8,620	51,700
9	P9-Oslo	47,375	19,250	5,250	71,875
Total		276,542	144,187	68,062	488,787

Part F

Proposed Revision of the Contract

No major revision is proposed by the co-ordinator.