QUANTUM CHEMICAL STUDIES OF SUPRAMOLECULAR COMPLEXES AND NANOCLUSTERS

Doctoral Dissertation

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Department of Engineering Physics and Mathematics
Optics and Molecular Materials

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Department of Engineering Physics and Mathematics
Optics and Molecular Materials

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Quantum chemical studies of supramolecular complexes and nanoclusters

Abstract

In this thesis, molecular structures occurring in nanotechnology and supramolecular polymer science have been investigated using methods of computational chemistry. Formation of pyridine-methanesulphonic acid complex and solvation effects affecting the hydrogen bond have been investigated. Torsional potentials of various bipyridines and their protonated analogues have been modelled and force field parameters obtained. The structure of a coordination compound formed by pyridine, zinc and a chelating ligand was used as a model to investigate the binding in a self-organizing polymeric system. Interactions between polyamide, phenolic resins and water was studied using small model molecules. Optical properties of silicon nanoclusters have been modelled to investigated their luminescence properties.

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Tiivistelmä

Tässä väitöskirjassa on tutkittu nanoteknologiassa ja supramolekyylisessä polymeeritieteessä esiintyviä molekyylirakenteita laskennallisen kemian keinoin. Työssä on tutkittu pyridiinin ja metaanisulfonihapon kompleksoitumista ja liuottimen vaikutusta vetysitoutumiseen. Työssä on määritetty torsiopotentiaaleja eri bipyridiineille ja niiden protonoiduille muodoille sekä laskettu voimakenttäparametrit. Pyridiinin, sinkin ja kelaattiyhdisteen muodostamaa koordinaatiokompleksia on käytetty mallina tutkittaessa itse-järjestyvän polymeerirakenteen rakennetta. Polyamidin, fenolihartsin ja veden käyttäytymistä tutkittiin käyttäen apuna pieniä mallimolekyylejä. Piin muodostamien nanoklustereiden optisia ominaisuuksia on mallinnettu tutkittaessa klustereiden luminesenssia.

The history of the human race is a continual struggle from darkness towards light. It is, therefore, to no purpose to discuss the use of knowledge; man wants to know, and when he ceases to do so, he is no longer man.

—Fridtjof Nansen

List of Publications

List of publications included in the thesis

I O. Lehtonen, J. Hartikainen, K. Rissanen, O. Ikkala and L.-O. Pietilä, *Hydrogen bonding and protonation in acid-base complexes: Methanesulfonic acid-pyridine*, J. Chem. Phys. **116**, 2417 (2002)

II O. Lehtonen, O. Ikkala and L.-O. Pietilä, *Density functional studies of torsion potentials of neutral and protonated bipyridines*, J. Mol. Struc. (Theochem) **91**, 663 (2003)

III S. Valkama, O. Lehtonen, K. Lappalainen, H. Kosonen, P. Castro, T. Repo, M. Torkkeli, R. Serimaa, G. ten Brinke, M. Leskelä and O. Ikkala, *Multicomb polymeric supramolecules and their self-organization: Combination of coordination and ionic interactions*, Macromol. Rapid Comm. **24**, 556 (2003)

IV J. Hartikainen, O. Lehtonen, T. Harmia, M. Lindner, S. Valkama, J. Ruokolainen and K. Friedrich, *Structure and morphology of polyamide 66 and oligomeric phenolic resin blends: Molecular modeling and experimental investigations*, Chem. Mat. **16**, 3032 (2004)

V O. Lehtonen and D. Sundholm, *Density-functional studies of excited states of silicon nanoclusters*, Phys. Rev. B **72**, 085424 (2005)

List of other publications

- M. Kalmi, M. Lahcini, P. Castro, O. Lehtonen, A. Belfkira, M. Leskelä and T. Repo, *Tetrakis Sn(IV) alkoxides as novel catalysts for living ring-opening polymerization of lactides*, J. Pol. Sci. A **42**, 1901 (2004)

- H. Santa, J. Kammonen, O. Lehtonen, J. Karimaki, O. Pastinen, M. Leisola and O. Turunen, *Stochastic boundary molecular dynamics simulation of L-ribose in the active site of Actinoplanes missouriensis xylose isomerase and its Val135Asn mutant with improved reaction rate*, Biochim. et Biophys. Acta **1749**, 65 (2005)

- O. Lehtonen and D. Sundholm, *Optical properties of sila-adamantane nanoclusters from density-functional theory*, Phys. Rev. B **74**, 045433 (2006)

- O. Lehtonen and D. Sundholm, *Bright luminescence from silane substituted and bridged silicon nanoclusters*, Phys. Chem. Chem. Phys. **8**, 4228 (2006)

- O. Lehtonen and D. Sundholm, *Coupled-cluster studies of the electronic excitation spectra of silanes*, J. Chem. Phys. **125**, 144314 (2006)

Author's contribution

   I The author has performed all the quantum chemical computations and related analysis and written the first version of the manuscript excluding the experimental part.

  II The author has performed all the quantum chemical computations and related analysis except the molecular mechanics part and the least squares fitting of the torsion potentials and written the first version of the manuscript.

 III The author has performed all the quantum chemical computations and related analysis and written parts of the manuscript related to computational work.

 IV The author has taken part in the initial design of the experiment, performed all the quantum chemical computations and related analysis and written parts of the manuscript related to computational work.

  V The author has performed all the quantum chemical computations and related analysis except computations related to small silanes. The manuscript was jointly written by both authors.

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Olli Lehtonen

Contents

Chapter 1

Introduction

Designing new materials and to understand phenomena occurring at the atomic level is often complicated and usually there are no simple models available. If one is able to construct a model based on fundamental physical theories, which is not specific to the system, theoretical modelling may become possible. At the smallest length scales experimental methods may not be able to probe the system accurately enough, and in this respect computer simulations are becoming increasingly important in order to understand physics and chemistry at the atomic level.

Performing 'experiments' with computers has become more and more attractive as the computing power has increased and efficient programs are available. Computer simulations may provide results with much less work than experiments; even more often computations and experiments complement each other, and computations can help to interpret experimental results better. In some cases computations are also able to provide information which is not accessible experimentally, or they can predict totally new phenomena yet to be observed.

Computations must be based on theoretical models developed to describe experimentally observed phenomena; the better the model the better agreement one should obtain with experiments. Although theoretical models are always simplifications of the reality and are not necessarily able to describe the true, complete behaviour of the nature, they can provide new insights into the system, which are otherwise impossible to obtain.

Although computations may appear to be much easier than experiments to perform and they may seem to offer an easy short cut to the results, the importance of understanding the theory behind the models, and especially its limitations, cannot be overemphasised. While experimental accuracy can often be estimated by repeating the measurement sufficiently many times, with computational results the errors are usually systematic and cannot be so easily assessed.

The main theme of this thesis has been to investigate molecular systems present in supramolecular and polymer chemistry using computational quantum chemistry methods. Many of these investigations originate from experimental needs to understand the underlying phenomena and observations more deeply. To be able to study these kinds of systems using quantum chemical methods only a small part of the system can be included in the model. In the summary part of this thesis basic theoretical methods relevant to the work are discussed and an overview on the publications included is given.

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Chapter 2

Theory

Computational chemistry is based on theoretical models describing the interactions between chemical elements. Different models vary significantly in their accuracy and computational cost, both of which are important factors to be considered when modelling is undertaken. Some models include all electrons explicitly, others consider atoms as classical points of mass connected by springs with characteristic spring constants. To choose the right model for a particular problem is not always straightforward, and often different models yield complementary information. However, more often the computational resources are the limiting factor in determining which model can be used.

Although the mathematical equations describing quantum systems, like atoms and molecules, were developed already in 1920s, there is still increasing effort to solve these equations even approximately; at the same time, the interesting systems become larger and more complex. An example of this ongoing effort is that in 1998 the Noble prize in chemistry was awarded to Walter Kohn and John Pople due to their contributions to computational chemistry. Usually the more the equations are approximated, the faster computations become. The drawback is that in this process the results also become less and less reliable.

Most of the computations presented in this thesis have been performed using density functional theory as many of the systems have been so large that other, more accurate, methods would have been exceedingly costly or impossible to use with the programs and computers available at the time of work. Other methods like the second-order Møller-Plesset perturbation theory, the approximate coupled cluster theory and semiempirical methods have been also used when appropriate.

In the following the most common electronic structure methods are described. Some of the methods are described, not because they are applied in this work, but to provide a consistent overview on available methods and to show the similarities and differences between the methods. Some of the methods are almost as old as quantum theory itself and some were invented only few decades ago.

2.1   Electronic structure methods

There are two main approaches to describe electronic structure of atoms and molecules: the wavefunction and density functional based methods. In the wave-

function based methods an approximation for the actual wavefunction is constructed and the molecular properties are calculated based on it. In the other approach the electron density is taken as the fundamental variable and this approach is known as the density functional theory. The aim in all electronic structure methods is to solve the Schrödinger equation, or in the relativistic case, the Dirac equation. Usually the solution is obtained within some well defined approximations. The three basic ingredients which affect the accuracy of different electronic structure methods are the choice of the basis set, the computational level and the Hamiltonian. Additionally, molecular properties show different kinds of dependence on these three components, and in order to model the particular molecular property accurately, the basis set, the computational level and the Hamiltonian must be chosen appropriately.

The Dirac equation [1, 2] offers an exact framework to describe relativistic effects[1] for a one-particle system, like an electron. However, there are further effects which are not included in the Dirac equation, like the Lamb shift [3] due to the quantization of the electromagnetic field. These effects can be included using quantum electrodynamics [4], but from the chemical point of view these effects are usually so small that they can be neglected.

In order to treat many-electron systems relativistically, one has to introduce interactions between the electrons. However, the classical Coulomb interaction between two charged particles is not Lorentz covariant, i.e. it does not satisfy the requirements of relativity. On the other hand, the fully relativistic interaction between charged particles is very complicated, and for chemical purposes it is usually sufficient to include only the first terms in the series expansion of the interaction potential and this approximative form is known as the Coulomb-Breit interaction; however, it not Lorentz covariant[2]. Adding this interaction into the Dirac equation results in the Dirac-Coulomb-Breit (DCB) Hamiltonian. The four-component equation can be reduced into two separate two-component equations using the Foldy-Wouthuysen transformation [6] (which is exact only in the absence of interactions). Application of this transformation with the DCB Hamiltonian leads to the Breit-Pauli Hamiltonian [7], which can be expanded as a series expansion in the inverse powers of the speed of light. The resulting terms in this Hamiltonian can be given a physical interpretation, such as the spin-orbit coupling, the mass-velocity correction, the Darwin correction, the dipole-dipole interaction between two spins, the Fermi contact interaction etc. These interactions are important, for example, in formulating expressions for quantum mechanical calculations of the magnetic properties. As these additional terms often give only small corrections to the energy, it is possible to include their effects perturbatively in a nonrelativistic treatment. Alternative methods to decouple large and small components in the Dirac equation are the zeroth-order regular approximation (ZORA) [8], the Douglas-Kroll transformation [9] and Kutzelnigg's formulation of direct perturbation theory [10].

There are different approaches to perform all-electron calculations including the relativistic effects. One can use the full DCB Hamiltonian with all four-components or the Dirac-Hartree-Fock method which ignores relativistic effects

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[1]With relativity in this context it is meant special relativity excluding any effects arising from gravity.

[2]Fully covariant treatment of two-particle problem results in the Bethe-Salpeter equation [5].

in the interaction term and solves the resulting four-component equations [11]. Another approach is to use the Breit-Pauli Hamiltonian terms as perturbational corrections in order to estimate relativistic corrections using some nonrelativistic reference state. However, this type of perturbation theory should be used only up to first order because it is not variationally stable [12].

The importance of relativistic effects is proportional to the second power of the nuclear charge [13], and for lighter elements the relativistic effects can often be neglected (the errors arising from other sources are often more significant). To describe a quantum mechanical system nonrelativistically, one can start directly from the Schrödinger equation[3]

$$i\frac{\partial \Psi}{\partial t} = \hat{H}\Psi, \tag{2.1}$$

where $\hat{H}$ is the Hamiltonian and Ψ the wavefunction. Solving the Schrödinger equation analytically, or even numerically, becomes intractable for systems with more than a few particles, and therefore different levels of approximations must be introduced. This results in a variety of computational methods with different levels of accuracy.

The complete Hamiltonian including electronic and nuclear degrees of freedom, results in the Schrödinger equation containing non-adiabatic coupling terms which mix different electronic states. In the adiabatic approximation the mixings between different electronic states are neglected and only diagonal coupling terms remain [14]. Furthermore, in the most frequently used Born-Oppenheimer (BO) approximation [15] even the diagonal terms are neglected, as they are proportional to the ratio of the electronic and nuclear masses. Within the BO approximation the electronic Hamiltonian in the Schrödinger equation becomes

$$\hat{H} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_i \sum_K \frac{Z_K}{|\boldsymbol{R}_K - \boldsymbol{r}_i|} + \sum_i \sum_{j>i} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_K \sum_{L>K} \frac{Z_K Z_L}{|\boldsymbol{R}_K - \boldsymbol{R}_L|}, \tag{2.2}$$

where $\boldsymbol{r}_i$ and $\boldsymbol{R}_K$ are the coordinates of ith electron and Kth nucleus, respectively, and Z_K is the charge of the Kth nucleus. The BO approximation is based on the fact that the nuclei are much more heavier than the electrons, and thus move more slowly. The nuclei are assumed to be stationary with respect to the electrons neglecting all coupling terms arising from the nuclear kinetic energy operator with the electronic wavefunction. In practice this means that the total wavefunction is written as a product of the nuclear and electronic wavefunctions and the electronic wavefunction depends parametrically on the nuclear positions. Usually errors arising from this approximation are negligible. A direct consequence of the BO approximation is potential energy surfaces (PESs), i.e. the energy surface as a function of nuclear coordinates. The minimum on a PES determines the equilibrium geometry of a molecule.

Both the BO and adiabatic approximations are good as long as different PESs do not come too close to each other energetically. If two PESs cross each other, and the wavefunctions have the same symmetry, the wavefunction changes its

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[3]Atomic units are used throughout.

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character close to the crossing and switches from one PES to the other in order to remain in the ground state. In one dimensional PES scan one sees that the PESs cannot actually cross but they make an avoided crossing [14]. If the BO approximation fails, the electronic character of the wavefunction does not change, and the molecule continues along the PES which is no longer the electronic ground state [16]. In general, such a point where two PESs with same symmetry become degenerate is called a conical intersection [17].

The solution of the Schrödinger equation is based on the variational principle. The variational principle establishes that the wavefunction resulting in the lowest possible energy is also the ground state wavefunction of the system, i.e. other wavefunctions correspond to a higher energy state, and the energy is always an upper bound for the exact ground state energy. This basic principle forms the foundation for many quantum chemical methods, where the aim is to find an approximate wavefunction that minimises the energy. In practice, the wavefunctions are represented through a set of parameters which in turn are optimised. Often these parameters are not independent but the optimisation has to be carried out with subject to some constraints. However, even if total energies given by this process were variational, it does not imply that the energy differences obtained by subtracting two variational total energies would also be variational. On the other hand, with error cancellation the absolute energies can still be quite far from the exact solution but the energy differences are much more accurate. This can be the case, for example, while calculating energy differences of different isomers.

Electrons are fermions and, therefore, their wavefunction must be antisymmetric with respect to interchange of any two particles. Electrons have spin angular momenta which allows two electrons with opposite spins to occupy the same energy level. Each electron state can be associated with a spin orbital. However, in order to satisfy the correct antisymmetry of the total wavefunction, all possible permutations of electrons with respect to the orbitals must be taken. This requirement is satisfied if the wavefunction is constructed using Slater determinants with spin orbitals as their elements

$$\Phi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\boldsymbol{x}_1) & \phi_2(\boldsymbol{x}_1) & \ldots & \phi_N(\boldsymbol{x}_1) \\ \phi_1(\boldsymbol{x}_2) & \phi_2(\boldsymbol{x}_2) & \ldots & \phi_N(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\boldsymbol{x}_N) & \phi_2(\boldsymbol{x}_N) & \ldots & \phi_N(\boldsymbol{x}_N) \end{vmatrix}. \tag{2.3}$$

Such a wavefunction is exact only for non-interacting particles but it can be used as an approximate wavefunction. In general, the wavefunction can be expressed as a linear combination of several Slater determinants. If the Slater determinants are combined in such a way that the state is an eigenfunction of the total spin operator, the combination is referred as a configuration state function (CSF).

Second quantisation [18, 19] provides an equivalent way to account for the correct antisymmetry properties of the wavefunction without the need to use explicit Slater determinants. Each Slater determinant in the Hilbert space can be represented by an abstract vector space (Fock space) element, and there exists one-to-one mapping between these elements and the Slater determinants [20, 21]. Basically, a Fock space element tells which spin orbitals are occupied by the electrons. In the second quantisation the operators in the Hamiltonian (e.g. kinetic

energy, electron-electron repulsion) are expressed using creation and annihilation operators combined with numerical coefficients, which can be computed as interaction integrals for the spin orbitals. The antisymmetry property of fermions is included by requiring that the creation and annihilation operators must satisfy specific fermionic anticommutation rules.

In the second quantisation the electronic Hamiltonian can be written as [21]

$$\hat{H} = \sum_{\substack{pq \\ \sigma\tau}} h_{p\sigma q\tau} \hat{a}_{p\sigma}^\dagger \hat{a}_{q\tau} + \frac{1}{2} \sum_{\substack{pqrs \\ \sigma\tau\mu\nu}} g_{p\sigma q\tau r\mu s\nu} \hat{a}_{p\sigma}^\dagger \hat{a}_{r\mu}^\dagger \hat{a}_{s\nu} \hat{a}_{q\tau} + h_{\text{nuc}}, \qquad (2.4)$$

where $\hat{a}^\dagger$ and $\hat{a}$ are the creation and annihilation operators obeying the fermionic anticommutation rules and $h_{p\sigma q\tau}$ and $g_{p\sigma q\tau\mu s\nu}$ are one- and two-electron integrals over the spin orbitals and first quantised operators

$$h_{p\sigma q\tau} = \int \phi_{p\sigma}^*(\boldsymbol{x}) \left(-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{|\boldsymbol{R}_I - \boldsymbol{r}|} \right) \phi_{q\tau}(\boldsymbol{x}) \, \mathrm{d}\boldsymbol{x} \qquad (2.5)$$

$$g_{p\sigma q\tau r\mu s\nu} = \iint \frac{\phi_{p\sigma}^*(\boldsymbol{x}_1)\phi_{q\tau}(\boldsymbol{x}_1)\phi_{r\mu}^*(\boldsymbol{x}_2)\phi_{s\nu}(\boldsymbol{x}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \, \mathrm{d}\boldsymbol{x}_1 \, \mathrm{d}\boldsymbol{x}_2, \qquad (2.6)$$

where integrations are over both spatial and spin degrees of freedom and Roman letters refer to the spatial orbitals and Greek letters to the spin part. The first quantised operators above are independent of spin and therefore it is possible to perform the spin part of the integrals and the sum over the spin indices. In the spin-free formalism the Hamiltonian becomes

$$\hat{H} = \sum_{pq} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{e}_{pqrs} + h_{\text{nuc}}, \qquad (2.7)$$

where the singlet one- and two-electron excitation operators are defined as

$$\hat{E}_{pq} = \hat{a}_{p\alpha}^\dagger \hat{a}_{q\alpha} + \hat{a}_{p\beta}^\dagger \hat{a}_{q\beta} \qquad (2.8)$$

$$\hat{e}_{pqrs} = \hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}. \qquad (2.9)$$

The integral terms are similar, except that they do not involve spin any more. If the Hamiltonian contains spin dependent operators, like spin-orbit terms, other types of excitation operators arise [21].

The total energy of a system described by a wavefunction $|\text{CSF}\rangle$ in the Fock space is obtained as an expectation value of the Hamiltonian

$$E = \sum_{pq} D_{pq} h_{pq} + \frac{1}{2} \sum_{pqrs} d_{pqrs} g_{pqrs} + h_{\text{nuc}}, \qquad (2.10)$$

where the one- and two-electron density matrices are defined as

$$D_{pq} = \langle \text{CSF}|\hat{E}_{pq}|\text{CSF}\rangle \qquad (2.11)$$

$$d_{pqrs} = \langle \text{CSF}|\hat{e}_{pqrs}|\text{CSF}\rangle. \qquad (2.12)$$

From the set of orthonormal molecular orbitals (MOs) which define $|\text{CSF}\rangle$, one can obtain a new set of orthonormal MOs using a unitary transformation

$$|\text{CSF}(\boldsymbol{\kappa})\rangle = \exp(-\hat{\kappa})|\text{CSF}\rangle, \qquad (2.13)$$

where $\hat{\kappa}$ is an anti-Hermitian one-electron operator

$$\hat{\kappa} = \sum_{p>q} \kappa_{pq} (\hat{E}_{pq} - \hat{E}_{qp}). \tag{2.14}$$

This transformation is also called an orbital rotation and it changes the orbitals in such a way that the orbitals remain orthogonal. Additional constraints are not needed. The exponential parametrisation of the orbital rotation matrix allows nonredundant optimisation parameters to be more easily identified. The electronic energy of the transformed orbitals can be written in the form

$$E(\boldsymbol{\kappa}) = \langle \text{CSF} | \exp(\hat{\kappa}) \hat{H} \exp(-\hat{\kappa}) | \text{CSF} \rangle. \tag{2.15}$$

By expanding the exponential operator in a series expansion in terms of the orbital rotation parameters $\boldsymbol{\kappa}$, one obtains expressions for the electronic gradient and electronic Hessian, i.e. for the first and second derivatives of the energy with respect to the wavefunction parameters. For real wavefunctions the electronic gradient becomes [21]

$$E_{pq}^{(1)} = \left. \frac{\partial E}{\partial \kappa_{pq}} \right|_{\boldsymbol{\kappa}=\boldsymbol{0}} = 2\langle \text{CSF} | [\hat{E}_{pq}, \hat{H}] | \text{CSF} \rangle. \tag{2.16}$$

Now imposing a condition that the energy becomes stationary, i.e. the electronic gradient vanishes for a unitary transformation, leads to necessary (but not sufficient) condition for an energy minimum to occur. Whether a stationary point is a true minimum or not, can be determined from the eigenvalues of the electronic Hessian. Using the commutator rules and definitions for density matrices, the expression for the gradient can be written as

$$E_{pq}^{(1)} = 2(F_{pq} - F_{qp}), \tag{2.17}$$

where F_{pq} is defined as a generalised Fock matrix

$$F_{pq} = \sum_r D_{pr} h_{qr} + \sum_{rst} d_{prst} g_{qrst}. \tag{2.18}$$

This general expression can be partitioned into inactive and active Fock matrices leading to a multi-configurational self-consistent field method [22] discussed later. On the other hand, in the Hartree-Fock method described next the density matrix elements have special values, which simplify the expressions considerably.

2.1.1 Hartree-Fock method

The Hartree-Fock (HF) approximation [23, 24] is based on estimating the wavefunction as a single Slater determinant and, by construction, it provides the best possible approximate wavefunction that can be obtained this way. However, this is only an approximation, and part of the electronic energy is not accounted for by the HF approximation. The energy difference between the exact (nonrelativistic) solution and the HF solution is usually referred as the correlation energy.

In closed shell molecules, where all the spins are paired, each orbital can be assumed to be occupied by two electrons with opposite spins. In the second quantised formulation the closed shell single determinant HF wavefunction can be expressed as

$$|\mathrm{CSF}\rangle = \prod_i \hat{a}_{i\alpha}^\dagger \hat{a}_{i\beta}^\dagger |\mathrm{vac}\rangle, \tag{2.19}$$

where i runs over the occupied orbitals. For this particular wavefunction, the density matrix elements are

$$D_{ij} = 2\delta_{ij} \tag{2.20}$$

$$d_{ijkl} = D_{ij}D_{kl} - \frac{1}{2}D_{il}D_{kj}, \tag{2.21}$$

where i, j, k and l refer to the occupied orbitals. The energy for a closed shell system is given by

$$E = 2\sum_i h_{ii} + \sum_{ij}\left(2g_{iijj} - g_{ijji}\right) + h_{\mathrm{nuc}}. \tag{2.22}$$

The h_{ii} is the kinetic and nuclear attraction energy, g_{iijj} is the Coulomb (or Hartree) term and g_{ijji} is the exchange term (which also cancels the self-interaction present in the Coulomb term). In order to evaluate this expression, one needs the numerical values for the integrals over the MOs. To determine the ground state of a molecule, the MOs have to be chosen to minimise the energy. If there are some symmetry constraints imposed into the system, the energy minimisation may converge into an excited state instead of the ground state.

In the previous section, the condition for the stationary state was derived using the generalised Fock matrix: the MOs must be determined so that the gradient vanishes. However, there are a few subtleties. Orbital rotations among the occupied and virtual orbitals themselves are redundant; for these kinds of rotations the gradient is always zero. Only rotations that change the energy (and have non-zero gradient) are those between the occupied and virtual orbitals. It follows that it is sufficient to require that the gradient vanishes for any orbital rotation between occupied and virtual orbitals. This imposes restrictions which the optimised HF state has to fulfil.

Using the density matrix elements obtained from the HF wavefunction, the generalised Fock matrix in equation (2.18) simplifies considerably, becoming $F_{pi} = 2f_{pi}$, where

$$f_{pi} = h_{pi} + \sum_j (2g_{pijj} - g_{pjji}), \tag{2.23}$$

and f_{pi} is defined as the Fock matrix (not to be confused with the generalised Fock matrix). When p is an occupied orbital, the gradient is zero. If p is a virtual orbital, the second F_{ip} term in the gradient is zero, and the only remaining term is F_{pi}, which is a nonredundant occupied-virtual orbital rotation. Therefore, it follows that the Fock matrix elements between the occupied and unoccupied elements must be zero, i.e. $f_{ai} = 0$, where a is a virtual and i an occupied orbital, in order to the HF energy to be stationary. This condition is satisfied, for example, when the Fock matrix is diagonal, i.e. only the diagonal elements are non-zero. A

block diagonal Fock matrix can also satisfy this condition, i.e. occupied and un-occupied orbitals can be mixed between themselves. The diagonalisation of the Fock matrix yields the canonical MOs as eigenvectors and the orbital energies as eigenvalues. However, the solution must be found in an iterative fashion as the one- and two-electron integrals, h_{pq} and g_{pqrs}, depend on the MOs themselves. This iterative procedure is known as a self-consistent field (SCF) method.

Starting with a set of orthonormal orbitals, one can form a symmetric Fock matrix and find its eigenvalues and eigenvectors. Using the eigenvectors to form a new set of orthonormal MOs, a new Fock matrix can be calculated. By repeating this procedure until the MOs do not change any more, the Fock matrix becomes diagonal, and the MOs correspond to a stationary state. The particular orbitals that diagonalise the Fock matrix are called the canonical orbitals and the eigenvalues are referred as the orbital energies.

The Hartree-Fock wavefunction provides an approximate solution for the exact Hamiltonian. Another way to look at the problem is to ask whether there is some approximate Hamiltonian for which this particular solution is exact. This kind of an effective one-electron operator, or a Fock operator, can be identified as

$$\hat{f} = \sum_{pq} f_{pq} \hat{E}_{pq}, \tag{2.24}$$

where the Fock matrix elements are given by equation (2.23). This is also the reason why in the Møller-Plesset perturbation theory the Hamiltonian is partitioned in a way that the unperturbed Hamiltonian is chosen to be a sum of the Fock operators, and the perturbation is the difference between the exact Hamiltonian and the unperturbed one.

Usually the MOs are represented as linear combinations of the atomic orbitals (AOs) and these AOs are referred as basis functions. In practice, the set of basis functions is finite, and this leads to an approximate solution of the HF equations. One could perform the computations by evaluating the matrix elements first in the AO basis, then transform back into the MO basis and perform the SCF procedure described above. However, this scheme scales as N^5 in terms of the number of basis functions due to the two-electron MO integrals. Therefore, it is better to formulate the problem so that one can perform computations directly in the AO basis. A MO can be expressed as

$$\phi_p = \sum_{\mu} C_{\mu p} \chi_{\mu}, \tag{2.25}$$

where χ_{μ} are AO basis functions and $C_{\mu p}$ are MO coefficients to be optimised. Inserting this into the energy expression gives the energy in terms of the MO coefficients. Although the MOs are orthonormal, the AO basis functions are usually not.

The HF equations in a matrix form are

$$\mathbf{FC} = \mathbf{SC}\varepsilon, \tag{2.26}$$

where $\mathbf{F}$ is the Fock matrix, $\mathbf{C}$ the MO coefficient matrix, $\mathbf{S}$ the overlap matrix of AO basis functions and ε is a diagonal matrix containing orbital energies. These

equations are called the Roothaan-Hall equations [25, 26]. The matrix elements of the Fock matrix in the AO basis are

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} D_{\rho\sigma}\left(g_{\mu\nu\rho\sigma} - \tfrac{1}{2}g_{\mu\sigma\rho\nu}\right), \qquad (2.27)$$

where the AO density matrix is defined as

$$D_{\rho\sigma} = 2\sum_i C_{\rho i} C_{\sigma i}, \qquad (2.28)$$

and the summation is over the occupied orbitals. The main advantage with the AO formulation is that the HF equations can be written as standard linear algebra equations and they are of the form of a generalised eigenvalue problem. Although the solution must usually be obtained through an iterative procedure without a guarantee that such a procedure will converge, the eigenvalues (orbital energies) and eigenvectors (MO coefficients) can in many cases be determined self-consistently.

In the canonical formulation the orbital energies can be interpreted using Koopmans' theorem [27]. An occupied orbital energy is equal to the change in the total energy if the electron is removed from that orbital while an unoccupied orbital energy corresponds to the change in the total energy if an electron is added to that orbital and all the other orbitals are supposed to remain the same. Especially, the energy of the highest occupied molecular orbital (HOMO) can be interpreted as an estimate for the (vertical) ionisation potential. Correlation effects, which are neglected in the HF approximation, will produce further corrections to the ionisation potential. Often the correlation effects and the error arising from not relaxing the orbitals tend to cancel each other, and values for the first ionisation potentials are estimated reasonably good. On the other hand, electron affinities are not estimated well using this approach as there the error cancellation does not work any more [28]. The spatial distribution of canonical orbitals seldom correlates with a notion of a localised chemical bond. However, occupied orbitals can be transformed to obtain localised orbitals for this purpose and there are several different schemes available [14].

In the case of closed shell molecules, instead of singly occupied spin orbitals, the orbitals can be taken to be doubly occupied, i.e. two spin orbitals are combined into a single spatial orbital which is occupied by two electrons with opposite spins. This is called the restricted HF (RHF) method. When each electron is allowed to occupy its own spatial orbital, without imposing double occupancy, the method is called the unrestricted HF (UHF) method [29]. The UHF method allows more flexibility for the wavefunction, and sometimes the UHF solution has a lower energy than the RHF solution. This phenomenon is called triplet instability due to the fact that the UHF wavefunction is not an eigenstate of the total spin operator but the wavefunction contains some triplet, quintuplet etc. character as well, which is also known as spin-contamination. A triplet instability indicates that the molecule has an open shell diradical state and such instability occurs usually when the molecular bonds are stretched. Singlet instabilities are less common and they occur when there exists a wavefunction with a lower energy which has lower symmetry than the molecule. In such case the electronic

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states cannot be classified according to the molecular point group. In addition to the RHF and UHF methods there is a restricted open shell HF (ROHF) method [30], where the wavefunction remains an eigenfunction of the total spin operator. The ROHF wavefunction is not restricted to a single determinant but can contain multiple determinants.

The SCF procedure is usually started with an initial guess for the orbitals obtained with some simple method (e.g. extended Hückel method) and iterated until the MO coefficients do not change any more (within some predefined tolerance). However, in general there is no guarantee that a SCF iteration should converge, and in practice one has to use additional schemes to assist the convergence. It is common that a SCF iteration oscillates between two states. These oscillations can be decreased by damping or level shifting. Damping can be introduced by taking a weighted average of consecutive density matrices. Oscillations can be reduced also by level shifting, i.e. by adding a constant value to the diagonal elements of the virtual orbitals in the Fock matrix in the MO basis, or by scaling down the off-diagonal elements between the occupied and virtual orbitals [31]. Another very efficient method to improve the convergence is the direct inversion of iterative subspace (DIIS) [32] in which the previous Fock matrices (or the density matrices) are used to construct a new Fock matrix (or a density matrix) as a linear combination. The weights of the old Fock matrices are chosen to minimise the norm of the error vector, which can be taken, for example, as the electronic gradient. A similar idea can be applied for a geometry optimisation as well. When even DIIS fails to converge (or a very tightly converged wavefunction is needed) second-order optimisation methods, like Newton's method, which need also the electronic Hessian, must be used.

For small molecules it is possible to store all two-electron integrals in the memory or on the disk. However, the number of integrals increases as N^4 in terms of the basis functions, and for large molecules storing all of them becomes impossible. Furthermore, reading the values from the disk is often slower than recomputing them. In the direct SCF approach the integrals are not stored but recomputed at each iteration, multiplied with the density matrix elements and added to the Fock matrix without the need to store them.

Although the number of two-electron integrals increases quartically, the number of significant integrals increases only quadratically when the system size becomes large enough [33]. This can be understood by considering an overlap integral between the localised basis functions. If the centres of basis functions are sufficiently far apart, their overlap is almost zero (below some threshold value). In order make use of this scaling, one has to determine before the integral is computed, whether it is significant or not. One way is to use the Schwarz inequality to derive an upper bound for the integral, but more sophisticated methods are also available [34]. The new Fock matrix can be obtained as a sum of the previous Fock matrix and a correction term which depends on the two-electron integrals and the difference between the consecutive density matrices. As the computation converges, the density matrices change less and less. Therefore, it is possible to consider only those two-electron integrals which are to be multiplied with a density matrix difference large enough to contribute to the Fock matrix [33].

The Roothaan-Hall approach described above involves always diagonalisation of a matrix and this scales as N^3. Instead of the molecular orbital coeffi-

cients, it is possible to perform the optimisation using the density matrix directly, avoiding the diagonalisation step altogether [35]. Multiplications of sparse matrices scale linearly and it is in principle possible to obtain a linearly scaling HF method for large enough systems. However, the optimisation of a density matrix is not an easy task [36], and additionally this type of approach provides only the occupied orbitals; the unoccupied orbitals are also needed for any correlation method which uses the HF state as a reference state.

2.1.2 Electron correlation methods

The energy difference between the exact nonrelativistic solution of the Schrödinger equation and the RHF energy is called the correlation energy. The difference is due to that the RHF approximation restricts the ground state wavefunction to be described by a single determinant with doubly occupied orbitals, but the many-body wavefunction cannot be represented in such a way. For some properties the HF method gives results which are in a qualitative agreement with more accurate methods. This is the case, for example, with energy differences between different molecular conformations, where the missing correlation energy is more or less constant and therefore cancels.

The correlation energy can be qualitatively divided into two contributions. In general, the wavefunction may contain multiple determinants other than the HF determinant, which have almost the same energy and which mix with the HF wavefunction. This deficiency is remedied by using a multiconfigurational wavefunction including all the necessary determinants. This type of correlation is called nondynamical (or static) correlation and although it is usually small for closed shell molecules near the equilibrium geometry, it becomes important as the bonds are distorted or broken.

Another deficiency in the HF approximation is that it is an independent particle approximation, i.e. an electron moves in an averaged field of the other electrons and it does not actually feel the instantaneous repulsion. The HF MOs do not minimise the actual electronic repulsion energy and, in reality, the electrons are further away from each other reducing the repulsion energy. This contribution to the correlation energy arising from the lack of instantaneous interelectronic interactions is referred as dynamical correlation. However, these definitions are only qualitative and there is no rigorous and unique way to distinguish between the two.

Electron correlation can be defined also from another point of view based on probabilities. There the electron correlation means that the probability to find two electrons at the specified locations is not just a product of their individual probability densities, i.e. the events are not statistically independent but they are correlated. The antisymmetry requirement excludes the possibility to find two electrons with parallel spins at the same location in space. Due to the continuity of the wavefunction, the probability to find an electron in the vicinity of an other electron with parallel spin is also diminished, and this phenomenon is called a Fermi hole. The Fermi hole is a consequence of the antisymmetry of the wavefunction having nothing to do with the Coulomb repulsion; it is already present in the HF wavefunction. On the other hand, Coulomb interactions are independent of the spin, and they reduce the probability of finding electrons close to

each other, as this is energetically more favourable. This leads to a Coulomb hole around the electron. These two concepts allow to partition electron correlation into Fermi and Coulomb correlation. As the Fermi hole can be considered to be a kinematical effect, i.e. having nothing to do with the electrostatic interactions between the electrons, the Coulomb hole is a dynamical effect due to the interactions.

Although the HF wavefunction does not include correlation effects, it is often used as a starting point to describe the electron correlation using more accurate methods. There are various approaches to include effects arising from the fact that electronic motions are correlated. In the following, some common correlation methods will be reviewed. Most of them are based on the idea of representing the wavefunction using the occupied and unoccupied orbitals obtained from the HF solution. An exception is the density functional theory, where the electron density (instead of the wavefunction) is taken to be the fundamental variable.

There are also other methods which can be used to calculated electronic correlation and some of them are mentioned here. In the R12 approach one constructs a trial variational wavefunction which contains an additional configuration with an explicit linear dependence on the interelectronic distances r_{ij} [37]. There are different implementations of R12 within configuration interaction, many-body perturbation and coupled cluster theories. The main advantages is that such a wavefunction satisfies the Coulomb cusp condition and results in more accurate energies. Even more flexibility can be added to the wavefunction by making it explicitly dependent on all powers of interelectronic distances, a form known as Hylleraas expansion [38].

In quantum Monte Carlo (QMC) methods, which basically rely on the generation of random numbers, the Scrödinger equation is solved directly and, in principle, errors are not due to additional approximations but arise from the statistical character of the method itself. There are different flavours of QMC methodology [39, 40, 41]. For example, in variational QMC the expectation value of the Hamiltonian is calculated using numerical integration making use of random sampling. In the diffusion QMC the idea is to interpret the Schrödinger equation as a diffusion equation. If the wavefunction is allowed to propagate long enough, the ground state part becomes dominant one, and the ground state wavefunction in terms of electron coordinates can be obtained. For some properties QMC can provide very accurate results.

The electronic many-particle problem can also be formulated using Green's function (instead of the wavefunction) techniques. From the Green's function one can derive various properties of the system. However, the exact Green's function is usually not known, and it must be obtained through the Dyson equation starting from the Green's function of a simple non-interacting system. This is the basis of the so-called GW approximation [42], which allows to calculate excited state properties by approximating the self-energy so that screening effects are still included [43].

There are other methods, which are actually not electronic structure methods, but include some of the correlation effects indirectly, and are computationally much less demanding than the actual electron correlation methods. Semi-empirical methods [14, 28] and molecular mechanics [14, 44] based methods include part of the correlation effects through predetermined parameters. In

semi-empirical methods some of the costly two-electron integral terms are obtained from predetermined parametric values and some are approximated to be zero. Only valence electrons are considered explicitly using minimum basis set. In molecular mechanics all interactions between atoms are parametrirsed and these parameters constitute a force field. Force field parameters are determined based on experimental data and/or computations and force fields are often parametrised for some particular purpose, e.g. to model small organic molecules, polymers or proteins.

Configuration interaction

Electron correlation can be taken into account by giving the wavefunction more flexibility than available in the HF approximation. A straightforward way to achieve this is to construct a wavefunction as a linear combination of multiple Slater determinants orthogonal to each other. Such determinants can be constructed using the orthonormal orbitals obtained from the canonical HF orbitals by exciting electrons from the occupied to unoccupied orbitals, i.e. replacing an occupied orbital with an unoccupied one in the determinant. This approach is called the configuration interaction (CI) method. Based on the variational principle, the solution is found by minimising the energy with respect to the expansion coefficients in front of the determinants.

If all possible determinants are included in the wavefunction expansion, the method is called full CI (FCI), and it gives an exact solution to the Schrödinger equation within the basis set used (with a finite basis set there is a finite number of determinants). FCI calculations are only possible with atoms or small molecules and are usually undertaken only for benchmark purposes. The full CI is an exceeding expensive method as the total number of CSFs increases factorially as a function of basis functions and depends also on the number of electrons [14]. The CI expansion for a wavefunction can be truncated, for example, taking into account only single and double excitations, which is usually called the CISD method. Single excitations do not mix with the HF reference, but affect only through the double and triple excitations. Therefore, in the CIS method the ground state properties are the same as in HF, but CIS can be useful to study excited states, at least qualitatively.

Instead of generating all the determinants, and calculating the expectation values thereof, the number of required determinants can be decreased by including only particular spin states. The main advantage in this approach is that one can specify the molecular spin state unambiguously beforehand. In atomic calculation, some additional problems with specifying spin and angular momentum may arise. The determinants can be combined so that they form CSFs, which are eigenfunctions of the total spin operator. Without spin-dependent operators, all expectation values between CSFs belonging to different spin states are zero. Use of CSFs usually reduces the dimension of the problem significantly.

A general CI wavefunction can be written as

$$|\text{CI}\rangle = \sum_i c_i |i\rangle, \tag{2.29}$$

where $|i\rangle$ are CSFs and c_i are expansion coefficients to be determined by the vari-

ational principle. The linear variation problem reduces into solving a secular equation [45], i.e. finding the eigenvalues and eigenvectors of a matrix equation

$$\mathbf{HC} = \mathbf{CE}, \tag{2.30}$$

where $\mathbf{H}$ is a matrix having the expectation values $\langle i|\hat{H}|j\rangle$ between different CSFs, $\mathbf{C}$ has the eigenvectors as columns and $\mathbf{E}$ the eigenvalues on its diagonal. The matrix elements of $\mathbf{H}$ can be expressed in terms of one- and two-electron integrals using Slater-Condon rules [46]. As the Hamiltonian contains only one- and two-electron operators, all the expectation values between CSFs which differ by more than two orbitals are zero. Additionally, all the matrix elements between the HF reference and singly excited CSFs are zero due to Brillouin's theorem [47]. Consequently, the $\mathbf{H}$ matrix has a block diagonal structure and many of its blocks are sparse; nonetheless, full diagonalisation of a large CI matrix can still be impossible. However, one is usually interested in the ground state (and maybe few lowest lying excited states), and the corresponding eigenvalues and eigenvectors can be found with iterative methods without the need to keep all the matrix elements in the memory [48, 49] and this kind of approach is called direct CI [50].

Both full and truncated CI methods are variational. However, the major drawback of all truncated CI methods is that the energy does not scale properly as a function of system size, and the dissociation of fragments yields incorrect complexation energies. These two properties are referred as size extensivity and size consistency [51]. Although these two concepts are sometimes used interchangeably, they are separate, however. These deficiencies in the truncated CI method are related to the exclusion of the particular excited state determinants from the wavefunction. As an example, CISD is equivalent to FCI for a hydrogen molecule, because there are only two electrons in the system. One could expect that for a system consisting of two non-interacting hydrogen molecules (e.g. at an infinite distance from each other), the CISD energy would be two times that of a single molecule. However, this is not the case. The total system has four electrons and the CISD lacks triply and quadruply excited states, which would be necessary to describe the system at the FCI level. The discrepancy becomes even worse, as the number of non-interacting molecules increases. Therefore, truncated CI methods are neither size consistent nor size extensive.

Size consistency is essential, for example, when relative energies are considered. A method which is not size consistent cannot give complexation energies in a proper manner. It is possible to reduce the error due to lack of size consistency using the Davidson correction [52]. On the other hand, size extensivity is a related, but a somewhat more general concept. It implies that the energy scales correctly with the particle number, and particles can also interact with each other. Size extensivity is a necessary requirement, for example, for computing potential energy surfaces correctly. Size consistency is always related to the fragmentation of two or more subunits to the infinite distance, and it additionally requires that the wavefunction behaves correctly. For example, for certain fragmentation processes the RHF wavefunction does not describe the system correctly, and, therefore, in these particular cases RHF is not size consistent, although the RHF method is always size extensive. Therefore, size extensivity does not imply size consistency.

Although FCI is an exact method and able to account for non-dynamical correlation and the multireference character in the wavefunction, truncated CI in general cannot. One way to include the multireference character in the wavefunction is to use multiple Slater determinants as reference states (instead of single HF determinant) in the CI expansion. This approach is called multireference configuration interaction (MRCI) [50] method, and it is able to account for both dynamical and non-dynamical correlation; nonetheless, it is not size extensive either.

Multiconfiguration self-consistent field

In the construction of the CI expansion, the molecular orbitals in the CSFs are taken from the HF solution, and they remain the same during the calculation. In the multiconfiguration self-consistent field (MCSCF) method the electronic energy is minimised with respect to both the molecular orbitals and the CSF coefficients. The MCSCF description of the wavefunction is necessary when the wavefunction is not even qualitatively described correctly by a single determinant. This may be the case with bond dissociation processes, excited states and sometimes also with ground states in which degenerate orbitals are only partially occupied, and the actual wavefunction is a linear combination of two (or more) electron configurations [53]. The MCSCF wavefunction is able to account for nondynamical correlation arising from degenerate electronic configurations, whereas methods like configuration interaction, Møller-Plesset perturbation theory and coupled cluster theory are based on improving the HF reference state, and to account for dynamical correlation. The MCSCF method is variational, as all the wavefunction parameters are optimised, and size extensive. It is also size consistent as far as all the appropriate orbitals are included into the configuration space.

The problematic part in MCSCF computations is often how to choose the configuration space so that all essential configurations are included. With larger systems this is perhaps not even possible, and one is able to include only part of the configurations. The computational cost increases fast with the size of the configuration space, and too many configurations make computations quickly infeasible. Although occupations obtained from the natural orbitals often give a good starting point [14], sometimes one must choose the orbitals by chemical insight or by trial and error. Due to the large number of parameters to be optimised, the optimisation may easily end up with a stationary point which is not a minimum, but this problem is usually remedied by increasing the configuration space. Instead of the iterative SCF procedure, MCSCF wavefunctions are usually optimised using other methods, such as the Newton-Raphson method, which make use of the second derivatives of the energy with respect to the wavefunction parameters in order to attain better convergence [54]. Due to these problems, the MCSCF wavefunction expansions must be kept shorter relative to the CI expansions and therefore MCSCF does not recover dynamical correlation as well as other methods.

One implementation of MCSCF is the complete active space SCF (CASSCF) method [55], in which the orbitals are partitioned into active and inactive orbitals. Within active orbitals all possible electron excitations are allowed, and these con-

figurations are included into the MCSCF wavefunction. Although all MOs are being optimised, electrons within inactive orbitals remain doubly occupied. The generalised Fock matrix can be partitioned into inactive and active parts

$$F_{ip} = 2(F_{ip}^I + F_{ip}^A) \tag{2.31}$$

$$F_{tp} = \sum_u D_{tu} F_{up}^I + 2 \sum_{uvw} d_{tuvw} g_{puvw}, \tag{2.32}$$

where

$$F_{pq}^I = h_{pq} + \sum_j (2g_{pqjj} - g_{pjjq}) \tag{2.33}$$

$$F_{pq}^A = \sum_{vw} D_{vw} \left(g_{pqvw} - \frac{1}{2} g_{pwvq} \right), \tag{2.34}$$

and i and j refer to the inactive and t, u, v and w to the active orbitals. The electronic MCSCF gradient can be calculated using these equations, and it is also possible to obtain an expression for the electronic Hessian in terms of the generalised Fock matrices, density matrices and AO integrals [22, 54]. Although all orbitals are optimised, the electron correlation is recovered only for electrons in the active orbitals. The rest of the correlation energy has to be accounted for using multireference CI methods, with MCSCF wavefunction as a reference wavefunction, or using multireference perturbation theory.

Coupled cluster

In the coupled cluster (CC) theory [56] the wavefunction is constructed by including excited state determinants into the HF ground state wavefunction, similar to the CI method. Whereas the truncation of the CI expansion resulted in the loss of size extensivity, in the CC approach size extensivity is retained. The configuration interaction method was not size consistent, because the CI wavefunction for two non-interacting systems could not be represented as an antisymmetric product of individual CI wavefunctions of both subsystems. The lack of higher excitations, which become more and more pronounced as the number of electrons increases, is the main reason for the lack of size extensivity.

In the CC approach the truncation is not done in the wavefunction but in the exponential operator generating the excitations. The basic idea is that in the wavefunction the amplitudes of higher order excitations (cf. CI coefficients) are expressed as products of lower order excitation amplitudes (disconnected terms) and as genuine amplitudes (connected terms) corresponding to the particular excitation level. When the truncation is done, the connected terms from a certain excitation level onwards are missing but all disconnected terms are still present up to infinite order. The CC wavefunction is usually built from the HF reference state, and in order to perform well, non-dynamical correlation effects should be absent [51].

The uncorrelated wavefunction can be represented by creation operators acting on the vacuum state. In the uncorrelated description all the electrons reside in the occupied orbitals, and no excitations to the unoccupied ones take place.

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When electron correlation is taken into account, the correlated motion of electrons is included through the excitations from the occupied to the virtual orbitals. Each excitation is accompanied by an amplitude related to the probability that the excitation occurs. In the CC method there are multiple ways to obtain excited configurations, each having an individual weight. The total probability amplitude of a configuration is the sum of these weights. The main idea of the CC theory is to make the wavefunction multiplicatively separable, which in turn makes the energy additively separable and guarantees size extensivity. This can be obtained by using an exponential excitation operator. In general, the CC wavefunction can be written as

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle, \tag{2.35}$$

where the cluster operator for a system containing N electrons is defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N, \tag{2.36}$$

and, for example, the operators for single and double excitations are given by

$$\hat{T}_1 = \sum_{ai} t_i^a \hat{a}_a^\dagger \hat{a}_i \tag{2.37}$$

$$\hat{T}_2 = \sum_{\substack{a>b \\ i>j}} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_i \hat{a}_b^\dagger \hat{a}_j, \tag{2.38}$$

where t_i^a and t_{ij}^{ab} are called cluster amplitudes. If the full cluster operator in (2.36) is used, the description is equivalent to the FCI method.

The remaining problem is to find the cluster amplitudes. The CC wavefunction (2.35) satisfies the Scrödinger equation

$$\hat{H}|\mathrm{CC}\rangle = E \exp(\hat{T})|\mathrm{HF}\rangle. \tag{2.39}$$

This equation can be projected onto the HF reference state and onto different excitations $|\mu\rangle$, and the resulting equations give a system of nonlinear equations

$$\langle \mathrm{HF}| \exp(-\hat{T}) \hat{H} \exp(\hat{T})|\mathrm{HF}\rangle = E \tag{2.40}$$

$$\langle \mu| \exp(-\hat{T}) \hat{H} \exp(\hat{T})|\mathrm{HF}\rangle = 0, \tag{2.41}$$

from which the values for amplitudes can be solved iteratively

Although the exponential operator is expressed as an infinite series, the projected equations contain no higher than quartic amplitude terms due to the structure of the cluster operator. With some approximate amplitude values, equations (2.41) are not zero, and these equations can be used to construct a vector function. In order to find a solution, this vector function can be optimised using, for example, Newton's method [21]. For practical purposes it is often more convenient to derive the amplitude equations using a similarity transformed Hamiltonian which yields the same energy and amplitudes [57].

The lowest order CC method giving corrections to the ground state energy is obtained when only the double excitations are present, and the cluster operator contains only the $\hat{T}_2$ term. In the exponential expression the contribution from

the double excitations are called as connected clusters. However, in the CCD wavefunction there are additional terms called disconnected clusters which arise as products of the $\hat{T}_2$ operators. Therefore, the amplitudes of the higher order (quadruple, hextuple, etc.) excitations are approximated as products of those of double excitations. These disconnected clusters are essential in making the CCD method size extensive. On the other hand, in the CID wavefunction only the doubly excited determinants would be present without contributions from any higher order terms.

The CCD method is the simplest CC approximation; including also single excitations gives the CCSD method, which scales as N^6, where N is the number of basis functions, and triple excitations the CCSDT method scaling as N^8. The contribution from the triple excitations can be also approximated perturbatively, and this approach is known as CCSD(T), which scales as N^7. One can also introduce additional approximations to the CCSD and CCSDT methods, and obtain computationally order of magnitude less demanding methods known as the approximate coupled cluster singles and doubles (CC2) model [58] and the approximate coupled cluster singles, doubles and triples (CC3) model [59]. Although the coupled cluster methods are not variational, they are size extensive, which is a major advantage as compared to the CI method.

For molecular properties the nonvariational projection method used to obtain the amplitude equations in the CC theory is not well suited because the wavefunction is not fully variational. This can be circumvented by formulating the CC energy expression in the presence of a perturbation using a new Lagrangian and a set of undetermined multipliers so that the new expression for the CC energy becomes fully variational with respect to both the amplitudes and the multipliers [57]. The properties of excited states can be obtained using the CC response theory by calculating the first derivatives of the corresponding CC energy with respect to the external field related to the property. Relaxed properties are calculated by allowing the orbitals to relax due to the external field already at the SCF stage [60], while in the unrelaxed case the orbitals do not response to the external field [58]. Closely related to the CC response theory is a so-called equation-of-motion CC (EOM-CC) method [61], which also allows the calculation of excited states. The excitations are generated from the CC wavefunction using a linear excitation operator similar to the CI method. This approach can be regarded as a conventional CI method using the similarity transformed Hamiltonian.

There is a variation of the CC theory which is based on the fact that the contribution from the single excitations is usually small when the canonical HF orbitals are used. This method is called the Brueckner coupled cluster theory [62], and there the MOs are optimised so that the amplitudes from single excitations are zero. Nonetheless, the results are usually very similar to those obtained with standard CC theory at the corresponding level.

Perturbation theory

Perturbation theory relies on the assumption that the unperturbed system described by the Hamiltonian $\hat{H}_0$ can be solved exactly, and the introduction of a small perturbation $\hat{V}$ changes the energies and wavefunctions only slightly compared to the unperturbed ones. The Schrödinger equation for the perturbed sys-

tem is

$$(\hat{H}_0 + \lambda\hat{V})|0\rangle = E|0\rangle, \tag{2.42}$$

and the exact wavefunction and energy are assumed to be given by series expansions

$$|0\rangle = \sum_{k=0}^{\infty} \lambda^k |0^{(k)}\rangle \tag{2.43}$$

$$E = \sum_{k=0}^{\infty} \lambda^k E^{(k)}, \tag{2.44}$$

where λ is a formal coupling parameter of the order of perturbation (in the final expressions $\lambda = 1$). Inserting the above series expansions into the Scrödinger equation and collecting the terms of the same order in λ together, gives a set of coupled equations. Through these equations it is possible to solve the energies and wavefunction corrections recursively up to any order. The total wavefunction is assumed to be intermediately normalised, i.e. all the corrections are orthogonal to the unperturbed wavefunction.

The Møller-Plesset (MP) perturbation theory [63] arises from the application of the Rayleigh-Schrödinger perturbation theory using the specific partitioning of the Hamiltonian into the unperturbed part and perturbation. In the MP method the unperturbed Hamiltonian is the sum of Fock operators, and the perturbation is the difference between the exact Hamiltonian (within the Born-Oppenheimer approximation) and the unperturbed Hamiltonian. The unperturbed wavefunction is the HF wavefunction, and any excited Slater determinant, obtained by replacing an occupied orbital by a virtual one, is orthogonal to the unperturbed wavefunction. The excited Slater determinants form a complete set, and corrections to the unperturbed wavefunction can be expressed in terms of these determinants.

The unperturbed total energy is a sum of orbital energies. The energy corrected to the first order is equal to the Hartree-Fock energy, and the first-order wavefunction correction involves doubly excited determinants as the contributions from singly excited states vanish due to Brillouin's theorem. The correction for correlation energy is not obtained until the second-order energy correction involving matrix elements of the perturbation between the ground state and doubly excited states. Eventually these terms reduce into an expression of two-electron integrals between occupied and virtual orbitals. The MP2 energy is the Hartree-Fock energy added with the second-order correction term

$$E^{(2)} = -\sum_{\substack{i>j \\ a>b}} \frac{|g_{aibj} - g_{ajbi}|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \tag{2.45}$$

where g is the two-electron MO integral and ε is the orbital energy. The two-electron MO integral evaluation also makes MP2 to scale as N^5 in terms of the number of basis functions. The scaling arises from the transformation of atomic orbitals into molecular orbitals. In general, there is no guarantee that the perturbation is small in order to satisfy the basic assumption of the theory; nonetheless, the second-order perturbation theory is often successful. On the other hand, it

has been demonstrated that the MP series may diverge even for simple systems, as the higher order terms become divergent, and in the case of a more complicated electronic structure, e.g. elongated bond, the divergence occurs already at lower orders [21].

Also higher order corrections to the energy and wavefunction can be evaluated. Third-order corrections (MP3) improve results only little and usually fourth-order corrections (MP4) are used instead. As the order of the correction increases, computational cost increases as well as higher order excitations are included, for example, MP4 scales already as N^7. It can be shown that in order to calculate the energy correction to order $2n + 1$ it is sufficient to have the wavefunction corrections to order n. This result is known as Wigner's $2n + 1$ rule [21]. The MP perturbation theory is size extensive, but another perturbation theory known as the Brillouin-Wigner perturbation theory is not. The MP perturbation theory is not variational, and thus the energy corrections may be too large.

The electron correlation of the core electrons is usually affected only little by chemical changes taking place at the valence shell, and it is often justified to neglect contributions from the core electrons. This approach is called frozen core approximation. If the correlation effects from the core electrons need to be taken into account, one must usually have additional basis functions at the core region to account for core correlation. Local correlation methods are based on the fact that in non-metallic systems the dynamical electron correlation is a short-range effect and therefore it is possible to use localised molecular orbitals to represent the HF reference wavefunction [64]. This reduces the number of required integrals in large systems. Similar approximation can be applied also for CC methods.

Instead of using the HF wavefunction as a reference, it is also possible to use a multiconfigurational wavefunction as a reference for perturbation theory. This approach is called multiconfigurational perturbation theory. However, the choice of an unperturbed Hamiltonian is not unambiguous as the MCSCF MOs are not eigenfunctions of any one-electron operator (cf. the Fock operator). One implementation of this type is the CAS perturbation theory (CASPT) [65, 66], where the reference state is taken to be a CASSCF wavefunction. With this approach one can include dynamical correlation effects after non-dynamical correlation is taken care of by the multiconfigurational wavefunction. It is also better suited to study excited states, because it is not based on the Hartree-Fock reference only.

2.1.3   Density functional theory

All the methods described so far are based on solving the wavefunction from the Schrödinger equation in some approximative fashion. Density functional theory (DFT) is different in a sense that there the basic variable is the electron density[4], not the wavefunction. In the original formulation, the foundation of DFT relies on the Hohenberg-Kohn (HK) theorems [67], which prove that all the ground state properties of the system are formally determined by the ground state electron density, which can be found by minimising the total energy. The energy is a functional of the density, and it is variational with respect to the density. The

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[4]DFT as such is generally applicable to any interacting system, not just electrons, but it is most often related to electronic structure calculations.

first HK theorem states that there is a one-to-one mapping between the electron density and the external potential. The proof assumes that there are two external potentials, which differ by more than a constant, but result in the same electron density. This assumption leads to a contradiction which proves that the external potential is determined uniquely by the density. The second HK theorem establishes the variational principle for the energy. The ground state energy is minimised if and only if the density corresponds to that of the ground state; all other densities give higher energies (assuming nondegenerate ground state).

In order to describe a physical system of electrons, the density has to be positive, it must be obtainable from an antisymmetric wavefunction and integrate to a given number of electrons (a property called N-representability) and it must be associated with some external potential. The last statement is related to the so-called v-representably problem; only those densities which are attainable from an antisymmetric wavefunction and related to a Hamiltonian with some external potential come into question. It is not known in general which conditions the density has to satisfy in order to be v-representable [68]. If the density is not v-representably, the HK theorems are no longer valid.

The original proof of the first HK theorem had to assume nondegenerate ground state and that the densities are v-representable. Another proof, based on constrained search formulation given by Levy [69], extends the validity of the HK theorems for degenerate states and requires the density to satisfy a weaker condition, namely N-representability. The functional $F[\rho]$ is constructed by

$$F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle, \tag{2.46}$$

where the minimisation is over all antisymmetric wavefunctions whose density is equal to $\rho(\boldsymbol{r})$. This formal procedure gives a universal form of the functional $F[\rho]$. The ground state energy is given by

$$
\begin{aligned}
E &= \min_{\Psi \to N} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}} | \Psi \rangle \\
&= \min_{\rho \to N} \left\{ F[\rho] + \int v_{\text{ext}}(\boldsymbol{r}) \rho(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} \right\},
\end{aligned}
\tag{2.47}
$$

where the final minimisation is over all those densities that yield N electrons. This theorem provides rigorous proof that the N-representable density can be used as a basic variable instead of the wavefunction, but none of the theorems cannot provide any practical scheme to actually perform computations. Such a method was suggested by Kohn and Sham [70] by using a fictitious system of noninteracting electrons.

Suppose that there are N noninteracting electrons moving in an effective potential. The orbitals are solutions of the single-particle Schrödinger, or Kohn-Sham (KS), equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{s}}[\rho](\boldsymbol{r}) \right) \varphi_j(\boldsymbol{r}) = \varepsilon_j \varphi_j(\boldsymbol{r}), \tag{2.48}$$

where the effective single-electron potential is

$$v_{\text{s}}[\rho](\boldsymbol{r}) = v_{\text{ext}}(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}\boldsymbol{r}' + v_{\text{xc}}[\rho](\boldsymbol{r}). \tag{2.49}$$

The first term is an external potential (e.g. due to the nuclei), the second term is the Hartree term due to the static Coulomb interaction arising from the electron density and the last term is the exchange-correlation potential. These fictitious electrons are still fermions so that the exact wavefunction is given by the Slater determinant constructed from the KS orbitals. The density of the system is obtained as

$$\rho(\boldsymbol{r}) = \sum_i |\varphi_i(\boldsymbol{r})|^2, \tag{2.50}$$

where the sum is over the occupied KS orbitals. The effective potential v_s is a functional of the density and depends on the external potential, and is therefore specific to the system itself. However, the exchange-correlation part is universal in a sense that it depends only on the electron density, and this functional has the same form for any system. If the exact functional form would be available, the KS scheme would give the same energy as the exact solution of the Schrödinger equation. The major advantage of the KS formulation is that a large part of the kinetic energy can be calculated straightforwardly, and everything that is not known exactly, i.e. all many-body effects, are accounted for by the exchange-correlation potential.

The Kohn-Sham scheme assumes that for an interacting system with an external potential and a given density there exists a corresponding noninteracting system with the same density, and the interactions can be described by an effective potential v_s. The HK theorems prove that this potential is unique, but do not guarantee that such a potential always exists. The problem whether one can always find an effective potential that yields the same ground state density is known as noninteracting v-representability problem. This can be proven to be true by formulating the kinetic energy functional using the density matrix which allows fractional occupations for KS orbitals [71].

For closed shell molecules the KS orbitals are usually taken to be occupied by two electrons with opposite spins, i.e. there is no spin polarisation. Unpaired spins and open-shell systems can be treated using unrestricted KS scheme in which each orbital is occupied only by one electron. Within DFT the spin-contamination has no similar meaning as in the HF method, as there is no wavefunction to calculate the expectation value of the total spin operator.

The exact form for the exchange-correlation potential in the KS equations is not known, and in order to perform actual computations with DFT some approximative form has to be used. Contrary to wavefunction methods, where accuracy can be increased simply by adding more flexibility into the wavefunction, there is no systematic way to construct more accurate functionals. Therefore, there exists a large variety of different functionals. Although DFT is variational in itself, it is no longer variational when approximate exchange-correlation functional is used. While most exchange-correlation functionals are size consistent, it is possible to construct functionals which are not size-consistent [72].

The simplest approximate form for the exchange-correlation potential is obtained from the uniform electron gas model. There the kinetic energy and exchange energy can be calculated analytically [73, 74], and for the correlation energy analytical solutions are known in the high and low density limits. At the intermediate densities the correlation energy can be computed using quantum Monte Carlo simulations [75]. This knowledge of the total energy as a function

of the density can be used to construct the local density approximation (LDA) for the exchange-correlation potential [76]. The LDA is a local functional of the density so that the energy at a given point depends only on the density at that point.

The LDA is exact for a uniform electron gas, and it is a good approximation for systems where the electron density varies sufficiently slowly. However, in systems where the electron density is inhomogeneous, like in molecules, the LDA is not that accurate anymore. Additionally, the LDA has incorrect asymptotic behaviour for the exchange energy density, and to correct the asymptotic behaviour, a gradient dependent functional was introduced [77, 78]. In order to account for irregularities in the density, the exchange-correlation potential can be made dependent on the gradient of the density as well. These kinds of functionals are known as generalised gradient approximations (GGAs) and are also referred as semi-local. The gradient dependent part can be added as a correction to the LDA exchange [77] and correlation parts [79, 80], or the correlation energy can be reparametrised completely [81]. Usually these functionals contain few parameters which are empirically fitted to produce particular set of results in the best possible way, but it is also possible to construct functionals without any empirical input [82].

The exchange-correlation potential can be made dependent also on the kinetic energy density obtained from the KS orbitals. These type of functionals are called meta-GGAs [83, 84]. Furthermore, the exchange-correlation functional can explicitly depend on the occupied orbitals themselves, and these functionals are called hyper-GGAs, including exact exchange and nonlocal correlation. This is the case, for example, with so-called hybrid functionals where the exact exchange term (cf. the Hartree-Fock theory) is mixed with the exchange in DFT in such a proportion that the resulting functional produces the desired quantities in the best possible way [85, 86, 87, 88, 89]. Some hybrid functionals have turned out to produce some molecular properties very well and gained wide popularity[5]. Further extensions like dependence on the unoccupied orbitals are also possible [72].

As all approximations, also approximate functionals have their shortcomings. From the Hartree term in the KS potential in equation (2.49) one can see that as the fictitious electron interacts with the electron density through the Coulomb interaction, it also interacts with itself. If the exchange-correlation potential were exact, it would precisely cancel this spurious effect known as self-interaction. However, with approximate exchange-correlation functionals this is not the case. The unphysical self-interaction causes orbitals to 'feel' an incorrectly large charge from the other electrons, and this makes orbitals to be spatially too extended [90].

One approach to remove the self-interaction is the optimised effective potential (OEP) method. In the OEP method the total energy is taken as a functional of ithe KS orbitals, e.g. with the exact exchange term. The effective potential in KS equations is determined variationally so that the orbitals satisfy the KS equations and simultaneously minimise the energy. This scheme is computationally very complicated leading to integral equations but approximative schemes are also available [91].

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[5]An example of this kind of 'unholy alliance' is the popular B3LYP functional.

The exact exchange-correlation potential should decay asymptotically as r^{-1} to zero, but approximate functionals usually exhibit exponential decay. This can be qualitatively understood by considering an electron taken away from an atom. As the electron is taken sufficiently far away from the other electrons and the nucleus, it experiences only the static Coulomb interaction with the net charge. However, in DFT the isolated electron still experiences repulsion of its own density through the Hartree term and this should be eliminated by the exchange term. Due to the incorrect decay, Rydberg states are usually missing in DFT [91].

Another phenomenon that can be seen when DFT is formulated using ensembles allowing fractional particle numbers, is that the exchange-correlation potential has a discontinuity as the number of particles passes through an integer [72]. This phenomenon is called derivative discontinuity. Current approximate functionals which are all continuous with respect to particle number cannot account for this behaviour. Other problematic issues with LDA and GGAs include heavy elements, negative ions, neglect of dispersion forces and strongly correlated systems [91].

Although DFT is a ground state method, it is possible to extend its applicability to time-dependent systems and their properties, like excitation energies, through time-dependent DFT (TDDFT) [92, 93]. Instead of actually solving the time-dependent KS equation, which is also possible, one can combine TDDFT with linear response theory. Using the property that the frequency dependent response has discrete poles at the excitation energies, allows the problem to be formulated as an eigenvalue equation [94], which results in the excitation energies and oscillator strengths. Usually TDDFT relies on the so-called adiabatic approximation, where the complicated time-dependent exchange-correlation kernel [90, 95, 96] is approximated simply by using the same functional as with the ground state ignoring the time-dependence. In addition to excitations, other frequency dependent properties can be calculated. Furthermore, it is possible to extend DFT to include phenomena like finite temperature, electric currents and magnetism [97] and relativity [98].

The Hartree term is equivalent to the interaction between two continuous charge distributions, and a direct evaluation in AO basis would require computation of four-centre two-electron integrals, similar to the HF method. However, the electron charge distribution can be approximated using auxiliary basis functions [99, 100, 101], which in turn reduce the integrals into three-centre integrals. Additional, if the centres corresponding to the remaining AO basis functions are sufficiently far apart, the integral can be neglected. The asymptotic scaling in this case becomes N^2. This method is called the density fitting or resolution of the identity[6] (RI). The errors introduced by this approximation are usually much smaller than other errors, such as due to finite basis sets [102]. A similar procedure can also be applied for the HF, MP2 and CC methods to speed up computations.

There are also other ways to speed up the evaluation of the Hartree term. One can solve Poisson's equation to find out the electrostatic potential due to the charge distribution, and use this potential in the integration over the space

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[6]This is not equivalent to the resolution of the identity used in the mathematics since the Coulomb metric is used.

to obtain the Coulomb energy. The Coulomb interaction can also be evaluated using so-called fast multipole method (FMM) [103], where the interaction of two charge distributions sufficiently far apart is approximated using the multipole moments of the charge distributions. With FMM it is possible to achieve linear scaling in the evaluation of the Coulomb interaction [104].

The local or semi-local exchange-correlation term, on the other hand, can be evaluated by numerical integration (quadrature), as it depends only on the density (and possibly its derivatives). The points of the integration grid are usually taken to be spherically distributed around the nuclei with varying radial density. This integration grid has similar role in the accuracy of the computation as the basis set: The grid has to be dense enough to accurately account for the exchange-correlation energy. The cost of this integration scales linearly for large enough systems [105].

2.2   Basis sets

Wavefunctions are represented using MOs, which in turn are functions of the electron coordinates. Of course, the wavefunctions and MOs could be represented using a grid of points. However, as the number of points and orbitals increases, this kind of approach becomes soon infeasible due to memory requirements as there are three spatial coordinates for each electron. There are real-space methods like finite element and finite difference methods which can take advantage of so-called multigrid techniques, and solve, for example, the Kohn-Sham equations, or sometimes also the Schrödinger equation for a few particles in a special geometry, as a differential equation with particular boundary conditions [106, 107]. Advantages of real-space methods are that linear scaling approaches are more straightforward to implement using multigrid techniques [108] and multiple-length scales can be included. There is no need to perform Fourier transforms between real and reciprocal spaces as in the plane wave approach described shortly. However, molecular properties depend on the grid, and the movement of nuclei with respect to the grid introduces artificial Pulay forces.

With MOs a more efficient way is to use basis functions, and expand the MOs as linear combinations in terms of these functions. The essence it to choose the basis functions in such a way that they 'resemble' the atomic orbitals, but on the other hand the computation of integrals must be efficient. A set of basis functions can be parametrised beforehand and thereafter used as such in computations. Basis functions in turn can be represented either numerically or algebraically. In numerical approach basis functions are evaluated in a set of grid points. However, this is computationally costly as every basis function has its own set of values at every grid point. In algebraic approach basis functions are represented using functions with a set of parameters determining their form.

The algebraic form of suitable basis functions depends on the problem at hand. With periodic boundary conditions periodicity is required also from the basis functions and, therefore, one can use plane waves [109]. Plane waves do not depend on the position of the nuclei; the Pulay forces are absent, and the basis set size is controlled by the energy cutoff only. Another advantage is that deriva-

tives in real-space become simply multiplications in the reciprocal space, and transformation between these spaces can be efficiently done using fast Fourier transform (FFT). An eigenvalue equation is solved for a set of reciprocal lattice points, which gives the energy bands as eigenvalues and wavefunction coefficients as eigenvectors. For DFT the total electron density in real-space is needed; it can be efficiently obtained by first transforming each wavefunction into the real-space with FFT and summing all contributions [110]. Plane wave methods are intimately connected to pseudopotentials, as an adequate description of the core electrons would need very high energy cutoffs.

On the other hand, in finite systems the basis functions are usually taken to be localised and centred at the nuclei. In the first approximation the MOs can be thought to arise from combinations of the atomic orbitals. Therefore, the Slater type orbitals (STOs), which are derived from analytic solutions of a hydrogenic one electron atom, would seem to be ideal candidates as basis functions. A general STO basis function has the form

$$\chi_{nlm}^{\text{STO}}(r, \theta, \varphi) = N Y_{lm}(\theta, \varphi) r^{n-1} \exp(-\zeta r),\tag{2.51}$$

where $Y_{lm}(\theta, \varphi)$ are spherical harmonics, n, l and m are the quantum numbers and N is the normalisation factor. However, the evaluation of the four-centre two-electron integrals turns out to be very difficult with STOs. The most time consuming step is usually to evaluate the required integrals over the basis functions. Therefore, the most widely used basis functions are Gaussian type orbitals (GTOs) [111], which allow the evaluation of integrals to be done almost analytically [21]. A spherical GTO basis function can be represented as

$$\chi_{nlm}^{\text{GTO}}(r, \theta, \varphi) = N Y_{lm}(\theta, \varphi) r^{2n-l-2} \exp(-\alpha r^2).\tag{2.52}$$

GTOs have no such physical interpretation as STOs; actually they behave differently at the nucleus (derivative is zero) and farther away decay faster than STOs. Therefore one usually needs more GTOs than STOs to achieve the same accuracy. In spite of these shortcomings, GTOs are nowadays used almost in all quantum chemistry packages, and even if integrals could be calculated using STOs, they would not necessarily be superior to GTOs [31]. GTOs can be represented with cartesian or spherical Gaussians. The latter choice is usually preferred, due to the fact that from d functions onwards cartesian Gaussians become linearly dependent with respect to lower angular momentum functions, but spherical Gaussians do not suffer from this problem [21].

There are number of different schemes to evaluate Gaussian integrals such as Obara-Saika [112] and McMurchie-Davidson [113], which employ recursive formulas for integrals. Both of these method reduce the numerical integration into evaluation of a so-called Boys function. Another way to do the integration is the Rys quadrature [114], which is based on the idea of using the Gauss quadrature to evaluate an integral over a polynomial and a weight function exactly. This reduces the integral evaluations into finding the roots and weights of the Rys polynomials. The details of the integral evaluation, especially for two-electron integrals, are often quite involved [21].

The Gaussian basis functions are accompanied by a set of parameters (coefficients and exponents), which give the functions their specific spatial distribution. Usually these parameters vary from one element and basis set to the other,

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and they are usually predetermined so that the same parameters can be used in different computations and the results are commensurate. There exists a wide variety of different kinds of Gaussian basis sets and there are several different approaches to construct them. A simple method to obtain a basis set is to make linear combinations of GTOs and fit them to STOs in the least squares sense [115]. Another way to construct a basis set is to optimise all the parameters in the linear combination of GTOs so that they minimise the SCF energy for an atom [116]. Instead of complete optimisation, the exponents can be required to be proportional (so-called even-tempered sequence) to each other and fewer parameters need to be optimised [21]. Instead of optimising all the parameters, which is costly, one can construct fixed linear combinations of primitive Gaussians with fixed contraction coefficients and use these predetermined contractions as basis functions in actual computations.

There are two different contraction schemes. In the segmented contraction scheme each contracted Gaussian has its own primitive Gaussians which do not contribute to any other contraction. Further flexibility and computational efficiency can be obtained with a general contraction scheme [117] where the same primitives occur in all contractions but with different coefficients. An example of basis sets using general contraction scheme are so-called correlation consistent basis sets cc-pVDZ, cc-pVTZ, etc. [118]. These basis sets are optimised to be used with correlation methods. Another example are atomic natural orbital (ANO) basis sets [119] which are especially designed for correlation methods. The basis functions are constructed so that they approximate the atomic natural orbitals obtained with the CI method. The ANO approach allows systematic improvement of the basis set in an optimal fashion.

When there is only one basis function for each orbital, the basis set is called minimal basis set. To increase the flexibility of a basis set (and accuracy of the computation), one can use more than one contraction (or primitive Gaussian) for each orbital. These kinds of basis sets are usually called double-ζ, triple-ζ etc. depending on the number of independent basis functions assigned for each orbital. As the core orbitals are usually only weakly affected by chemical bonding, they are often represented by a single contraction, and it is sufficient to add more flexibility to the valence orbitals only. This kind of basis set is called a split-valence basis set.

In molecules the electron distribution is often different from atoms using which the basis sets are usually optimised. This can be compensated by polarisation functions which are otherwise similar to normal basis function but are of higher angular momentum type than the valence orbitals in the element. In the case the electron distribution differs much from the ground state, it may be necessary to add diffuse functions which have small exponent allowing the electrons to spread farther away. Diffuse functions can be needed with anions, excited states and intermolecular complexes. A simple rule of thumb with basis sets is, the larger the better; however, one must keep in mind that some molecular properties are more affected by the basis set than others. Simply taking one of the standard basis sets and including all polarisation and diffuse functions is sometimes just not enough. For example, when the core electrons are included in a correlation calculation or properties which are strongly affected by the core electrons are studied, special basis sets including the core polarisation functions are

required.

On the other hand, with heavy elements the number of core orbitals becomes very large compared to valence orbitals, even though the core would be represented using a minimal basis only. The contribution of the core electrons and the nucleus can be combined and represented using effective core potentials (ECPs) [120, 121] (also known as pseudopotentials). ECPs are potentials which have a particular radial structure, and they combine the effects of the nucleus and the core electrons together. The valence (and possibly sub-valence) electrons see only this effective potential without explicit core electrons. ECPs are designed to reproduce the valence electron structure based on an all-electron calculation. Although the valence electrons themselves are only little affected by relativity, the core electrons in very heavy elements can reach velocities which are comparable to the speed of light. Therefore the core electron orbitals get contracted, which in turn enhances the nuclear screening and expands the orbitals of the valence electrons. With ECPs it is possible to include part of the relativistic effects (scalar relativistic effects) without using any relativistic correction to the Hamiltonian. This requires that ECPs have been parametrised using methods including relativistic effects. On the other hand, spin-orbit effects cannot be accounted for without explicit terms in the Hamiltonian.

2.3   Molecular properties

So far the only molecular property that has been discussed is the total energy which is to be minimised in order to obtain the ground state wavefunction. However, there are many properties which can be experimentally measured and are therefore of computational interest. As the system is perturbed, its total energy changes and the energy can be expressed as a Taylor expansion in terms of the perturbation. The derivatives of the energy with respect to the perturbation are evaluated at zero perturbation strength, and the derivatives are system specific and related to molecular properties [122]. In principle, these derivatives could be obtained using numerical differentiation, e.g. by calculating the total energy at different perturbation strengths. However, this is computationally costly and often numerically inaccurate. A better way to obtain the derivatives is to derive analytic expressions for them and evaluate these expressions directly [123]. For example, the analytic evaluation of nuclear or molecular gradients enables efficient geometry optimisations for molecules. Analytic derivatives can be derived also using second quantisation, which isolates all basis set effects from the Hamiltonian, and there is no need to incorporate orthonormality of MOs into the energy expression [124].

The energy depends on the perturbation explicitly through the Hamiltonian (e.g. electric field, geometric perturbation) and implicitly through the wavefunction parameters (e.g. MO coefficients, cluster amplitudes). The change of the wavefunction due to the perturbation is called the wavefunction response. For fully variational wavefunctions the energy is stationary and its derivative with respect to all wavefunction parameters is zero.

The Hellmann-Feynman theorem [125, 126] states that the derivative of the energy with respect to some parameter is equal to the expectation value of the

derivative of the Hamiltonian with respect to the same parameter. The Hellmann-Feynman theorem is valid for exact wavefunctions and, additionally, to approximate wavefunctions which are fully variational (variational with respect to all wavefunction parameters), like the Hartree-Fock or MCSCF wavefunction[7]. Truncated CI is not fully variational even if the energy is determined by the variational principle. However, the Hellmann-Feynman theorem holds no longer with perturbation-dependent basis sets, e.g. with basis functions depending on the nuclear positions. In this case, there appears additional terms which are called wavefunction response and they arise from the changes in the MO coefficients with respect to the perturbation. For example, with nuclear gradients there arises terms called Pulay forces [128] due to the derivatives of basis functions with respect to nuclear coordinates; in the complete basis set limit these forces vanish. For wavefunctions which are not fully variational, like truncated CI, coupled cluster theory or perturbation theory, the Hellmann-Feynman theorem is not valid even in the complete basis set limit, meaning that the expectation values of the operators do not agree with the values obtained as derivatives of the energy.

For fully variational wavefunctions the explicit evaluation of the wavefunction response is not needed in order to calculate the molecular gradient, as the energy is stationary with respect to all wavefunction parameters. For molecular Hessian, i.e. the second-order derivatives, the first-order wavefunction response is needed. In general, for fully variational wavefunctions the nth order derivatives of the wavefunction parameters determine the energy derivatives up to order $2n + 1$.

For nonvariational wavefunctions also the wavefunction response is needed for the molecular gradient, as the energy is not variational with respect to all wavefunction parameters and it has to be evaluated for all perturbations separately. However, there is a way to avoid this. The problem can be formulated so that nonvariational wavefunction parameters are constrained using Lagrange's method of undetermined multipliers. This is done by imposing a constraint including a new set of parameters which are chosen so that the new energy expression, or Lagrangian, is fully variational with respect to all parameters and its value coincides with that of the energy. As soon as the undetermined multipliers are determined from a set of linear equations, the gradient of the Lagrangian can be evaluated as any other fully variational energy expression [124]. Instead of solving the first-order response equations for each perturbation separately, it suffices to solve a single set of linear equations. The Lagrange multipliers can be taken as wavefunction parameters of the Lagrangian. For Lagrange multipliers there is actually a rule that the derivatives of the Lagrange multipliers of order n determine the energy derivatives up to order $2n + 2$ [129]. Therefore, to calculate the molecular gradient only the Lagrange multipliers, but not their derivatives, need to be solved.

The equilibrium geometry is probably to most important molecular property. Within the BO approximation the total energy of the system may be described as a function of nuclear coordinates. The surface formed by the energy and the nu-

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[7]If the MCSCF wavefunction is based on the RHF reference, it is not variational with respect to triplet rotations, and so-called restricted-unrestricted approach is needed [127].

clear coordinates is usually called a potential energy surface (PES). The equilibrium and transition state structures correspond to stationary points on the PES. In order to locate stationary points, one needs to evaluate molecular gradients (first derivatives of the total energy) with respect to the nuclear coordinates and find out when they become zero. Employing some optimisation algorithm in combination with molecular gradients allows one to do geometry optimisation for the molecular structure [130].

The nature of the stationary point can be characterised using the second derivatives of the total energy with respect to normal coordinates, which is also called molecular Hessian, to determine whether the point is a local minimum or saddle point. This computation also yields the harmonic frequencies of the molecule. For a SCF wavefunction, the second derivatives can be calculated efficiently using analytic derivative method. However, the second derivatives of the energy involve first derivatives of the density matrix and MO energies as well [14]. They can be obtained by solving the so-called coupled perturbed Hartree-Fock equations. In practice, these equations determine how much the MOs are changed to the first order by the perturbation. If the Hessian has no negative eigenvalues, the stationary point corresponds to an equilibrium structure; on the other hand, at least one negative eigenvalue corresponds to a transition state.

Other important molecular properties include the response to the external electric and magnetic fields. In general, properties of a system can be measured by perturbing the system and measuring its response. Often the perturbations are weak and response is linear, i.e. it is linearly proportional to the strength of the perturbation. This proportionality constant can be defined as a property of the system. For example, an induced dipole moment is proportional to the electric field and the proportionality constant is called polarisability. Response theory can be extended beyond linear regime to include non-linear responses as well.

Magnetic properties can be measured using NMR techniques [131]. An external magnetic field may change the equilibrium electron distribution and induce additional current density and magnetic moments in a molecule. These kinds of induced magnetic fields give rise to quantities like nuclear magnetic shielding tensor (related to chemical shift) and indirect nuclear spin-spin coupling tensor, which can be theoretically computed [132]. However, including magnetic field into the Hamiltonian is more complicated. The magnetic field couples through the kinetic energy operator in a form of the magnetic vector potential. Although the magnetic field is unique, the magnetic vector potential depends on the choice of the origin. This origin is usually called the gauge origin, and with finite basis sets and approximate wavefunctions the results are dependent on the choice of the gauge origin. In gauge-including atomic orbitals (GIAO) method this problem is circumvented by including the gauge origin into the basis functions themselves so that the gauge origin dependence cancels. In individual gauge for localised orbitals (IGLO) approach the idea is to use different gauge origins for different MOs and try to minimise the error.

2.4 Solvation models

Chemistry in a gas phase can often be described using only isolated molecules due to low molecular density of the system. On the other hand, chemical processes taking place in a condensed phase (liquid or solid) may be affected by the interactions arising from the surrounding molecules and therefore intermolecular interactions may have important role in the chemistry of the system. An obvious way to account for intermolecular interactions is to include surrounding molecules explicitly into the system. However, the number of molecules in the vicinity of the chemical species in question can easily become very large and computationally infeasible. Another way the include solvation effects is to use implicit solvation models, also known as continuum solvation models [133]. Nevertheless, static calculations with explicit or implicit solvation models cannot account for dynamical effects arising from the movement of molecules. They can be accessed only by performing molecular dynamics simulations.

In the continuum solvation model the solute molecule is placed into a cavity and its interactions with the solvent molecules are taken into account using simplified approximations. Of course, in case the solvent molecules form bonds with the solute, continuum solvation models cannot account for such effects. Also specific interactions, like hydrogen bonding and hydrophobic interactions, latter of which arise from the orientational rearrangements of water molecules in the vicinity of hydrocarbon molecules in the first solvation shell, cannot be accounted for. Continuum solvation models are able to account for the electrostatic interactions, but do not take into account other interactions explicitly. For example, to account for dispersion interactions even qualitatively, a correlated computational model (e.g. coupled-cluster or perturbation theory) has to be used. The model system should also include explicit solvent molecules in order to have dispersion interactions present in the first place. Another approach is to parametrise the dispersion energy based on experimental or theoretical data, and use them as an empirical input for the dispersion contribution in the solvation energy.

The main contributions of the solvation free energy arise from creating the cavity and from dispersion and electrostatic interactions between solvent and solute [134]. The creation of the cavity involves rearrangement of solvent molecules in order to make a void into the medium and it destabilises the system. On the other hand, dispersion interactions are attractive and therefore stabilise the system. Usually these two interactions are accounted for by using empirical parameters derived from experimental solvation data, which depends on the particular atom types, and this contribution is made proportional to the surface area of the cavity. The shape of the cavity and the dispersion interactions are usually determined by the first solvation shell, and are therefore short-range effects. The electrostatic interactions are due to the interaction of solute and solvent charge distributions, and they are long-range effects. The charge distribution of the solute creates an electric field which can be represented by a charge distribution on the surface of the cavity. The dependence is governed by electrostatics and depends on the dielectric constant of the medium. The charge distribution on the surface of the cavity in turn creates an electrostatic potential which interacts with the charge distribution of the solute. This additional interaction term can be added to the Hamiltonian, and thereby determine both the charge distribution

on the surface and the wavefunctions (which give arise to the charge distribution of the solute) iteratively so that the total energy is minimised. If the charge distributions are obtained in a self-consistent manner so that one charge distribution polarises the other and vice versa, until they are in equilibrium, the model is called a self-consistent reaction field (SCRF) solvation model [135].

In the most simple case the shape of the cavity, which the solute is placed in, can be assumed spherical. Depending on the charge and the dipole moment of the solute, different kinds of interaction models for the electrostatic interaction can be derived, like the Born and Onsager models [14]. If the dipole moment is not a constant but determined from the charge distribution of the solute, these become SCRF models. It is also possible to generalise electrostatic interactions into higher multipole moments. Although numerically appealing, a spherical cavity is not necessarily a very good approximation and it is better to create the cavity based on the structure of the solute molecule.

One implementation of the SCRF method is the polarised continuum model (PCM) and its variations [136]. In the first approximation the cavity is formed as an intersection of the spheres with specified radii located at the nuclei. Isodensity surface of the electron charge density can also be used to define the cavity (this model is called IPCM). The cavity surface is further partitioned, or tesselate, into triangular elements each with a point charge at the centre. These charges give arise to the reaction field and are determined iteratively based on how they interact with the molecular charge distribution. Additionally, the appropriate boundary conditions for the electric field and the potential at the solute-solvent interface has to satisfied [137].

Instead of using dielectric boundary conditions, one can simplify equations by using scaled conductor boundary conditions. This model is known as the conductor-like screening model (COSMO) [138]. When the continuum is approximated as a conductor, the electrostatic potential at the solute-solvent boundary vanishes. The screening charges on the boundary are chosen so that this condition is satisfied. The finite dielectric constant can be accounted for by scaling the screening charges by an appropriate factor [139]. An extension of COSMO is COSMO-RS [140, 141] which uses COSMO results as an input to calculate thermodynamic quantities.

2.5   Accuracy of methods

Computations are usually made using some model which is an approximation of the exact theory. Therefore, computational results always include some error, i.e. they differ from the exact result. Basically, these errors are due to the choice of the basis set, the approximate wavefunction used and the choice of the Hamiltonian, i.e. at what level relativistic effects are included. Additionally, there may arise some numerical error due to the finite precision of computers; however, these errors are usually insignificant compared to other sources of error.

Detailed discussion and actual comparison of different computational levels is beyond the purpose of this introduction and there exists extensive literature on the subject; here are mentioned just a few general references: Comparison of different wavefunction methods for properties of small molecules has been inves-

tigated in [21]. An overview of the performance of different exchange-correlation functionals has been discussed in [142]. Comparison of basic molecular properties, including both density functional theory and wavefunction methods, can found in [14, 28, 143, 144].

In order to obtain accurate results, the method should be able to describe the system sufficiently well, i.e. if the molecule has a complicated multi-reference electronic character there is little hope that any single-reference based method will work. Depending on the molecular property and the computational method used, it may be possible to achieve the basis set limit, i.e. the results do not change anymore with increasing the number of basis functions. However, in practice this is not always possible and the basis set limit has to be estimated by extrapolating [21].

Wavefunction based electron correlation methods are inherently more accurate than the Hartree-Fock approximation. However, the convergence of the results in terms of the basis set is also slower and electron correlation methods require significantly larger basis sets in order to describe the effects of electron correlation properly. Using electron correlation methods with inadequate basis sets is not expedient. Even if the computed results would appear to agree with experimental values, this does not necessarily mean that the method is as accurate as it seems to be, or that the computational level is sufficient; it may be due to cancellation of errors. There the different errors are of opposite sign and cancel.

In the context of this thesis some molecular properties are of special interest and they are discussed next. In determining the equilibrium geometry and the interaction energy of a molecular complex, the intermolecular interactions and their accurate description are essential. There are two different types of approaches to calculate interaction energies in a molecular complex: perturbational and supermolecular [145]. In the perturbational approach the unperturbed ground state wavefunction is taken to be a product of the ground state wavefunctions of the individual fragments while the perturbation operator contains all the intermolecular electrostatic operators. Contributions to the Coulomb, induction and dispersion energies are obtained as first- and second-order corrections. In symmetry-adapted perturbation theory (SAPT) [146] there are additional terms which account for the Pauli exclusion principle and introduce the exchange energy contribution to the total interaction energy. The interaction energy is a sum of all these contributions. In the supermolecular approach the interaction energy is obtained as a difference between the total energies of the complex and the individual fragments. In order to work, the computational method must be size consistent and the basis set superposition error has to be accounted for [147].

A hydrogen bonded system is a special kind of molecular complex. A hydrogen bond is formed when a proton acceptor with lone pair electrons or polarisable π electrons interacts with a proton donor, in which the hydrogen is covalently bonded to an electronegative atom and the hydrogen proton is partly deshielded as the electron density is moved towards the electronegative atom [148]. There exists a large variety of different kinds of hydrogen bonds with different bond energies varying from about 10 kJ/mol to over 100 kJ/mol. Although hydrogen bonds are much weaker than covalent bonds, they are usually stronger than van der Waals interactions [149].

At a conceptual level it is possible to partition the different energy contribu-

tions in a hydrogen bond into different parts [150]. The electrostatic interaction between the molecules is due to their static charge distributions. Next contributions is due to the antisymmetry of the wavefunction and it leads usually to a repulsive force between the molecules and due to this it is called the exchange repulsion energy. In reality, the charge distributions in the molecules are not static but they are able to deform one another leading to a redistribution of the electron density. This contribution is called the induction energy. All of these contributions can be already accounted for at the Hartree-Fock level. However, including the correlation affects also these energy contributions as well. The energy contribution which is not present at a non-correlated level, or in approximate density functionals, is dispersion energy. It is due to charge fluctuations in molecules and it is an attractive interaction present between all molecules [149]. Although dispersion is not a dominating part of the interaction in a hydrogen bond, it may be significant, especially if the other contributions are not very strong. These components of the interaction energy can give some insight into the interaction itself but it is only the total interaction energy which is physically observable.

There has been a number of studies of computational modelling of hydrogen bonds [151, 152, 153, 150, 154]. The lowest computational level is often said to be MP2 with sufficiently large valence double zeta basis set including polarization and diffuse functions at the non-hydrogen atoms in order to obtain reliable geometries; nevertheless, for accurate prediction of energies even larger basis sets are usually required [155]. In general, density functional theory with gradient corrected or hybrid functionals yields qualitative agreement with MP2 calculations. Although energetic and structural properties are rather good, intramolecular frequency splittings involving the hydrogen are rather poorly described as compared to MP2 [156]. Coupled cluster calculations, e.g. at the CCSD and CCSD(T) levels, give also reliable results for hydrogen bonds but they are not applicable for very large systems [154]. Although standard density functional theory often works for some properties of hydrogen bonds, there are energy contributions which are completely missing; dispersion interactions are not accounted for by standard exchange-correlation functionals [157, 158]. Dispersion interaction originates from the correlations between dynamic electron density fluctuations at well separated positions and cannot be accounted for by local or semi-local functionals [90]. However, dispersion interaction can be estimated by calculating the second-order dispersion energy contributions through electric polarisabilities using time-dependent density functional theory. This approach yields results in a reasonable agreement with MP2 as far as appropriate hybrid functionals are used [159].

Chapter 3

Results

Various chemical systems have been investigated, and several computational methods have been applied in the course of this work. These studies offer different perspectives on what can be done using computational modelling. In this chapter the articles included in the thesis are discussed. The computational studies include number of topics. Hydrogen bonding and solvent effects in a pyridine-methanesulphonic acid acid-base complex have been studied, torsion potentials of bipyridines were parametrised for a force field, metal coordination in a supramolecular complex was modelled, hydrogen bonding between polyamide and phenolic resins and the effect of water was studied and optical properties of silicon nanoclusters were investigated.

In most of the molecular systems studied here the computational methods were used to investigate phenomena more closely, and from another point of view as compared to experiments. Often it was also necessary to restrict the system size considerably to be able to use quantum chemical methods in the first place. Many of the obtained results were either inaccessible with experimental techniques, or the experiments would have been very difficult to perform. Different computational methods have been applied in this work. Density functional theory was used in all studies, but wavefunction based methods such as perturbation theory and coupled cluster theory were also applied when appropriate. Most of the computations were performed using GAUSSIAN program packages [160, 161] except in Paper V where TURBOMOLE 5.7 program package [162] was used.

3.1   Pyridine-methanesulphonic acid

Pyridine based molecules, e.g. bipyridines and other derivatives, are very versatile building blocks for supramolecular structures due to their ability to form coordination compounds with metal atoms and hydrogen bonds with acids (see e.g. [163, 164]). The pyridine-methanesulphonic acid complex is a common subunit in many supramolecular materials and thus an interesting model system to study. To model the interactions between pyridine and methanesulphonic acid, and to account for solvation effects, appropriate computational methods have to be chosen. The main interaction in the complex is hydrogen bonding, different aspects of which have been studied computationally [151, 152, 155, 165, 166, 153].

Comparisons of different properties, such as vibrational frequencies and NMR chemical shifts obtained both computationally and experimentally have been carried out [167, 168]. Predictions of the energy of the hydrogen bond can be done by calculating the energies of the isolated monomers and their complex, which in principle is straightforward but involves basis set superposition error (BSSE) leading usually to overestimation of complexation energies. BSSE can be estimated using counterpoise correction (CP) scheme [145], in which two separate single point computations for both fragments are performed first using their own basis functions only and then also basis functions from the other fragment. The difference yields an estimate for the energy correction due to BSSE.

Polarised continuum models (PCMs) and explicit cluster models for hydrogen bonds have been investigated using ammonia-hydrogen halide complexes as a model system [169]. In aqueous environment, i.e. in solvents with high dielectric constants, both the cluster model and PCM can predict proton transfer. The results obtained using both approaches are in good agreement for strongly interacting complexes. However, for less acidic proton donors, PCM does not predict proton transfer although the explicit cluster model does, whereas in nonpolar solvents, the explicit cluster model and PCM agree reasonably well for all cases.

The presence of water molecules has been found to assist the intramolecular proton transfer by lowering the energy barrier in tautomers of adenine [170]. Intramolecular hydrogen bonding and proton transfer due to electronic excitations has been modelled with a variety of different methods [171]. Conventional quantum chemical calculations can be combined with transition state theories to obtain dynamical information about hydrogen bonds and their reactions [172]. Intramolecular proton transfer rate was enhanced by adding water to bridge the proton donor and acceptor sites, and it was also observed that proton transfer takes place via a concerted mechanism.

Pyridine-water complexes have been studied computationally and comparisons with experimental FT-IR data have been made [173]. Both DFT with the B3LYP functional and MP2 methods with double zeta valence basis including polarisation and diffuse functions on all atoms are found to give sufficiently reliable results for intermolecular distances, interaction energies and vibrational properties. However, when the water molecule is bonded to the π electrons of the methyl-substituted pyridine, DFT cannot adequately account for dispersion interactions present in such a bond [174]. Pyridine-HCl complexes have been studied using computational methods and NMR and FT-IR spectroscopy in argon and nitrogen matrices [175]. It was found that the complex has a traditional hydrogen bond in argon matrix, but an ionic hydrogen bond in nitrogen matrix suggesting that the nitrogen environment influences the complex.

Pyridine and related nitrogen containing six-member ring molecules and the effect of hydrogen bonding in different solvents has been studied by Takahashi *et al.* using vibrational spectroscopy [176]. They found that several pyridine vibrations shifted significantly to higher frequencies (as much as $+10$ cm^{-1}) for solvents which were able to make hydrogen bonds with pyridine. In non-hydrogen bonding solvent the shifts were only ± 2 cm^{-1}. They concluded that the shifts were due to hydrogen bonding and not due to plain solvent effects. The influence of chemical substitutions on the protonation of pyridine was studied at different

computational levels and compared with experimental results [177]. The best agreement with experiment was obtained at the MP2 level using the isodensity PCM method to consider the environmental effects.

Methods based on density functional theory have been shown to be capable to describe hydrogen bonds and their properties reasonably well [156]. The second-order Møller-Plesset perturbation theory (MP2) has also been established to perform well in hydrogen bonded systems [145]. The MP2 method is able to account for dispersion interactions, which are often of importance for an accurate description of hydrogen bonds [153]. Both computational methods require that errors arising from BSSE are taken into account, either by employing the CP correction or by using large enough basis sets. In order to describe intermolecular interactions, such as hydrogen bonding, basis sets are required to have at least polarisation functions included, and often diffuse functions are also necessary.
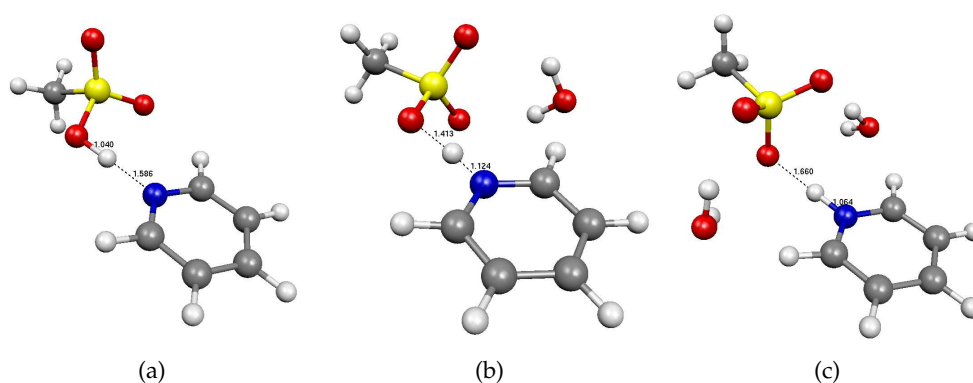

Figure 3.1. Equilibrium structures of (a) pyridine-methanesulphonic acid complex with a hydrogen bond, (b) pyridine-methanesulphonic acid with one water molecule showing proton transfer and (c) with two water molecules while proton transfer is further enhanced. All structures are optimised at B3LYP/6-31++G(d,p) level.

In Paper I the hydrogen bonding between pyridine and methanesulphonic acid and the effect of solvation on it was studied. Methanesulphonic acid is a strong acid, though it is not usually considered as a superacid [178]. Similar hydrogen bond formation occurs in many polymer based supramolecular materials where an amphiphilic molecule is hydrogen bonded to the polymer backbone [179, 180, 181]. The resulting structure resembles comb copolymers but the difference is that the amphiphilic side chains are not covalently bonded to the backbone. Non-polar tails of the amphiphiles have a tendency to phase separate, but if the polymer-amphiphile interaction is strong enough only microphase separation can occur. This microphase separation leads to an ordered structure at the nanoscale level, even though at the macroscopic level the material is homogeneous, i.e. there is no phase separation [179]. Because the strength of the hydrogen bond determines whether microphase separation can occur or whether the material macrophase separates, it is interesting to study this interaction at a more accurate quantum chemistry level. Especially interesting is the possibility of proton transfer occurring in the system, which may have influence on the proton conductivity in such materials, and the effect of which other molecules, like

water, have on the interaction.

Experimentally it has been observed that atactic poly(4-vinyl pyridine) can be protonated by p-dodecylbenzene sulphonic acid, and the resulting interaction between the polymer and the amphiphile is strong ionic hydrogen bond [182]. These conclusions have been based on the results obtained with FT-IR spectroscopy. A similar system, but with a reduced interaction strength, is poly(4-vinyl pyridine) with an amphiphilic 3-pentadecyl phenol molecule. In this case the interaction is hydrogen bonding without proton transfer [183]. Poly(4-vinyl pyridine) can be made protonically conducting by mixing it with methanesulphonic acid or toluenesulphonic acid [184] and one can obtain self-organised lamellar structures by adding 3-pentadecyl phenol amphiphiles [179].

In Paper I it was shown that in the absence of solvent, the pyridine in the pyridine-methanesulphonic acid complex is not protonated but there is a hydrogen bond between the molecules, as can be seen from figure 3.1(a). The hydrogen bond potential energy surface (PES) was also investigated and it turned out to be a single minimum potential in the gas phase, as presented in figure 3.2. However, when the complex was surrounded by a dielectric medium using a PCM the form of the PES changed. In a dielectric medium corresponding to acetone (ε_r=21), the PES exhibited double minimum character, and when dielectric constant was increased still to that corresponding to water (ε_r=78), the PES changed to a single minimum potential again, but now the minimum was located close to the pyridine, i.e. the pyridine was protonated. Energetically the global minima in acetone and water are 35 and 63 kJ/mol below the global minimum in the gas phase.

The pyridine-methanesulphonic acid complex was also studied using explicit water molecules to mimic the solvation. Already one water molecule was enough to change the proton transfer state to the equilibrium one, which is shown in figure 3.1(b). With two water molecules the proton transfer was further enhanced with shorter N–H bond distance as shown in figure 3.1(c). The presence of water molecules affects the equilibrium structure of the complex. To investigate this effect more closely, the PES of the proton was calculated with and without the water molecule at the pyridine-methanesulphonic acid-H_2O complex geometry. Without the water molecule the PES was very flat exhibiting a slight minimum closer to methanesulphonic acid, suggesting hydrogen bonding but with the water molecule the PES had a distinct minimum closer to pyridine.

The structural effect was further investigated by calculating the PES at the experimental crystal structure determined by X-ray diffraction and using PCM to model the environment. Without any solvation, the PES had almost symmetrical double minimum structure. With acetone as a solvent, the minimum close to methanesulphonic acid vanished and only the other minimum remained. In the presence of water this effect was further intensified. Based on these results, already a small change in the geometrical structure of pyridine-methanesulphonic acid complex affects the PES of the proton so that proton transfer becomes possible. Solvation effects, either by explicit hydrogen bonds and/or from the dielectric environment, further enhance this effect. Therefore it is likely that in real materials a spectrum of different kinds of states varying from hydrogen bonded state to proton transfer states occur between pyridine-methanesulphonic acid fragments, and that this distribution is affected both by dielectric effects and by
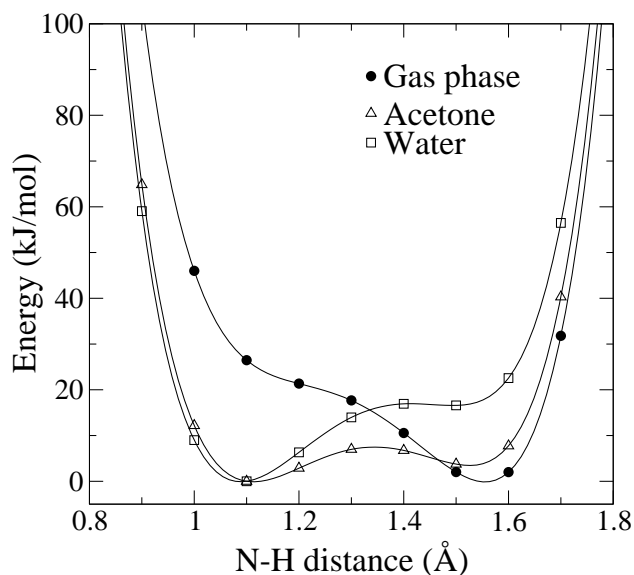
Figure 3.2. Potential energy surfaces of the proton in gas phase, in acetone and in water solvents at the optimised pyridine-methanesulphonic acid geometry obtained in gas phase using the PCM and B3LYP/6-31++G(d,p) method.

explicit interactions from neighbouring molecules.

The models used here do not take into account the quantum behaviour of the proton, i.e. that the proton is able to tunnel through the potential barrier in a double minimum potential. Experimentally the solvent effect on the hydrogen bond could be studied, for example, using NMR techniques [185].

The present study showed that the PES experienced by the proton in the pyridine-methanesulphonic acid complex is strongly dependent on the dielectric environment and water molecules present in the vicinity of the complex. This can explain why the complex is sometimes referred as hydrogen bonded and sometimes described as a proton transfer system.

3.2 Bipyridines

Polypyridine is a π-conjugated rod-like polymer much like poly(p-phenylene). However, due to the nitrogen, it is able to form hydrogen bonds with acids or co-ordinate with a metal, forming supramolecular structures. Polypyridine is also more easily soluble than poly(p-phenylene) due to the heteroatom. Polypyridine has been found to be a luminescent and very stable material with respect to oxidation [186], making it an interesting material for practical applications. Although difficult to oxidise, polypyridine can be reduced to yield an electrically conductive form. Due to these optical and electrical properties pyridine-based conjugated polymers are promising materials for light emitting diode (LED) applications with a reasonable quantum yield [187, 188]. Hydrogen bonding or protonation can be used also to achieve supramolecular structures with polypyridine. Polypyridine protonated with methanesulphonic acid and complexed with octyl gallate has been demonstrated to form lamellar nanostructures [189].

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As a consequence of these interesting properties there has been a lot of effort to study polypyridine and related materials both experimentally and theoretically. The solid state structure of polypyridine has been determined by using X-ray diffraction [190]. It shows that the polypyridine rods are stacked parallel on top of each other and the pyridine rings are in a planar conformation. The interchain packing distance was measured to be about 3.6 Å.

Electronic properties of periodic structures of conjugated polymers, including polypyridine, have been investigated computationally [191], and photophysical properties of polypyridine and the effect of protonation by different acids have been studied experimentally [192]. Sulphonic acids, which protonate polypyridine, were observed to have the largest effect on the optical properties. At the highest acid concentrations, both green and blue emission is observed. The green emission is characteristic for the solid state while blue emission is observed in solution. This can be explained by the changes in the band gap due to variations in the conformation. In the solid state the pyridine rings are more planar, but on protonation interchain interactions change and the torsion angle is allowed to relax back to slightly distorted equilibrium structure, similar to solution.

Similar kinds of studies of optical properties have been performed for bipyridine containing poly(*p*-phenylene-vinylene) polymers [193]. The colour observed from photoluminescent devices manufactured from these materials was adjustable by changing the concentrations of acids and bases used in preparation of samples.

Torsional potentials for a number of conjugated polymers and the effect of torsion angle on their electrical properties were investigated already some time ago [194, 195]. In a more recent study torsional properties of pyridine dimers, tetramers and polypyridine have been investigated computationally using DFT methods [196]. The torsional potential was found to be dependent on the configuration of the molecules, i.e. the position of nitrogen atoms on rings. In most of the configurations the adjacent rings are not planar but the deviation is only few tens of degrees, and related barrier energies are relatively small so that it was concluded that in a solid state the system is planar. The torsion angle was also observed to approach planarity as the number of monomers in an oligomer increased. Torsional properties of some substituted conjugated biphenyl derivatives have been studied including HF, MP2 and DFT methods [197]. All of these methods gave similar results, although in some conformations DFT predicted lower or higher torsional barriers than MP2 and HF.

The polypyridine inspired us to investigate the torsion behaviour of its subunits, and how the conformation of the two adjacent pyridine units is affected by protonation since it has significant effect on the photophysical properties and probably also on the solubility behaviour. This subject was studied in Paper II. Different torsion potentials were also parametrised for a force field, and the effect of atomic partial charges obtained with different methods was analysed.

Conjugated systems containing heteroatoms, such as nitrogen, and their conformational properties have been studied using DFT methods before [198]. Comparison with the MP2 method showed that DFT performs well for most systems, and the properties studied, including energy differences, vibrational frequencies and electrostatic potential derived charges, are in good agreement with those obtained with different density functionals. However, some of the torsional bar-

riers were overestimated and some minima predicted too shallow with DFT. The overestimation of torsional barriers is due to DFT to bias towards too delocalised π-electron structure. In some of the molecules it was also observed that partial charges were dependent on the conformation. Comparison with the semi-empirical AM1 method revealed that the semi-empirical method was not able to produce the correct torsional behaviour and, therefore, it could not be used for parametrisation of torsional potentials.

The transferability of the force field parameters of a conjugated bond has been investigated using simple model molecules [199]. It has been shown that the conformation of the molecule can significantly influence the molecular charge distribution and the intermolecular hydrogen bond energies [200]. Therefore, the approximation that partial charges are conformation independent may not always be valid, and in some cases it may lead to wrong results.

In Paper II three different bipyridines were investigated. The bipyridines were 2,3′-, 2,2′- and 3,3′-bipyridine of which 2,3′-bipyridine was also studied

Table 3.1. Selected structural parameters and relative energies of the optimised minimum energy structures of neutral and protonated bipyridines (BPy) computed at B3LYP/6-31G(d,p) level.

|		Torsion angle (°)	C–C bond length (Å)	Relative energy (kJ/mol)
2,2′-BPy	TS	0.0	1.499	33.2
	cis	35.1	1.494	29.2
	TS	84.4	1.503	37.5
	trans	180.0	1.490	0.0
2,3′-BPy	TS	0.0	1.488	3.6
	cis	21.0	1.485	2.9
	TS	88.8	1.496	20.5
	trans	161.0	1.486	0.0
	TS	180.0	1.488	0.5
3,3′-BPy	TS	0.0	1.488	9.1
	cis	39.3	1.480	0.6
	TS	89.5	1.491	10.1
	trans	140.9	1.480	0.0
	TS	180.0	1.488	8.3
2-Py-2′-PyH$^+$	*cis*	0.0	1.480	0.0
	TS	92.8	1.497	53.0
	trans	165.7	1.479	31.0
	TS	180.0	1.480	31.2
2,2′-BPyH$^+$	TS	0.0	1.488	27.6
	cis	58.2	1.489	7.6
	TS	77.3	1.496	8.0
	trans	136.2	1.484	0.0
	TS	180.0	1.486	12.4
3-Py-2′-PyH$^+$	TS	0.0	1.469	6.8
	cis	35.1	1.468	0.0
	TS	88.8	1.496	14.6
	trans	144.6	1.465	1.6
	TS	180.0	1.469	8.3
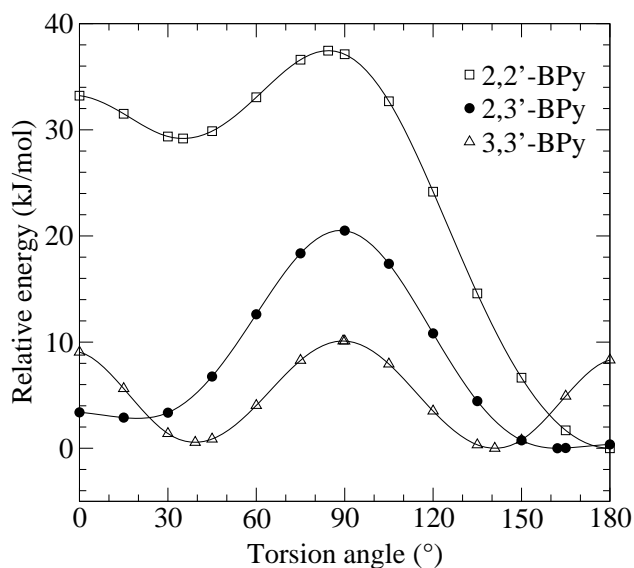
Figure 3.3. Relative torsion energies of 2,2'-, 2,3'- and 3,3'-bipyridine calculated at B3LYP/6-31G(d,p) level.

as singly protonated, and 2,2-bipyridine both as singly and doubly protonated. The torsion potential is rather symmetric for 3,3'- and 2,3'-bipyridine and slightly twisted *cis* and *trans* conformations are close in energy, but for 2,2'-bipyridine the planar *trans* conformation is energetically more favourable than the *cis* conformation, as can be seen from figure 3.3.

The protonation has different kinds of effects on the torsion potential in the different bipyridines, as shown in table 3.1. The singly protonated 2,2'-bipyridine has the minimum energy at the planar *cis* conformation. However, there is a potential barrier between the singly protonated planar *trans* conformation and the new global minimum, indicating that if 2,2'-bipyridine is protonated in the planar *trans* conformation, it can stay in this metastable state. If 2,2'-bipyridine is doubly protonated, the global minimum is the slightly twisted *trans* conformation and the *cis* conformation has only a very weak minimum. 2,3'-bipyridine is not affected as much as 2,2'-bipyridine by protonation. The global minimum is shifted from twisted *trans* conformation to twisted *cis* conformation, and the torsion potential barrier is lowered by 5 kJ/mol.

Atomic partial charges were obtained from density functional computations by fitting to the electrostatic potential (ESP) with CHelpG scheme [201]. These results were compared with less accurate schemes to obtain partial charges, like the bond increment method [202], the charge equilibration method [203] and the charge equalisation method [204]. However, these methods were not able to reproduce the partial charges based on ESP. The best agreement with computed torsion potentials was obtained by using the partial charges derived from the ESP, and including also the fourth order terms into the cosine expansion of the force field.

The degree of protonation turned out to be an important factor affecting the torsional potential of bipyridines. Therefore, the protonation is likely to affect

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also the conformation of polypyridine and its properties.

3.3   Metal coordination

Supramolecular structures can also be obtained by forming a coordination compound of chemical species using a metal cation as glue between the ligands. This type of approach was illustrated in Paper III where the supramolecular self-organisation is achieved as a combination of coordination and ionic bonding resulting in multicomb polymeric structures. The metal cation acts as a bridge between the pyridine unit of poly(4-vinyl pyridine) and the side-chain ligand 2,6-bis(octylaminomethyl)pyridine, which is a chelating ligand as it has three lone pairs which can coordinate with Zn. The most common coordination numbers for zinc are 4, 5 and 6 [205]. The dodecylbenzenesulphonate counterions contribute also as side-chains and therefore cylindrical organisation was observed experimentally. Based on FT-IR spectroscopy the formation of supramolecular entities can be observed. Since the material is not crystalline, determination of atomic positions by diffraction techniques is not possible, and a natural way to study the coordination was by quantum chemical calculations.

Due to the size of the system, density functional theory was considered as an appropriate method to perform the modelling. DFT has proven to be a very successful alternative for Hartree-Fock based ab initio methods to model transition metal containing complexes [206]. Especially the introduction of gradient corrected and hybrid functionals has given it almost the same accuracy as correlated ab initio methods have with a fraction of the cost [207]. There has been studies of zinc complexes performed with density functional theory previously. Stability of hydrated zinc complexes has been studied with density functional theory [208, 209] and compared also with other doubly charged metal ions [210]. The hybrid functional B3LYP has been found to perform well for these systems and also for other organometallic compounds [211]. Zinc is a first row transition metal and therefore only little influenced by relativistic effects [212]. Nevertheless, in the calculations the core electrons were replaced by an effective core potential based on numerical, relativistic Hartree-Fock calculations [213] and thereby including part of the relativistic effects.

The computational methods used were DFT with the B3LYP functional and the LanL2DZ basis set, which consists of D95V valence double-zeta basis set [214] with an effective core potential for zinc. The frequency calculations performed at the same level confirmed the minimum character of the optimised structure. The optimised structure is shown in figure 3.4. The dodecylbenzenesulphonate counterions were not included in the model system in order to keep the size computationally feasible. The coordination is tetrahedral-like. The Zn–N distances to the nitrogens on both sides of the ligand are significantly longer that the Zn–N distances to the nitrogens in the pyridine rings. In an isolated ligand, the aminomethyl groups may have different conformations, but the coordination with Zn constrains significantly their movement. The role of dodecylbenzene-sulphonate counterions was not investigated computationally. It is likely that they are located in the vicinity of Zn and interact through an ionic interaction due to opposite charges. In principle it could be possible for zinc to form a six co-
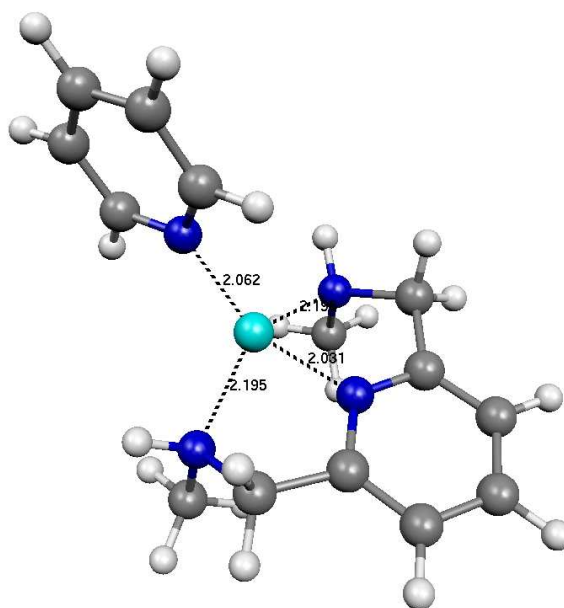
Figure 3.4. The optimised structure of pyridine, Zn^{2+} and 2,6-bis(methylamino-methyl)pyridine calculated at B3LYP/LanLDZ level.

ordinated compound with two ligands, as there are known amine ligands which form such a structure with zinc [205]. However, this is not observed, and the reason maybe that such a structure is not entropically favourable, or that ionic interactions with dodecylbenzenesulphonate become energetically unfavourable due to the steric hindrance caused the octyl-chains of the ligands.

The computations showed that coordination of Zn^{2+} with pyridine and the chelating ligand was possible and supported the suggested experimental structure.

3.4 Polyamide and phenolic resin

Polyamide based polymers have excellent mechanical properties with good resistance to different chemicals [215]. The properties of polyamides can be further improved by mixing them with phenolic containing resins. Phenolic group is able to form a hydrogen bond with the polyamide chain and bind different polyamide chains together. In Paper IV the interaction between polyamide and phenol formaldehyde resins were investigated using small model systems, enabling the use of quantum chemical methods. Polyamide was represented as N-methylacetamide molecule and its complexation with itself, phenol and water was studied. The aim was to investigate energetics of the complexation and compare different systems with each other.

Geometries of the complexes were optimised using DFT, and both DFT and MP2 levels were used to calculate interaction energies including corrections for BSSE, which can lead to significant errors if they are not accounted for. Standard basis sets were augmented with polarisation and diffuse functions in order to

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describe molecular complexes adequately. The BSSE was estimated using the CP correction [145].

Although the agreement between the DFT and MP2 results was found to be rather good, it must be remembered that the basis sets used for MP2 calculations are not large enough to give quantitative values for complexation energies. To demonstrate this, the CP corrected complexation energy of the N-methylacetamide-phenol complex at the RI-MP2/aug-cc-pVTZ level is -45.8 kJ/mol while BSSE is still -5.8 kJ/mol. On the other hand, DFT results do not change much with larger basis set; at B3LYP/aug-cc-pVTZ level energies are -38.7 and -1.7 kJ/mol, respectively. Of course, instead of the absolute values of the complexation energies, one is more interested in the relative differences between different complexes.

N-methylacetamide complex with itself was observed to be somewhat weaker than N-methylacetamide-water complex, implying that water should be able to disrupt the hydrogen bonds between polyamide chains. On the other hand, the N-methylacetamide-phenol complex was observed to have largest complexation energy. This result suggests that phenolic groups bind strongly with polyamide, and phenolic resins may act as glue between polyamide chains inhibiting water to disrupt the network structure.

The partial atomic charges of atoms were also calculated using the CHelpG scheme [201]. The partial charge of the CO carbon in N-methylacetamide was noted to decrease due to the complexation with phenol as compare to the dimer complex. The carbon atom in polyamide is known to be prone to react with water and such a reaction will cleave the polymer backbone. One could argue that the complexation with phenol decreases the reactivity and in some degree suppresses the hydrolysis reaction. Usually hydrolysis of amides requires acidic or basic catalyst combined with heating, and water alone is not sufficient to hydrolyze most amides [216]. Therefore, it is difficult to make any conclusions based on this.

These computational results gave some new insights into the behaviour of polyamides and phenolic resins with water, and suggested why phenolic resins have favourable effects on the properties of polyamides.

3.5   Silicon nanoclusters

Crystalline silicon is known to have poor optical properties due to its indirect band gap, and in the past most of the research in semiconductor optoelectronics has been focussed on compound semiconductors, like GaAs, having direct band gap which enables efficient light emission. However, the recent discovery of the photoluminescence of nano sized silicon clusters have shown that even silicon can be an interesting optical material.

Porous silicon was observed to be photoluminescent already in 1984 [217] at cryogenic temperatures and later at room temperature [218]. Visible photoluminescence from porous silicon occurs from red to yellow, while the blue emission is weak. The luminescence has been contributed to various different phenomena such as quantum confinement, nanocrystal surface states, defects, molecules or structural disorder [219]. However, the quantum confinement model is found

to be in the best agreement with experimental results. Nonetheless, it has even been proposed that the observed light would not be photoluminescence at all, but due to thermal radiation emitted by silicon nanoparticles [220], showing that the origin of luminescence has by no means been simple to understand.

According to the quantum confinement model the generated electron-hole pair, or exciton, is confined inside a nanocrystal, and in the radiative recombination of the electron-hole pair light is emitted. Whereas in indirect band gap semiconductors the optical transitions are forbidden, unless phonons (i.e. lattice vibrations) are involved in order to the conserve crystal momentum [221], in nanocrystals the spatial confinement of electrons and holes increases the uncertainty of the crystal momentum and optical transitions become allowed [222]. Luminescence efficiency is attributed to the hydrogen terminated surface with only few dangling bonds, suppressing undesired non-radiative pathways. As the size of the nanocrystal decreases, the photoluminescence energy increases due to spatial confinement [222]. In the quantum confinement model the nanocrystal acts as a potential energy well for the generated electron-hole pair. As the size of the nanocrystal decreases, the wavefunction becomes spatially more confined, and the energy levels recede form each other. This trend is clearly visible in figure 3.5, where the optical gap of different sized nanoclusters is shown. In bulk silicon, which is an indirect band gap semiconductor, the electron-hole pair cannot recombine radiatively unless assisted by a phonon and recombination is more likely to occur nonradiatively at a defect site or at the surface. Therefore, in bulk silicon non-radiative recombination channels are dominant.

More recently silicon nanoparticles of about 1 nm in diameter were observed to be strongly photoluminescent with blue emission [223]. Excitation with UV radiation results in blue emission visible with plain eye while nanoparticles are suspended in a colloid. The brightness of these silicon nanoparticles is measured to be four times larger that that of the fluorescein standard. In general, the lu-
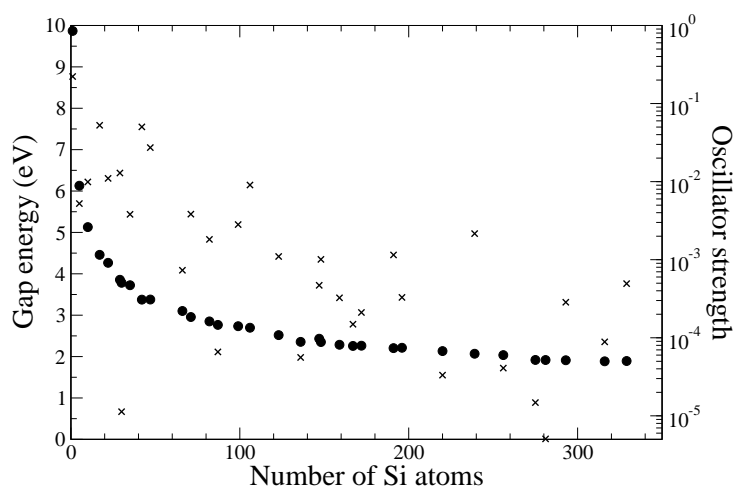

Figure 3.5. Optical gap (•) and oscillator strength (×) for silicon clusters of different size as a function of the number of silicon atoms calculated using TDDFT at MARIJ-BP/def2-SV(P) level.

minescence from different sized nanoparticles is observed at the visible region of

the spectrum [224], and this is explained using the same quantum confinement model as in the porous silicon. The wavelength of the emitted radiation depends on the size of the nanocluster.

There has been different suggestions to explain the intense luminescence, such as self-trapped surface states [225] and oxygen defects at the surface of the cluster [226]. Silane groups attached to the surface have also been suggested as a possible explanation for the bright luminescence, as the observed and calculated oscillator strengths are in good agreement with each other [227]. The nanocluster surface can be hydrogen or oxygen terminated; however, the surface passivation does not directly influence the luminescence [228]. There are also silicon nanocrystals with non-crystalline structure with spherical and prolate shapes [229].

In Paper V the properties of three different silicon clusters, about 1 nm in diameter, $Si_{29}H_{24}$, $Si_{29}H_{36}$, and $Si_{35}H_{36}$ were investigated using computational methods. In some studies it has been suggested that $Si_{29}H_{24}$ is the most probable candidate for the luminous cluster [230]. Other studies have suggested that $Si_{29}H_{36}$ is also a possible candidate [231], and showed that it is unlikely that there is a double well potential, a model which has been used to explain luminescence, in the excited state, as required by the self-trapped surface state model [232]. Various computational methods has been used in previous computational studies making comparison difficult; therefore, it was important to obtain properties of these clusters at the same computational level making comparison easier.

All the three clusters are about 1 nm in size, and possible candidates for luminescent nanoparticles observed experimentally. Number of silicon atoms in these clusters are structural magic numbers [233], i.e. all structures have the symmetry of $T_{\rm d}$ point group. The structures were optimised both for the ground state and for the lowest excited state using DFT and time-dependent DFT, respectively. TDDFT was used to calculate excitation energies and oscillator strengths of the clusters. In order to model the emission process, it was assumed, according to the Franck-Condon principle, that after a vertical absorption process the structure may relax leading to the Stokes shift, i.e. the emission energy becomes red shifted relative to the absorption energy [234]. This was accounted for by relaxing the structure at the first excited state and calculating the optical excitations at the relaxed geometry. Comparing the lowest excitation energies at the ground state and at the excited state structures, it was possible to derive the corresponding Stokes shifts for the clusters.

In $Si_{29}H_{36}$ the calculated Stokes shift was 0.70 eV which is in rather good agreement[1] with experimentally observed values 0.5–0.6 eV [235]. For the two other clusters, the shifts were significantly larger. However, the oscillator strengths of all clusters in the spectral region of interest were found to be much less than would be expected from the intense luminescence observed experimentally. For comparison, a fluorescein molecule has oscillator strengths of about 0.2 calculated at the same level at the visible region. Based on experimental measurements, is has been estimated that in silicon nanoclusters the oscillator strength of the transition involved is 0.92 [236] which is almost two orders of magnitude

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[1]Later it was found that $Si_{29}H_{36}$ has still a lower energy excited state structure where the Stokes shift becomes 2.19 eV

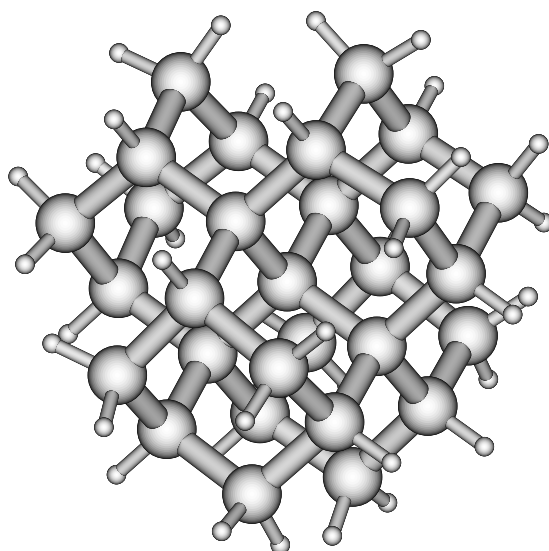**Figure 3.6.** The structure of $Si_{29}H_{36}$ optimised at BP/TZVP level.

higher than obtained computationally. The lifetime of the transition was measured to be few nanoseconds, confirming that the radiation is fluorescence.

Additionally, the optimisation of the triplet state was performed using unrestricted KS scheme. It was observed that one of the Si–Si bonds became elongated. The elongation was observed to be dependent on the functional used; the local density approximation predicted shorter bond lengths that gradient corrected functionals. Similar bond elongations were also obtained for the triplet state, optimised using plane waves and local density approximation [237]. These results are probably due to the LDA's tendency to overbind, i.e. to yield too short bond lengths.

The computed energies for $Si_{29}H_{36}$ cluster are in accordance with experimental data, but for the other two clusters the energies are too low to explain blue luminescence. However, in all clusters the computed oscillator strengths are significantly lower than experimental values, suggesting that the structure of the actual luminous nanocluster is different of those studied here, or that the radiative transition cannot be modelled as a single photon transition in the dipole approximation.

Chapter 4

Conclusions

The work presented in this thesis contains a number of different areas of computational chemistry: solvation effects, torsion potentials for force fields, bonding of a metal cation with ligands, complexation energies and electronic excited states. Most of the computations have been done using density functional theory although wavefunction methods have also been applied when possible. Some of the molecular systems modelled here have also been studied experimentally and computations have been done in order to better understand experimental observations.

Chemical moieties similar to pyridine-methanesulphonic acid complex are present in many supramolecular structures. Modelling the complex provided new information on the effects of the molecular environment on the hydrogen bond in the complex. Solvation studies revealed that both dielectric environment, with high enough dielectric constant, and explicit hydrogen bonds enhance protonation in the complex. Another structural unit used in supramolecular chemistry are oligopyridines. The modelling of bipyridines and their torsion potentials helped to understand the effects due to the protonation and the differences between the bipyridine structures. It was also observed that partial charges are strongly dependent on the conformation, and simple methods to obtain partial charges for force fields do not always work.

A supramolecular polymer system was studied by using only a small part of the actual system to investigate molecular interactions between the polymer and the sidechains. The study of coordination of ligands with a metal showed that this approach can yield useful information which helps to understand the system better. The idea of using small model molecules was also applied to investigate interaction in polyamide and phenolic resin system with water. The complexation energies supported the notion that phenolic resins stabilise polyamide and inhibit water to break intermolecular hydrogen bonds.

With silicon clusters the experimental methods to determine the actual molecular structure of luminescent clusters are not available, and the only way is to computationally study different types of clusters and their properties. The study revealed that the oscillator strengths of all the cluster were significantly smaller than those observed experimentally.

These computational studies have given new insight into the systems and have provided information which is unaccessible experimentally. Of course, the static molecular structure obtained by geometry optimisation gives only a

glimpse of what is actually going on in the system with all dynamical effects present.

Computational chemistry has also evolved during this work; not only due to faster computers but also due to the development of methods and program packages. Although programs become more and more accessible and computing power continues to increase, in the end it is up to user how to interpret the results and to estimate their accuracy. In this sense, the computational and experimental research methodologies do not differ much from each other after all.

References

[1] P. A. M. Dirac. *Proc. R. Soc. A* **117**, 610 (1928).

[2] P. A. M. Dirac. *Proc. R. Soc. A* **118**, 351 (1928).

[3] W. E. Lamb, Jr. and R. C. Retherford. *Phys. Rev.* **72**, 241 (1947).

[4] I. J. R. Aitchison and A. J. G. Hey. *Gauge Theories in Particle Physics*. Institute of Physics Publishing, Bristol, 3rd ed., 2003.

[5] H. Bethe and E. E. Salpeter. *Quantum Mechanics of One and Two-Electron Atoms*. Springer-Verlag, Berlin, 1957.

[6] L. L. Foldy and S. A. Wouthuysen. *Phys. Rev.* **78**, 29 (1950).

[7] K. Balasubramanian. *Relativistic Effects in Chemistry Part A: Theory and Techniques*. John Wiley & Sons, 1997.

[8] E. van Lenthe, E. J. Baerends and J. G. Snijders. *J. Chem. Phys.* **99**, 4597 (1993).

[9] M. Douglas and N. M. Kroll. *Ann. Phys.* **82**, 89 (1974).

[10] W. Kutzelnigg. *Phys. Rev. A* **54**, 1183 (1996).

[11] P. Strange. *Relativistic Quantum Mechanics*. Cambridge University Press, Cambridge, 1998.

[12] W. Kutzelnigg. *Z. Phys. D* **15**, 27 (1990).

[13] P. Pyykkö. *Chem. Rev.* **88**, 563 (1988).

[14] F. Jensen. *Introduction to Computational Chemistry*. Wiley, 1999.

[15] M. Born and R. Oppenheimer. *Ann. Phys.* **84**, 457 (1927).

[16] L. J. Butler. *Annu. Rev. Phys. Chem.* **49**, 125 (1998).

[17] D. R. Yarkony. *Rev. Mod. Phys.* **68**, 985 (1996).

[18] P. A. M. Dirac. *Proc. R. Soc. A* **113**, 621 (1927).

[19] P. Jordan and E. P. Wigner. *Zeits. Phys.* **47**, 631 (1928).

[20] P. P. Jørgersen and J. Simons. *Second Quantization-Based Methods in Quantum Chemistry*. Academic Press, New York, 1981.

[21] T. Helgaker, P. Jørgersen and J. Olsen. *Molecular Electronic-Structure Theory*. Wiley, 2000.

[22] P. E. M. Siegbahn, J. Almlöf and A. Heigerg B. O. Roos. *J. Chem. Phys.* **74**, 2384 (1981).

[23] D. R. Hartree. *Proc. Cambridge Phil. Soc.* **24**, 89 (1928).

[24] V. Fock. *Z. Physik* **61**, 126 (1930).

[25] C. C. J. Roothaan. *Rev. Mod. Phys.* **23**, 69 (1951).

[26] G. G. Hall. *Proc. R. Soc. (London)* **A205**, 541 (1951).

[27] T. A. Koopmans. *Physica* **1**, 104 (1933).

[28] C. J. Cramer. *Essentials of Computational Chemistry*. John Wiley & Sons, Chichester, 2002.

[29] J. A. Pople and R. K. Nesbet. *J. Chem. Phys.* **22**, 571 (1954).

[30] C. C. J. Roothaan. *Rev. Mod. Phys.* **32**, 179 (1960).

[31] J. Almlöf and R. Ahlrichs. Notes on Hartree-Fock Theory and Related Topics. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 1, p. 170–239. Lund Universitet, 2000.

[32] P. Pulay. *J. Comp. Chem.* **3**, 556 (1982).

[33] M. Häser and R. Ahlrichs. *J. Comp. Chem.* **10**, 104 (1989).

[34] D. S. Lambrecht and C. Ochsenfeld. *J. Chem. Phys.* **123**, 184101 (2005).

[35] R. McWeeny. *Rev. Mod. Phys.* **32**, 335 (1960).

[36] H. Larsen, J. Olsen, P. Jørgersen and T. Helgaker. *J. Chem. Phys.* **115**, 9685 (2001).

[37] W. Kutzelnigg. *Theoret. Chim. Acta* **68**, 445 (1985).

[38] E. A. Hylleraas. *Adv. Quant. Chem.* **1**, 1 (1964).

[39] A. Luchow and J. B. Anderson. *Annu. Rev. Phys. Chem.* **51**, 501 (2000).

[40] W. M. C. Foulkes, L. Mitas, R. J. Needs and G. Rajagopal. *Rev. Mod. Phys.* **73**, 33 (2001).

[41] J. B. Anderson. Diffusion and Green's Function Monte Carlo. In J. Grotendorst, D. Marx and A. Muramatsu (eds.), *Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms*, vol. 10 of *NIC Series*, p. 25–50. NIC, Forschungszentrum Jülich, 2002.

[42] L. Hedin. *Phys. Rev. A* **139**, 796 (1965).

[43] F. Aryasetiawan and O. Gunnarsson. *Rep. Prog. Phys.* **61**, 237 (1998).

[44] A. R. Leach. *Molecular Modelling: Principles and Applications*. Prentice Hall, 2nd ed., 2001.

[45] A. Szabo and N. S. Ostlund. *Modern Quantum Chemistry*. Dover, 1996.

[46] E. U. Condon and G. H. Shortley. *The Theory of Atomic Spectra*. Cambridge University Press, 1967.

[47] L. Brillouin. *Actualités Scientifiques et Industrielles* (159) (1934).

[48] Y. Saad. *Numerical Methods for Large Eigenvalue Problems*. John Wiley & Sons, New York, 1992.

[49] C. F. Van Loan G. H. Golub. *Matrix Computations*. The Johns Hopkins University Press, Baltimore, 3rd ed., 1996.

[50] P. E. M. Siegbahn. The Configuration Interaction Method. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 1, p. 241–284. Lund Universitet, 2000.

[51] P. R. Taylor. Coupled-Cluster Methods in Quantum Chemisty. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 2, p. 361–429. Lund Universitet, 2000.

[52] S. R. Langhoff and E. R. Davidson. *Int. J. Quant. Chem.* **8**, 61 (1974).

[53] M. W. Schmidt and M. S. Gordon. *Annu. Rev. Phys. Chem.* **49**, 233 (1998).

[54] B. O. Roos. Multiconfigurational (MC) Self-Consistent (SCF) Theory. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 2, p. 285–359. Lund Universitet, 2000.

[55] B. O. Roos, P. R. Taylor and P. E. M. Siegbahn. *Chem. Phys.* **48**, 157 (1980).

[56] J. Čížek. *J. Chem. Phys.* **45**, 4256 (1966).

[57] T. D. Crawford and H. F. Schaefer. An introduction to coupled cluster theory for computational chemists. In K. B. Lipkowitz and D. B. Boyd (eds.), *Reviews in Computational Chemistry*, vol. 14 of *Reviews in Computational Chemistry*, p. 33–136. Wiley-VCH, 2000.

[58] O. Christiansen, H. Koch and P. Jørgensen. *Chem. Phys. Lett.* **243**, 409 (1995).

[59] H. Koch, O. Christiansen, P. Jørgensen, A. M. S. de Merás and T. Helgaker. *J. Chem. Phys.* **106**, 1808 (1997).

[60] O. Christiansen, C. Hättig and P. Jørgensen. *Int. J. Quant. Chem.* **68**, 1 (1998).

[61] J. F. Stanton and R. J. Bartlett. *J. Chem. Phys.* **98**, 7029 (1993).

[62] K. A. Bruecker. *Phys. Rev.* **96**, 508 (1954).

[63] C. Møller and M. S. Plesset. *Phys. Rev.* **46**, 618 (1934).

[64] H.-J. Werner, M. Schützl and A. Nicklaß. Local Electron Correlation Methods with Density Fitting in MOLPRO. In J. Grotendorst (ed.), *High Performance Computing in Chemistry*, vol. 25 of *NIC Series*, p. 53–82. NIC, Forschungszentrum Jülich, 2005.

[65] B. O. Roos, P. Linse, P. E. M. Siegbahn and M. R. A. Blomberg. *Chem. Phys.* **66**, 197 (1982).

[66] K. Andersson, P.-Å. Malmqvist and B. O. Roos. *J. Chem. Phys.* **96**, 1218 (1992).

[67] P. Hohenberg and W. Kohn. *Phys. Rev.* **139**, B864 (1964).

[68] R. G. Parr and W. Yang. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press, New York, 1989.

[69] M. Levy. *Proc. Natl. Acad. Sci.* **76**, 6062 (1979).

[70] W. Kohn and L. J. Sham. *Phys. Rev.* **136**, A1133 (1965).

[71] R. M. Dreizler and E. K. U. Gross. *Density Functional Theory*. Springer-Verlag, Berlin, 1990.

[72] J. P. Perdew and S. Kurth. Density functionals for non-relativistic coulomb systems in the new century. In C. Fiolhais, F. Nogueira and M. A. L. Marques (eds.), *A Primer in Density Functional Theory*, number 620 in Lecture Notes in Physics, p. 1–55. Springer-Verlag, Berlin, 2003.

[73] P. A. M. Dirac. *Proc. R. Soc. A* **123**, 714 (1929).

[74] J. C. Slater. *Phys. Rev.* **81**, 385 (1951).

[75] D. M. Ceperly and B. J. Alder. *Phys. Rev. Lett.* **45**, 566 (1980).

[76] S. J. Vosko, L. Wilk and M. Nusair. *Can. J. Phys.* **58**, 1200 (1980).

[77] A. D. Becke. *Phys. Rev. A* **38**, 3098 (1988).

[78] N. C. Handy. Density Functional Theory. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 2, p. 506–547. Lund Universitet, 2000.

[79] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais. *Phys. Rev.* **B46**, 6671 (1992).

[80] J. P. Perdew. *Phys. Rev. B* **33**, 8822 (1986).

[81] C. Lee, W. Yang and R. G. Parr. *Phys. Rev. B* **37**, 785 (1988).

[82] J. P. Perdew, K. Burke and M. Ernzerhof. *Phys. Rev. Lett.* **77**, 3865 (1996).

[83] J. P. Perdew, S. Kurth, A. Zupan and P. Blaha. *Phys. Rev. Lett.* **82**, 2544 (1999).

[84] J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria. *Phys. Rev. Lett.* **91**, 146401 (2003).

[85] A. D. Becke. *J. Chem. Phys.* **98**, 5648 (1993).

[86] P. J. Stephens, J. F. Devlin, C. F. Chabalowski and M. J. Frisch. *J. Phys. Chem.* **98**, 11623 (1994).

[87] A. D. Becke. *J. Chem. Phys.* **98**, 1372 (1996).

[88] J. P. Perdew, M. Ernzerhof and K. Burke. *J. Chem. Phys.* **105**, 9982 (1996).

[89] V. N. Staroverov, G. E. Scuseria, J. Tao and J. P. Perdew. *J. Chem. Phys.* **119**, 12129 (2003).

[90] E. K. U. Gross, J. F. Dobson and M. Petersilka. Density functional theory of time-dependent phenomena. In R. F. Nalewajski (ed.), *Density Functional Theory II*, vol. 181 of *Topics in Current Chemsitry*, p. 81–172. Springer-Verlag, Berlin, 1996.

[91] E. Engel. Orbital-dependent functionals for the exchange-correlation energy. In C. Fiolhais, F. Nogueira and M. A. L. Marques (eds.), *A Primer in Density Functional Theory*, number 620 in Lecture Notes in Physics, p. 55–122. Springer-Verlag, 2003.

[92] E. Runge and E. K. U. Gross. *Phys. Rev. Lett.* **52**, 997 (1984).

[93] R. van Leeuwen. *Int. J. Mod. Phys. B* **15**, 1969 (2001).

[94] M. E. Casida. Time-dependent density-functional response theory for molecules. In D. P. Chong (ed.), *Recent Advances in Density Functional Methods, Part I*, p. 155. World Scientific, Singapore, 1995.

[95] M. A. L. Marques and E. K. U. Gross. Time-dependent density functional theory. In C. Fiolhais, F. Nogueira and M. A. L. Marques (eds.), *A Primer in Density Functional Theory*, number 620 in Lecture Notes in Physics, p. 144–184. Springer-Verlag, 2003.

[96] M. A. L. Marques and E. K. U. Gross. *Annu. Rev. Phys. Chem.* **55**, 427 (2004).

[97] A. Nagy. *Phys. Rep.* **298**, 1 (1998).

[98] R. M. Dreizler. Relativistic density functional theory. In C. Fiolhais, F. Nogueira and M. A. L. Marques (eds.), *A Primer in Density Functional Theory*, number 620 in Lecture Notes in Physics, p. 123–143. Springer-Verlag, 2003.

[99] S. F. Boys and I. Shavitt. University of wisconsin, report wis-af-13. Technical report, 1959.

[100] B. Dunlap, J. Conolly and J. Sabin. *J. Chem. Phys.* **71**, 3396 (1979).

[101] J. Mintmire and B. Dunlap. *Phys. Rev. A* **25**, 88 (1982).

[102] F. Weigend, A. Köhn and C. Hättig. *J. Chem. Phys.* **116**, 3175 (2001).

[103] L. Greengard and V. Rokhlin. *J. Comp. Phys.* **60**, 187 (1985).

[104] H. Dachel. Continuous Fast Multipole Method. In J. Grotendorst (ed.), *High Performance Computing in Chemistry*, vol. 25 of *NIC Series*, p. 109–131. NIC, Forschungszentrum Jülich, 2005.

[105] R. Alhrichs and K. May. DFT functionality in TURBOMOLE. In J. Grotendorst (ed.), *High Performance Computing in Chemistry*, vol. 25 of *NIC Series*, p. 7–27. NIC, Forschungszentrum Jülich, 2005.

[106] T. A. Arias. *Rev. Mod. Phys.* **71**, 267 (1999).

[107] T. L. Beck. *Rev. Mod. Phys.* **72**, 1041 (2000).

[108] S. Goedecker. *Rev. Mod. Phys.* **71**, 1085 (1999).

[109] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos. *Rev. Mod. Phys.* **64**, 1045 (1992).

[110] R. M. Martin. *Electronic Structure: Basic Theory and Practical Methods.* Cambridge University Press, Cambridge, 2004.

[111] S. F. Boys. *Proc. Roy. Soc.* **A100**, 542 (1950).

[112] S. Obara and A. Saika. *J. Chem. Phys.* **89**, 1540 (1988).

[113] L. E. McMurchie and E. R. Davidson. *J. Comp. Phys.* **26**, 218 (1978).

[114] M. Dupuis, J .Rys and H. F. King. *J. Chem. Phys.* **65**, 111 (1976).

[115] K. O-Ohata, H. Taketa and S. Huzinaga. *J. Phys. Soc. Jap.* **21**, 2306 (1966).

[116] S. Huzinaga. *J. Chem. Phys.* **42**, 1293 (1965).

[117] R. C. Raffenetti. *J. Chem. Phys.* **58**, 4452 (1973).

[118] T. H. Dunning. *J. Chem. Phys.* **90**, 1007 (1989).

[119] J. Almlöf and P. R. Taylor. *J. Chem. Phys.* **92**, 551 (1990).

[120] H. Hellmann. *J. Chem. Phys.* **3**, 61 (1935).

[121] U. Wahlgren. An introduction to Relativistic Quantum Chemistry and Effective Core Potentials. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 3, p. 599–639. Lund Universitet, 2000.

[122] J. Gauss. Molecular properties. In J. Grotendorst (ed.), *Modern Methods and Algorithms of Quantum Chemistry*, vol. 3 of *NIC Series*, p. 541–592. NIC, Forschungszentrum Jülich, 2nd ed., 2000.

[123] Y. Yamaguchi, J. D. Goddard, Y. Osamura and H. Schaefer. *A New Dimension to Quantum Chemistry: Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory.* Oxford University Press, Oxford, 1994.

[124] T. Helgaker. Analytic Gradient Theory. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 2, p. 431–469. Lund Universitet, 2000.

[125] H. Hellmann. *Einführung in die Quantenchemie*. Deuticke & Co, 1937.

[126] R. P. Feynman. *Phys. Rev.* **56**, 340 (1939).

[127] B. Fernandez, P. Jørgensen, J. Byberg, J. Olsen, T. Helgaker and H. J. Aa. Jensen. *J. Chem. Phys.* **97**, 3412 (1992).

[128] P. Pulay. *Mol. Phys.* **17**, 197 (1969).

[129] T. Helgaker and P. Jørgersen. Calculation of geometrical derivatives in molecular electronic structure theory. In S. Wilson and G. H. F. Diercksen (eds.), *Methods in Computational Molecular Physics*, p. 353–421. Plenum Press, New York, 1992.

[130] T. Helgaker. Optimization of Minima and Saddle Points. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 2, p. 471–504. Lund Universitet, 2000.

[131] Harald Günther. *NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry*. John Wiley & Sons, 2nd ed., 1995.

[132] T. Helgaker, M. Jaszuński and K. Ruud. *Chem. Rev.* **99**, 293 (1999).

[133] J. Tomasi, B. Mennucci and C. Cappelli. Interactions in solvents and solutions. In G. Wypych (ed.), *Handbook of Solvents*, p. 419–504. ChemTec Publishing, 2000.

[134] C. J. Cramer and D. G. Truhlar. Continuum solvation models: Classical and quantum mechanical implementations. In K. B. Lipkowitz and D. B. Boyd (eds.), *Reviews in Computational Chemistry*, vol. 6, p. 1–73. Wiley-VCH, New York, 1995.

[135] C. J. Cramer and D. G. Truhlar. *Chem. Rev.* **99**, 2161 (1999).

[136] J. Tomasi and M. Persico. *Chem. Rev.* **94**, 2027 (1994).

[137] M. Cossi and V. Barone. Solvent Effects by Effective Hamiltonian Model. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 2, p. 549–597. Lund Universitet, 2000.

[138] A. Klamt and G. Schüürmann. *J. Chem. Soc. Perkin Trans.* **2**, 799 (1993).

[139] M. Diedenhofen. Conductor-like Screening Model COSMO. In J. Grotendorst (ed.), *High Performance Computing in Chemistry*, vol. 25 of *NIC Series*, p. 133–149. NIC, Forschungszentrum Jülich, 2005.

[140] A. Klamt. *J. Phys. Chem.* **99**, 2224 (1995).

[141] A. Klamt, V. Jonas, T. Buerger and J.C.W. Lohrenz. *J. Chem. Phys.* **102**, 5074 (1998).

[142] W. Koch and M. C. Holthausen. *A Chemist's Guide to Density Functional Theory*. Wiley-VCH, Weinheim, 2001.

[143] P. R. Taylor. Accurate Calculations and Calibration. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 2, p. 641–718. Lund Universitet, 2000.

[144] P. E. M. Siegbahn. Computational and Molecular Models in Quantum Chemistry. In B. O. Roos and P.-O. Widmark (eds.), *European Summer School in Quantum Chemistry*, vol. 3, p. 719–770. Lund Universitet, 2000.

[145] J. G. C. M. Van Duijneveldt-van de Rijdt and F. B. Van Duijneveldt. Ab initio methods applied to hydrogen-bonded systems. In D. Hadži (ed.), *Theoretical treatments of Hydrogen Bonding*, p. 13–47. John Wiley & Sons, 1997.

[146] B. Jeziorski, R. Moszynski and K. Szalewicz. *Chem. Rev.* **94**, 1887 (1994).

[147] N. R. Kestner and J. E. Combariza. Basis set superposition errors: Theory and practice. In K. B. Lipkowitz and D. B. Boyd (eds.), *Reviews in Computational Chemistry*, vol. 13, p. 99–132. Wiley-VCH, New York, 1999.

[148] G. A. Jeffrey. *An Introduction to Hydrogen Bonding*. Oxford University Press, Chichester, 1997.

[149] J. N. Israelachvili. *Intermolecular and Surface Forces*. Academic Press, London, 2nd ed., 1991.

[150] S. Scheiner. *Hydrogen Bonding*. Oxford University Press, New York, 1997.

[151] D. A. Smith. *Modelling the Hydrogen Bond*. American Chemical Society, Washington, 1994.

[152] D. Hadži. *Theoretical treatments of Hydrogen Bonding*. John Wiley & Sons, 1997.

[153] S. Scheiner. Calculating the properties of hydrogen bonds by ab initio methods. In K. B. Lipkowitz and D. B. Boyd (eds.), *Reviews in Computational Chemistry*, vol. 2, p. 165–218. Wiley-VCH, 1991.

[154] J. E. Del Bene. Hydrogen bonding 1. In P. von R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III and P. R. Schreiner (eds.), *Encyclopedia of Computational Chemistry*, vol. 2, p. 1263–1271. John Wiley & Sons, Chichester, U.K., 1998.

[155] J. E. Del Bene and M. J. T. Jordan. *J. Mol. Struct. (Theochem)* **573**, 11 (2001).

[156] H. Guo, S. Sirois, E. I. Proynov and D. R. Salahub. Density functional theory and its applications to hydrogen-bonded systems. In D. Hadži (ed.), *Theoretical treatments of Hydrogen Bonding*, p. 49–74. John Wiley & Sons, 1997.

[157] E. J. Meijer and M. Sprik. *J. Chem. Phys.* **105**, 8684 (1996).

[158] S. Tsuzuki and H. P. Lüthi. *J. Chem. Phys.* **114**, 3949 (2001).

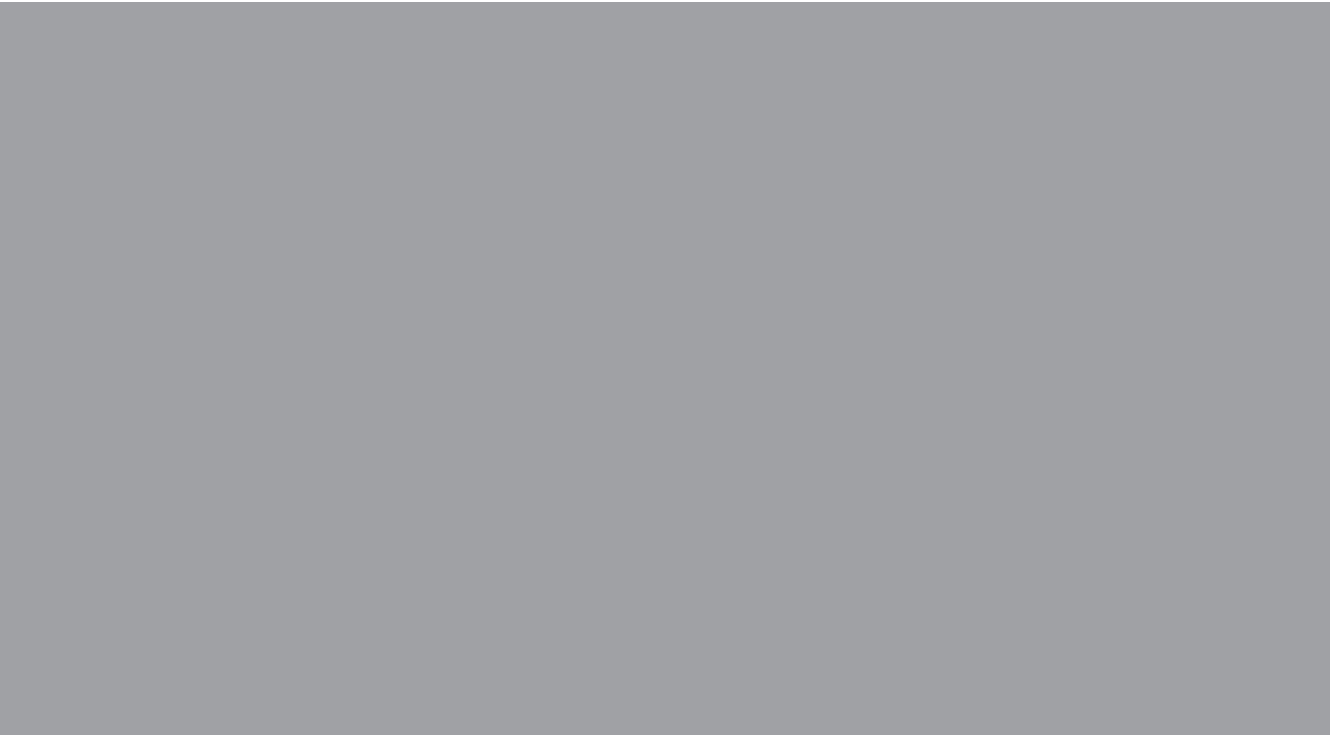[159] A. Heßelmann and G. Jansen. *Chem. Phys. Lett.* **367**, 778 (2003).

[160] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople. *Gaussian 98 (Revision A.11)*. Gaussian, Inc., Pittsburgh, PA, 1998.

[161] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople. *Gaussian 03 (Revision B.03)*. Gaussian, Inc., Pittsburgh, PA, 2003.

[162] R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel. *Chem. Phys. Lett.* **162**, 165 (1989). For current version see www.turbomole.com.

[163] F. Vögtle. *Supramolecular Chemistry*. Wiley, Chichester, 1993.

[164] J.-M. Lehn. *Supramolecular Chemistry*. VCH, Weinheim, 1995.

[165] M. Lozynski, D. Rusinska-Roszak and H.-G. Mack. *J. Phys. Chem. A* **102**, 2899 (1998).

[166] M. S. Gordon and J. H. Jensen. *Acc. Chem. Res.* **29**, 536 (1996).

[167] J. E. Del Bene and M. J. T. Jordan. *J. Am. Chem. Soc.* **122**, 4794 (2000).

[168] M. J. T. Jordan and J. E. Del Bene. *J. Am. Chem. Soc.* **122**, 2101 (2000).

[169] A. Abkowicz-Bieńko, M. Biczysko and Z. Latajka. *Comp. & Chem.* **24**, 303 (2000).

[170] J. Gu and J. Leszczynski. *J. Phys. Chem. A* **103**, 2744 (1999).

[171] T. Kar, S. Scheiner and M. Čuma. *J. Chem. Phys.* **111**, 849 (1999).

[172] R. L. Bell and T. N. Truong. *J. Chem. Phys.* **101**, 10442 (1994).

[173] A. Dkhissi, L. Adamowicz and G. Maes. *J. Phys. Chem. A* **104**, 2112 (2000).

[174] I. Papai and G. Jancsò. *J. Phys. Chem. A* **104**, 2132 (2000).

[175] K. Chapman, D. Crittenden, J. Bevitt, M. J. T. Jordan and J. E. Del Bene. *J. Phys. Chem. A* **105**, 5442 (2001).

[176] H. Takahashi, K. Mamola and E. K. Plyler. *J. Mol. Spect.* **21**, 217 (1966).

[177] I.-J. Chen and D. MacKerell Jr. *Theo. Chem. Acc.* **103**, 483 (2000).

[178] G. A. Olah and G. K. Surya Prakash. *Superacids*. Wiley, New York, 1985.

[179] J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Mäkelä, R. Serimaa, G. ten Brinke and O. Ikkala. *Science* **280**, 557 (1998).

[180] O. Ikkala, J. Ruokolainen, M. Torkkeli, J. Tanner, R. Serimaa and G. ten Brinke. *Colloids and Surfaces* **147**, 241 (1999).

[181] H. Kosonen, S. Valkama, J. Hartikainen, H. Eerikäinen, M. Torkkeli, K. Jokela, R. Serimaa, F. Sundholm, G. ten Brinke and O. Ikkala. *Macromolecules* **35**, 10149 (2002).

[182] J. Ruokolainen, J. Tanner, G. ten Brinke, O. Ikkala, M. Torkkeli and R. Serimaa. *Macromolecules* **28**, 7779 (1995).

[183] J. Ruokolainen, G. ten Brinke, O. Ikkala, M. Torkkeli and R. Serimaa. *Macromolecules* **29**, 3409 (1996).

[184] R. Mäki-Ontto, K. de Moel, E. Polushkin, G. A. van Ekenstein, G. ten Brinke and O. Ikkala. *Adv. Mat.* **14**, 357 (2002).

[185] A. Bagno and G. Scorrano. *Acc. Chem. Res.* **33**, 609 (2000).

[186] T. Yamamoto, T. Maruyama, Z.-H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda and K. Kubota. *J. Am. Chem. Soc.* **116**, 4832 (1994).

[187] M. Onoda. *J. Appl. Phys.* **78**, 1327 (1995).

[188] M. Halim, I. D. W. Samuel, E. Rebourt and A. P. Monkman. *Synth. Met.* **84**, 951 (1997).

[189] O. Ikkala, M. Knaapila, J. Ruokolainen, M. Torkkeli, R. Serimaa, K. Jokela, L. Horsburgh, A. Monkman and G. ten Brinke. *Adv. Mater.* **11**, 1206 (1999).

[190] E. J. Samuelsen, A. P. Monkman, L. A. A. Pettersson, L. E. Horsburgh, K. E. Aasmundtveit and S. Ferrer. *Synth. Met.* **124**, 393 (2001).

[191] M. E. Vaschetto, A. P. Monkman and M. Springborg. *J. Mol. Struct. (Theochem)* **468**, 181 (1999).

[192] A. P. Monkman, M. Hamil, I. D. W. Samuel and L. E. Horsburgh. *J. Chem. Phys.* **109**, 10372 (1998).

[193] Y. Eichen, G. Nakhmanovich, V. Gorelik, O. Epshtein, J. M. Poplawski and E. Ehrenfreund. *J. Am. Chem. Soc.* **120**, 10463 (1998).

[194] J. L. Brédas, G. B. Street, B. Thémans and J. M. André. *J. Chem. Phys.* **83**, 1323 (1985).

[195] J. L. Brédas and A. J. Heeger. *Macromolecules* **23**, 1150 (1990).

[196] M. E. Vaschetto, B. A. Retamal, A. P. Monkman and M. Springborg. *J. Phys. Chem. A* **103**, 11096 (1999).

[197] J.F. Pan, X. Y. Hou, S. J. Chua and W. Huang. *Phys. Chem. Chem. Phys.* **4**, 3959 (2002).

[198] B. Mannfors, J. T. Koskinen, L.-O. Pietilä and L. Ahjopalo. *J. Mol. Struct. (Theochem)* **393**, 39 (1997).

[199] B. Mannfors, L.-O. Pietilä and K. Palmö. *J. Mol. Struct.* **328**, 287 (1994).

[200] U. Koch and A. J. Stone. *J. Chem. Soc. Faraday Trans.* **92**, 1701 (1996).

[201] C. M. Breneman and K. B. Wiberg. *J. Comp. Chem.* **11**, 361 (1990).

[202] J. R. Maple, M. J. Hwang, T. P. Stockfisch, U. Dinur, M. Waldman, G. S. Ewig and A. T. Hagler. *J. Comp. Chem* **15**, 162 (1994).

[203] A.K. Rappe and W.A. Goddard III. *J. Phys. Chem.* **95**, 3358 (1991).

[204] J. Gasteiger and M. Marsili. *Tetrahedron* **36**, 3219 (1980).

[205] F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann. *Advanced Inorganic Chemistry*. John Wiley & Sons, 6th ed., 1999.

[206] T. Ziegler. Density-functional theory as a practical tool in studies of transition metal chemistry and catalysis. In M. Springborg (ed.), *Density-Functional Methods in Chemistry and Materials Science*, p. 69–103. John Wiley & Sons, New York, 1997.

[207] P. E. M. Siegbahn and M. R. A. Blomberg. *Chem. Rev.* **100**, 421 (2000).

[208] R. Roe and Y.-P. Pang. *J. Mol. Model.* **5**, 134 (1999).

[209] M. Hartmann, T. Clark and R. van Eldik. *J. Mol. Model.* **2**, 354 (1996).

[210] M. Pavlov, P. E. M. Siegbahn and M. Sandström. *J. Phys. Chem. A* **102**, 219 (1998).

[211] T. R. Cundari (ed.). *Computational Organometallic Chemistry*. Marcel Dekker, 2001.

[212] M. Diedenhofen, T. Wagener and G. Frenking. The accuracy of quantum chemical methods for the calculation of transition metal compounds. In T. R. Cundari (ed.), *Computational Organometallic Chemistry*, p. 69–121. Marcel Dekker, 2001.

[213] P. J. Hay and W. R. Wadt. *J. Chem. Phys.* **82**, 270 (1985).

[214] T. H. Dunning Jr. and P. J. Hay. In H. F. Schaefer III (ed.), *Modern Theoretical Chemistry*, vol. 3 of *Modern Theoretical Chemistry*, p. 1–28. Plenum Press, New York, 1976.

[215] F. W. Billmeyer. *Textbook of Polymer Science*. John Wiley & Sons, 3rd ed., 1984.

[216] M. B. Smith and J. March. *March's Advanced Organic Chemistry*. John Wiley & Sons, 5th ed., 2001.

[217] C. Pickering, M. L. J. Beale, D. J . Robbins, P. J . Pearson and R. Greef. *J. Phys. C* **17**, 6535 (1984).

[218] L. T. Canham. *Appl. Phys. Lett.* **57**, 1046 (1990).

[219] L. Canham. Visible photoluminescence from porous silicon. In L. Canham (ed.), *Properties of Porous Silicon*, p. 249–255. Institution of Engineering and Technology, 1997.

[220] P. Roura and J. Costa. *Eur. J. Phys* **23**, 191 (2002).

[221] G. Burns. *Solid State Physics*. Academic Press, 1985.

[222] D. Kovalev, H. Heckler, G. Polisski and F. Koch. *Phys. Stat. Sol. B* **215**, 871 (1999).

[223] M. H. Nayfeh, N. Barry, J. Therrien, O. Akcakir, E. Gratton and G. Belomoin. *Appl. Phys. Lett.* **78**, 1131 (2001).

[224] G. Belomoin, J. Therrien, A. Smith, S. Rao, R. Twesten, S. Chaieb, M. H. Nayfeh, L. Wagner and L. Mitas. *Appl. Phys. Lett.* **80**, 841 (2002).

[225] G. Allan, C. Delerue and M. Lannoo. *Phys. Rev. Lett.* **76**, 2961 (1996).

[226] L. N. Dinh, L. L. Chase, M. Balooch, W. J. Siekhaus and F. Wooten. *Phys. Rev. B* **54**, 5029 (1996).

[227] O. Lehtonen and D. Sundholm. *Phys. Chem. Chem. Phys.* **8**, 4228 (2006).

[228] M. Nirmal and L. Brus. *Acc. Chem. Res.* **32**, 407 (1999).

[229] F. Baletto and R. Ferrando. *Rev. Mod. Phys.* **77**, 371 (2005).

[230] M. H. Nayfeh. Stimulated Blue Emission from Ultrasmall Si Nano Particles (A New Phase of Silicon). In N. Bloembergen, N. Rahman and A. Rizzo (eds.), *Conference Proceedings Vol. 71: Atoms, Molecules and Quantum Dots in Laser Fields: Fundamental Processes*, p. 83–96. Societa' Italiana di Fisica, Bologna, 2001.

[231] D. Sundholm. *Nano Lett.* **3**, 847 (2003).

[232] D. Sundholm. *Phys. Chem. Chem. Phys.* **6**, 2044 (2004).

[233] P.-G. Reinhard and E. Suraud. *Introduction to Cluster Dynamics*. Wiley-VCH, 2004.

[234] N. J. Turro. *Modern Molecular Photochemistry*. University Science Books, Sausalito, California, 1991.

[235] S. Rao, J. Sutin, R. Clegg, E. Gratton, M. H. Nayfeh, S. Habbal, A. Tsolakidis and R. M. Martin. *Phys. Rev. B* **69**, 205319 (2004).

[236] A. Smith, Z. H. Yamani, N. Roberts, J. Turner, S. R. Habbal, S. Granick and M. H. Nayfeh. *Phys. Rev. B* **72**, 205307 (2005).

[237] A. Franceschetti and S. T. Pantelides. *Phys. Rev. B* **68**, 033313 (2003).