Computational investigations of nuclear magnetic resonance and magneto-optic properties at the basis-set limit

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Abstract

Theoretical examination of traditional nuclear magnetic resonance (NMR) parameters as well as novel quantities related to magneto-optic phenomena is carried out in this thesis for a collection of organic molecules. Electronic structure methods are employed, and reliable calculations involving large molecules and computationally demanding properties are made feasible through the use of completeness-optimized basis sets.

In addition to introducing the foundations of NMR, a theory for the nuclear spin-induced optical rotation (NSOR) is formulated. In the NSOR, the plane of polarization of linearly polarized light is rotated by spin-polarized nuclei in an NMR sample as predicted by the Faraday effect. It has been hypothesized that this could be an advantageous alternative to traditional NMR detection. The opposite phenomenon, i.e., the laser-induced NMR splitting, is also investigated. Computational methods are discussed, including the method of completeness optimization.

Nuclear shielding and spin-spin coupling are evaluated for hydrocarbon systems that simulate graphene nanoflakes, while the laser-induced NMR splitting is studied for hydrocarbons of increasing size in order to find molecules that may potentially interest the experimentalist. The NSOR is calculated for small organic systems with inequivalent nuclei to prove the existence of an optical chemical shift. The existence of the optical shift is verified in a combined experimental and computational study. Finally, relativistic effects on the size of the optical rotation are evaluated for xenon, and they are found to be significant. Completeness-optimized basis sets are used in all cases, and extensive analysis regarding the accuracy of results is made.
Acknowledgements

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Finally, a thank you goes to Mikko. You keep my feet on the ground and your ease with day-to-day practicalities brings me a great deal of support and stability. You also remind me that things should not be taken too seriously, making everyday life enjoyable.
List of Abbreviations

AO Atomic orbital
B3LYP Becke 3-parameter Lee-Yang-Parr hybrid DFT functional
BH\text{and}HLYP Becke-Half-and-Half-LYP hybrid DFT functional
BLYP Becke-Lee-Yang-Parr GGA DFT functional
CC Coupled cluster
CC2 Coupled cluster with approximate inclusion of double excitations
CCSD Coupled cluster singles and doubles
co completeness-optimized (basis set)
CPL Circularly polarized light
DDFT Dirac density functional theory
DFT Density functional theory
DHF Dirac-Hartree-Fock
DS Diamagnetic shielding
DSO Diamagnetic nuclear spin-electron orbit
FC Fermi-contact
GGA Generalized gradient approximation
GTO Gaussian type orbital
HF Hartree-Fock
KS Kohn-Sham
LC Large component
LCAO Linear combination of atomic orbitals
LDA Local density approximation
LPL Linearly polarized light
MO Molecular orbital
NMR Nuclear magnetic resonance
NR Nonrelativistic
NSOR Nuclear spin-induced optical rotation
OZ Orbital Zeeman
<table>
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<th>Abbreviation</th>
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<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof GGA DFT functional</td>
</tr>
<tr>
<td>PBE0</td>
<td>Perdew-Burke-Ernzerhof hybrid DFT functional</td>
</tr>
<tr>
<td>PSB11</td>
<td>11-cis-retinal protonated Schiff base</td>
</tr>
<tr>
<td>PSO</td>
<td>Orbital hyperfine (or paramagnetic nuclear spin-electron orbit)</td>
</tr>
<tr>
<td>SC</td>
<td>Small component</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-consistent field</td>
</tr>
<tr>
<td>SD</td>
<td>Spin-dipolar</td>
</tr>
<tr>
<td>STO</td>
<td>Slater type orbital</td>
</tr>
<tr>
<td>VIS/NIR</td>
<td>Visible/near-infrared</td>
</tr>
<tr>
<td>X2C</td>
<td>Exact two-component</td>
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List of Publications

List of Publications Included in the Thesis and the Author’s Contributions


IV J. Shi, S. Ikäläinen, J. Vaara, and M. V. Romalis, "Observation of optical chemical shift by precision nuclear spin optical rotation measurements and calculations" *submitted for publication*.


S.I. performed all of the calculations in papers I, III, and V. Preparation of all and execution of most calculations was done by S.I. for II and IV, respectively. The author also carried out the analysis of all computational data and wrote the first versions of the manuscripts for I-III and V of the listed publications, as well as the theoretical part of IV. The publications are referred to in the text by the Roman numerals.

List of Other Publications

1 T. S. Pennanen, S. Ikäläinen, P. Lantto, and J. Vaara, "Nuclear spin optical rotation and Faraday effect in gaseous and liquid water" *submitted for publication*. 
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1 Introduction

Nuclear magnetic resonance (NMR) is an important phenomenon that is applied in various fields of research including, e.g., materials science and medical imaging [1,2]. The effect arises from the behavior of certain magnetic nuclei in an external magnetic field. The NMR signal is extremely sensitive to the chemical surroundings of the nucleus, which allows gathering of detailed information of atomic and electronic structure, dynamics, and order (e.g., of liquid crystal phase) of the investigated sample. The information that is acquired through traditional NMR experiments is incorporated in the spectral parameters, which include nuclear shielding, spin-spin coupling, and quadrupole coupling. Theoretical NMR studies are conducted through electronic structure calculations of these parameters. Drawbacks of the traditional NMR method include limited spatial resolution and the requirement of large sample volumes. Recently, studies [3–13] have been conducted that suggest that magneto-optic phenomena, in particular the Faraday effect [14], could enhance the detection of NMR. In the Faraday effect, a parallel magnetic field causes the plane of polarization of linearly polarized light (LPL) to rotate. Analogously, the field arising from spin-polarized nuclei in an NMR sample causes rotation in the plane of polarization of incident LPL in a phenomenon called the nuclear spin-induced optical rotation (NSOR) [10]. In the opposite, inverse Faraday effect, incident circularly polarized light (CPL) induces a current density in the electron cloud of the sample in an NMR experiment [3, 4]. This corresponds to a static magnetic field at the nucleus, which leads to a laser-induced shift of the NMR lines. The NSOR was first observed experimentally in Ref. [10], and can easily be converted into the corresponding NMR shift and vice versa.

Computational science is a rapidly and continuously evolving field, which has become increasingly important in the last decades [15–17]. In addition to complementing experiments, computational methods allow realistic investigation of phenomena that have not yet been studied experimentally. The field of quantum chemistry involves solving the Schrödinger equation for molecules through different types of approximations. One of these approximations involves the construction of the single-particle states or molecular orbitals (MOs) through a set of functions called a basis set. The quality of the basis set used in a calculation will largely determine the accuracy of the results. Usually, a larger number of basis functions will lead to an improved result. The computational time increases, however, with the number of basis functions. As computer resources are limited, calculations involving large molecules and high-quality
basis sets quickly become unfeasible. Completeness optimization [18] (co) has been introduced as a novel method for the generation of compact, yet high-quality basis sets, which enable accurate calculations of large molecules. The first-principles computational studies conducted in this thesis investigate traditional NMR parameters as well as parameters involving magneto-optic phenomena. Many of these parameters require the use of very high-quality basis sets, which led to the utilization of completeness optimization. Using traditional basis sets, a large part of the calculations involved would not have been possible.

This thesis consists of an introductory part that addresses the theory of the main concepts that are considered in the five research articles, which are then discussed. Graphene, comprising of a single layer of carbon atoms, has raised considerable interest in recent years. The outstanding properties of this material lead to many possible applications in electronics and optics. Paper I predicted the nuclear shielding and spin-spin coupling parameters of large planar hydrocarbons that simulate increasingly large carbon nanoflakes, finite graphene fragments. Convergence of the parameters with system size is observed, allowing the prediction of the magnitude of the parameters at the large-system limit for finite fragments of graphene. In this study, the co basis set generation scheme was applied for the first time for the calculation of the properties of nanosystems.

In Paper II, the laser-induced NMR shift was evaluated for hydrocarbon molecules ranging in size from ethene ($\text{C}_2\text{H}_4$) to fullerene ($\text{C}_{60}$). This study, along with Refs. [5, 6, 8, 9], deemed the magnitude of the shift in most cases too small for detection. It was seen, however, that the shift increases with system size and laser frequency, with amplification by many orders of magnitude around optical resonances. Here, the co basis sets pioneered in computationally demanding magneto-optic properties.

In Paper III, the first-principles theory of NSOR, which is analogous to the theory for the Verdet constant, was formulated. The magnitude of the NSOR angle was then evaluated for water, ethanol, nitromethane, urea, and the light-sensitive retinal model PSB11. Chemical distinction between different molecules and inequivalent nuclei in the same molecule was observed. This implies an optical chemical shift, which can be seen as an analog of the chemical shift of traditional NMR, which arises from nuclear shielding. Improved distinction is found between the different chromophores in PSB11 at laser frequencies approaching the excitation energies of this molecule. Excellent agreement with experimental NSOR for $^1\text{H}$ in water [10] is observed.

Paper IV continued with the NSOR in a joint computational and experimental study. The NSOR was evaluated for $^1\text{H}$ in liquid water, methanol, ethanol, propanol, isopropanol, hexene, hexane, and cyclohexane, as well as for $^{19}\text{F}$ in perfluorohexane. Qualitative agreement between theory and computations was achieved only by using a correction term to the theoretical rotation resulting from the bulk magnetization field [19] present in the experiments performed in condensed media.

In Ref. [10], experimental $^{129}\text{Xe}$SOR seemed to be very close to that corresponding to the computational nonrelativistic (NR) antisymmetric polarizabilities obtained in Ref. [9]. However, it was thereafter noticed that the theoretical analysis in [9] is lacking a factor of two, thus revealing a discrepancy between experiment and the NR
computations. The aim of Paper V was therefore to estimate the effects of using relativistic theory on the magnitude of the nuclear spin-induced optical rotation for $^{129}$Xe. As xenon is a heavy element, it is expected that its hyperfine properties, including the NSOR, should be dependent on relativistic phenomena [20]. It is found that the use of relativistic methods brings the results closer to experimental ones, although intermolecular interaction effects remain yet to be fully taken into account. Paper V is also the first application of co basis sets in fully relativistic calculations.
2 Magnetic Interactions

2.1 Nuclear Magnetic Resonance

Protons, neutrons, and electrons possess a property called spin, which can be considered as an intrinsic angular momentum that also gives rise to a magnetic moment. The spin of these particles has a magnitude of $\frac{1}{2}$ in units $\hbar = h/2\pi$, where $h$ is Planck’s constant. The spin also has a direction, up or down, and opposite spins of electrons or nucleons will cancel each other out when filling single-particle states. Thus, if the nucleus of an atom contains any unpaired protons or neutrons, it will possess a non-zero nuclear spin quantum number $I$. For example, $^{13}\text{C}$ has one unpaired neutron and accordingly has a net nuclear spin equal to $\frac{1}{2}$. In a magnetic field, the nuclear spin has $2I+1$ possible orientations corresponding to spin projection quantum numbers $m_I = -I, -I+1, \ldots, I$. The magnetic moment associated with the spin can be expressed as

$$m = \gamma I,$$

where $\gamma$ is the gyromagnetic ratio (a constant for each nucleus). The interaction Hamiltonian between $m$ and an external magnetic field $B_0$ is $H = -m \cdot B_0$. Thus, when placed in the field, the interaction energy associated with each $m_I$ is

$$E = -\gamma h m_I B_0.$$

In thermal equilibrium, these Zeeman energy levels are populated according to the Boltzmann distribution. Radiation with energy $\Delta E = E(m_I) - E(m_{I-1})$ will cause a transition between two consecutive Zeeman levels. After excitation, the nuclear system relaxes back to its equilibrium state, emitting radiation with the same frequency. In NMR, the system is perturbed with a radiofrequency magnetic field, causing transitions at the resonance frequency, and the emitted radiation at the resonance frequency $\nu = \Delta E/h$ is then observed.

The behavior of magnetic nuclei in an external magnetic field is determined by the standard NMR spin Hamiltonian [1]

$$H = -\frac{1}{2\pi} \sum_K \gamma_k I_K \cdot (1 - \sigma_K) \cdot B_0 + \sum_{K<L} I_K \cdot (D_{KL} + J_{KL}) \cdot I_L + \sum_K I_K \cdot \Theta_K \cdot I_K,$$

given in frequency units $E/h$. The terms in the Hamiltonian represent different inter-
actions that affect the resonance frequency of a nucleus. Equation (2.2) corresponds to a bare nucleus in an external magnetic field. In atoms and molecules, however, electrons alter the magnetic field that is experienced by a nucleus. The first term in Equation (2.3) is equivalent to Equation (2.2), but contains the nuclear shielding tensor $\sigma$, which takes into account the surrounding electrons. $B_0$ induces a current density in the electron cloud that in most cases, according to Lenz’s law, creates an opposing magnetic field. The nucleus is thus shielded from the external field, resulting in a weakened effective field $B = (1 - \sigma)B_0$.

The second term in Equation (2.3) involves the spin-spin coupling, i.e., the interaction between nuclear spins that are close enough to alter each other’s effective magnetic field. The interaction between magnetic moments of two bare nuclei is taken into account through the direct spin-spin coupling tensor $D_{KL}$, while the indirect spin-spin coupling tensor $J_{KL}$ is a correction arising from the presence of the electron cloud.

In Equation (2.3), the last term contains the quadrupole coupling tensor $\Theta_K$, which represents the interaction between the electric quadrupole moment of a nucleus with spin quantum number $I$ greater than or equal to 1, and the electric field gradient at the position of the nucleus arising from the distribution of electrons in the electron cloud.

### 2.1.1 Spectral Parameters

The modifications that external magnetic and electric fields cause in a molecular system as well as the internal hyperfine interactions are very small in comparison to the Coulomb interactions between electrons and nuclei. Perturbation theory is hence appropriate for the study of these effects. When a molecular system is exposed to static perturbations $\beta_1, \beta_2, ...$, the energy of the system may be expressed as a power series in the perturbations:\[ E(\beta_1, \beta_2, ...) = E_0 + \sum_n E_n \beta_n + \frac{1}{2!} \sum_{m,n} E_{mn} \beta_m \beta_n + \mathcal{O}(\beta^3). \] (2.4)

The coefficients $E_n, E_{mn}$ describe the response of the system to the perturbations and are known as molecular properties, which can be calculated as derivatives of the energy with respect to the perturbations, at $\beta_m = \beta_n = 0$. In NMR, the external magnetic field and the field due to the nuclear spins may be considered as perturbations, leading to the energy expression [22]

\[
E(B_0, I_K) = E_0 + B_0 \cdot E_{B_0} + \sum_K I_K \cdot E_{I_K} + \frac{1}{2} B_0 \cdot E_{B_0^2} \cdot B_0 \\
+ \sum_K I_K \cdot E_{I_K \cdot B_0} \cdot B_0 + \frac{1}{2} \sum_{K,L} I_K \cdot E_{I_K \cdot I_L} \cdot I_L + \ldots
\] (2.5)

For closed-shell systems the first-order terms vanish, as observable molecular proper-

\[\text{[In the case of time-dependent perturbations, the energy levels are also time-dependent, and formulation is carried out through the molecular property in question [21].}\]
ties are symmetric with respect to time reversal (\( B_0 \) and \( I_K \) on their own are antisymmetric). Comparing Equation (2.5) to Equation (2.3) and taking into account that only the second-order terms are treated (third-order terms do not contribute significantly from the point of view of current NMR accuracy), it may be shown that the nuclear shielding and indirect spin-spin coupling tensors can be obtained through

\[
\sigma_K = \frac{1}{\gamma_K \hbar} \left. \frac{\partial^2 E(I_K, B_0)}{\partial I_K \partial B_0} \right|_{I_K = B_0 = 0} + 1
\]  \tag{2.6}

and

\[
J_{KL} = \frac{1}{\hbar} \left. \frac{\partial^2 E(I_K, I_L)}{\partial I_K \partial I_L} \right|_{I_K = I_L = 0} - D_{KL}.
\]  \tag{2.7}

Here, the contributions from the bare nuclei are subtracted, as \( \sigma_K \) and \( J_{KL} \) include only the effects arising from the electronic cloud, while \( E(B_0, I_K) \) and \( E(I_K, I_L) \) include the energy terms corresponding to the bare nuclei as well.

The second-order perturbation expression for the energy is given by [21]

\[
E^{(2)}_0 = |0\rangle \langle H^{(2)} |0\rangle + \sum_{n \neq 0} \frac{|0\rangle \langle H^{(1)} |n\rangle \langle n| H^{(1)} |0\rangle}{E_0 - E_n},
\]  \tag{2.8}

where \( H^{(1)} \) and \( H^{(2)} \) refer to first- and second-order perturbations and \(|0\rangle, |n\rangle\) is the basis of the eigenfunctions of the unperturbed system. Here, it is convenient to adopt the notation of response theory, which is used to formulate perturbation theory to describe the interaction between a system and a (generally) time-dependent external field. The expectation value of an operator \( A \), in a system exposed to the perturbation \( V \) can be written as a series [23]

\[
\langle A(t) \rangle = \langle 0| A |0\rangle + \int_{-\infty}^{\infty} d\omega_1 e^{-i\omega_1 t} \langle \langle A; V^{\omega_1} \rangle \rangle_{\omega_1}
\]

\[
+ \frac{1}{2} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 e^{-i(\omega_1 + \omega_2)t} \langle \langle A; V^{\omega_1}, V^{\omega_2} \rangle \rangle_{\omega_1, \omega_2}
\]

\[
+ \frac{1}{6} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 e^{-i(\omega_1 + \omega_2 + \omega_3)t} \langle \langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle \rangle_{\omega_1, \omega_2, \omega_3}
\]

+ \ldots,
\]  \tag{2.9}

where \( \langle 0| A |0\rangle \) is the unperturbed expectation value and \( V^{\omega} \) is the perturbation operator at frequency \( \omega \). The second term characterizes the response to a single perturbation, and contains the linear response function \( \langle \langle A; V^{\omega_1} \rangle \rangle_{\omega_1} \). The third and fourth terms involve two or three perturbation operators, and contain quadratic and cubic response functions. E.g., \(\langle \langle A; V^{\omega_1} \rangle \rangle_{\omega_1} \) can be written as a sum over the eigenstates of the unperturbed Hamiltonian

\[
\langle \langle A; V^{\omega_1} \rangle \rangle_{\omega_1} = \sum_{n \neq 0} \frac{|0\rangle \langle n| V^{\omega_1} |0\rangle}{\omega_1 - (E_n - E_0)} - \sum_{n \neq 0} \frac{|0\rangle \langle n| V^{\omega_1} |n\rangle A |0\rangle}{\omega_1 + (E_n - E_0)}.
\]  \tag{2.10}

The higher-order response functions accordingly contain all contributions that are
Magnetic Interactions

linear in all the involved perturbation operators. Using Equation (2.10), (2.8) can be expressed as

\[ E_0^{(2)} = H_0^{(2)} + \frac{1}{2} \langle \langle H^{(1)}; H^{(1)} \rangle \rangle_{\omega=0}, \]  

(2.11)

through which the traditional, static spectral parameters of NMR may be calculated. For nuclear shielding and spin-spin coupling, (2.6) and (2.7), respectively, the \( H^{(1)} \) contain either \( B_0 \) or \( I_K \), and \( H^{(2)} \) contains \( B_0 \) with \( I_K \) or \( I_K \) with \( I_L \).

2.2 Magneto-Optic Phenomena

2.2.1 Optical Rotation Through the Faraday Effect

In an optically active substance, the plane of polarization of LPL rotates as it passes through the medium. Consider the electric field \( \mathbf{E} \) of a LPL beam, which can be split into CPL components (with \( \mathbf{E}^+ \) corresponding to right CPL and \( \mathbf{E}^- \) corresponding to left CPL) propagating in the \( Z \) direction as \([21]\)

\[ \mathbf{E} = \mathbf{E}^+ + \mathbf{E}^- \]

\[ \mathbf{E}^- = \mathbf{E}i \cos \phi_- - \mathbf{E}j \sin \phi_- ; \quad \mathbf{E}^+ = \mathbf{E}i \cos \phi_+ + \mathbf{E}j \sin \phi_+ , \]  

(2.12)

where \( \mathbf{E} \) is the amplitude of the electric field, \( i \) is the unit vector in the \( x \) direction, and \( j \) the unit vector in the \( y \) direction. The phase angles \( \phi_{\pm} \) are given by

\[ \phi_{\pm} = \omega t - \frac{2\pi Z}{\lambda_{\pm}} = \omega t - \frac{n_{\pm} \omega Z}{c} , \]  

(2.13)

where \( \omega \) is the frequency at which the field oscillates and \( n_{\pm} \) are the indices of refraction of the medium for \( \mathbf{E}^{\pm} \). If the indices of refraction of the medium are different for left and right CPL, \( \mathbf{E} \) can be expressed as

\[ \mathbf{E} = 2\mathbf{E} \cos \phi \{ i \cos(Z\omega \Delta n/2c) - j \sin(Z\omega \Delta n/2c) \} \]  

(2.14)

through the identities:

\[ \phi = \omega t - n \omega Z/c \]  

(2.15)

\[ n = \frac{1}{2}(n_+ + n_-) \]  

(2.16)

\[ \Delta n = n_+ - n_- . \]  

(2.17)

This corresponds to LPL that is inclined at an angle \( \theta = Z \omega \Delta n/2c \) with respect to the plane of polarization of the incident LPL. For path length \( l \) through the medium, \( \theta = lw(n_+ - n_-)/2c \). Now \( n_+ = n_{XY} \) and \( n_- = n_{YX} \) (with the LPL beam propagating in the \( Z \) direction), and the complex index of refraction is given, for \( n \approx 1 \), by \([24]\)

\[ n_{\epsilon r} = \delta_{\epsilon r} + \frac{N}{2\epsilon_0} \langle \alpha_{\epsilon r} \rangle , \]  

(2.18)
where $\langle \alpha_{\epsilon \tau} \rangle$ is the average polarizability and $N$ is number density. In the presence of a magnetic field, the wave function of the system is complex, and $\langle \alpha_{\epsilon \tau} \rangle$ can be broken down into a symmetric and antisymmetric part, so that $\alpha_{\epsilon \tau} \to \alpha_{\epsilon \tau} + \mathbf{i} \alpha'_{\epsilon \tau}$. $\alpha_{\epsilon \tau}$ is the conventional symmetric polarizability, while $\alpha'_{\epsilon \tau}$ is the antisymmetric polarizability, which can be expressed as a power series with respect to the external field and nuclear spin as [11,24,25]

$$\alpha'_{\epsilon \tau} = \sum_{\nu} \alpha'_{\epsilon \tau,\nu}(B_0) B_{0,\nu} + \sum_{\nu} \alpha'_{\epsilon \tau,\nu}(I_K) I_{K,\nu} + \mathcal{O}(B_0^3, I_K^3).$$

(2.19)

The measurable rotation angle $\Phi = \text{Re} \theta$, realizing that $\alpha_{\epsilon \tau} = \alpha_{\tau \epsilon}$ and $\alpha'_{\epsilon \tau} = -\alpha'_{\tau \epsilon}$, can be written as

$$\Phi = N l \omega^2 \varepsilon_0 c \text{Im} \langle \alpha'_{XY} \rangle.$$

(2.20)

Far away from resonances, $\alpha'$ is purely imaginary due to the magnetic perturbation [25]. The antisymmetric polarizability may be induced by the external magnetic field or the field due to the nuclear spins. For the external field $B_0 = B_0 \hat{Z}$ (with $\hat{Z}$ indicating a unit vector in the Z direction) or the average spin polarization $\langle I_K \rangle = \langle I_{K,Z} \rangle \hat{Z}$, in a medium where isotropic molecular tumbling of molecules occurs,

$$\langle \alpha'_{XY} \rangle = \left\{ \frac{B_0}{6} \sum_{\epsilon,\tau,\nu} \varepsilon_{\epsilon \tau \nu} \alpha'_{\epsilon \tau,\nu}(B_0) \langle I_{K,Z} \rangle \right\}.$$

(2.21)

Here, $\varepsilon_{\epsilon \tau \nu}$ is the Levi-Civita symbol, $\epsilon, \tau$, and $\nu$ are coordinates in the Cartesian molecule-fixed frame, and $\langle I_{K,Z} \rangle$ is the degree of spin polarization.

Through the perturbation $V^\pm(t) = -\mu \cdot \mathbf{E}^\pm(t)$, where $\mu$ is the electric dipole moment, and response theory [Equation (2.9)], $\alpha'_{\epsilon \tau,\nu}(I_K)$ can be expressed as quadratic response functions

$$\alpha'_{\epsilon \tau,\nu}(B_0/I_K) = -\langle \langle \mu_\epsilon; \mu_\tau, h^{\text{OZ/PSO}} \rangle \rangle_{\omega,0}.$$

(2.22)

In Equation (2.22), the expression of the conventional dynamic electric dipole polarizability, $\alpha(\omega) = -\langle \langle \mu; \mu \rangle \rangle_{\omega}$, is modified by a third, static magnetic operator $h$. $h^{\text{OZ}}$ and $h^{\text{PSO}}$ refer to the Zeeman and orbital hyperfine operators, which are defined in Section 2.3. The Verdet constant $V$ of Faraday rotation and the NSOR rotation angle $V_K$ (normalized to unit concentration $[\cdot] = N/N_A$ of the polarized nuclei $K$) are then obtained through [III]

$$V = \frac{\Phi_F}{B_0 l} = -\frac{1}{2} \omega N \mu_0 c \sum_{\epsilon,\tau,\nu} \varepsilon_{\epsilon \tau \nu} \text{Im} \langle \langle \mu_\epsilon; \mu_\tau, h^{\text{OZ}} \rangle \rangle_{\omega,0}$$

(2.23)

and

$$V_K = \frac{\Phi_{\text{NSOR}}}{[\cdot] l} = -\frac{1}{2} \omega N_A \mu_0 c \langle I_{K,Z} \rangle \sum_{\epsilon,\tau,\nu} \varepsilon_{\epsilon \tau \nu} \text{Im} \langle \langle \mu_\epsilon; \mu_\tau, h^{\text{PSO}} \rangle \rangle_{\omega,0}.$$

(2.24)

$V$ and $V_K$ do not take into account the effect of the bulk magnetization field $B_b$, which is present in an experimental sample. The magnetization of the other
molecules in the medium will affect the magnetic field experienced by the molecule treated through equations (2.23) and (2.24). This effect is discussed in detail in Ref. [19], and is negligible for Faraday rotation. For the NSOR, the magnitude of the effect is relevant for protons [26]. The magnetization field is obtained through

$$B_b = \mu_0 \left( \frac{1}{3} - \eta \right) M,$$  \hspace{1cm} (2.25)

where $\eta$ is a shape factor depending on the geometry of the sample and the bulk magnetization $M$, through Equation (2.1), is given by $M = \mathcal{N} h \gamma_K \langle I_K \rangle$. The presence of this field results in an additional rotation analogous to the Faraday rotation, given by $\Phi_b = V l B_b$. A bulk correction $V_b$ must then be added to $V_K$ in order to be fully comparable to experimental results. For a cylindrical sample volume, $\eta = 0$ and the bulk correction is, hence, given by

$$V_b = \Phi_b = \frac{1}{3} \mathcal{N} A \mu_0 \langle I_{K,Z} \rangle h \gamma_K V.$$

The samples used for the $^1H$ experiments discussed in this thesis have the shape of a long cylinder with the axis along the direction $(Z)$ of the magnetization.

The experimental setup for NSOR detection is portrayed in Figure 2.1. The sample is placed in a cylindrical container of length $l$ along the $Z$-axis, along which the LPL beam is also directed. The magnetic field $B$ is parallel to the light beam.

**Figure 2.1:** Experimental setup for a Faraday rotation experiment. $B$ arises either from an external source or from prepolarized nuclei.

### 2.2.2 NMR Shift Induced by the Inverse Faraday Effect

The effect of impinging circularly polarized light onto an NMR sample, i.e., the laser-induced NMR shift, also involves the antisymmetric polarizability that is present in the expressions for the Verdet constant and NSOR. The interaction of the electric field of the CPL with the electron cloud in an atom induces a current density. The first-order current density oscillates with the laser frequency, and cannot be detected through NMR, as effects having optical frequency average to zero on the NMR timescale [3]. The second-order current density will give a time-independent contribution [3], and can produce effects that are in principle observable in NMR. In this inverse Faraday effect, the current density corresponds to a magnetic moment...
and causes a magnetic interaction corresponding to a static magnetic field at each nucleus, which is directed along the light beam [3].

The hyperfine magnetic field (arising from electronic motion) at the site of nucleus K, \( B_{PSO}^{K} \), is modified by the same perturbation \( V^{\pm}(t) \) as was used above for the Verdet constant and NSOR. The \( \epsilon \) component of the static perturbed magnetic field can be written as [4]

\[
B_{PSO}^{K,\epsilon} = \frac{1}{2\omega} \sum_{\tau\nu} b_{K,\epsilon}^{\tau\nu} \left( E_{\epsilon}^{\pm} \dot{E}_{\nu}^{\pm} - \dot{E}_{\epsilon}^{\pm} E_{\nu}^{\pm} \right),
\]

(2.27)

where the dot refers to differentiation with respect to time. \( B_{PSO}^{K,\epsilon} \) is parallel to the CPL beam and is in opposite directions for right and left CPL [9]. Reduction to the isotropic rotational average due to molecular tumbling is again applied, so that the coefficient \( b_{K,\epsilon}^{\tau\nu} \) reduces to

\[
b_{K,\epsilon} = \frac{1}{6} \sum_{\epsilon\tau\nu} \epsilon_{\epsilon\tau\nu} b_{K,\epsilon}^{\tau\nu}. \]

(2.28)

The induced field \( B_{PSO}^{K,\epsilon} \) couples to the magnetic moment \( m_{K} \) of the nucleus with the interaction Hamiltonian

\[
H_{\pm}^{\pm} = -m_{K} \cdot B_{PSO}^{K,\epsilon},
\]

(2.29)

where \( I_{K,Z} \) is the component of \( I_{K} \) along the light beam. \( H_{NMR}^{\pm} \) is added to the NMR spin Hamiltonian [Equation (2.3)], and corresponds to frequency shifts of the Zeeman states by \( \Delta/2 \) and \(-\Delta/2\) for the two differently polarized beams. Transitions with \( \Delta m_{I} = \pm 1 \) take place, and \( H_{NMR}^{\pm} \) gives a shift of resonance frequencies of

\[
\Delta = \frac{1}{4\pi} \gamma_{K} b_{K} \epsilon_{N},
\]

(2.30)

Figure 2.2 illustrates the effect of a CPL beam on the Zeeman energy levels of a nucleus with \( I = 1/2 \), while Figure 2.3 shows how the transitions would appear in the spectral lines. The splitting in the spectral lines upon switching between right and left CPL is \( 2\Delta \).

Upon recognizing that the intensity of the laser beam \( I_{0} = \frac{1}{2} c \epsilon_{0} E^{2} \), where \( \epsilon_{0} \) is the permittivity of a vacuum, \( \Delta \) can be expressed in terms of beam intensity as

\[
\frac{\Delta}{I_{0}} = \frac{1}{2\pi} \gamma_{K} c \mu_{0} b_{K}.
\]

(2.31)

The coefficient \( b \) may be equated with \( \alpha' \), as the same antisymmetric polarizability is responsible for both the NSOR and the laser-induced NMR splitting. The two phenomena may thus be interconverted through the relation [III,10]

\[
\Phi_{NSOR} = -h\omega N_{A} \langle I_{K,Z} \rangle \frac{\Delta}{I_{0}}.
\]

(2.32)
Figure 2.2: Effect of a CPL beam on the Zeeman energy levels of a nucleus with $I = 1/2$ ($\gamma$ is assumed to be positive). The red arrows denote transitions.

Figure 2.3: Splitting of the NMR spectral lines on the frequency scale as a result of irradiation with a CPL beam.
2.3 The Molecular Hamiltonian

The Hamiltonian that is used in electronic structure calculations to obtain NMR parameters contains the external magnetic field and the nuclear magnetic moments:[27]

\[ H = \frac{1}{2m_e} \sum_i \pi_i^2 + \frac{e \hbar}{2m_e} g_i \sum_i s_i \cdot B^{\text{tot}}(r_i) - \frac{e^2}{4\pi\epsilon_0} \sum_{iK} \frac{Z_K}{r_{iK}} + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i\neq j} \frac{1}{r_{ij}}, \]  

(2.33)

where \( s_i \) is the spin of electron \( i \), \( B^{\text{tot}}(r_i) \) is the magnetic field at \( i \), and \( \pi_i \) is the momentum operator given by

\[ \pi_i = -i\hbar \nabla_i + eA^{\text{tot}}(r_i). \]  

(2.34)

\( A^{\text{tot}}(r_i) \) is the vector potential at \( i \). The magnetic induction may be written in terms of the vector potential as

\[ B^{\text{tot}}(r_i) = \nabla_i \times A^{\text{tot}}(r_i). \]  

(2.35)

The vector potential as well as the magnetic induction may be expressed through contributions from the external field and each nucleus

\[ A^{\text{tot}}(r_i) = A_0(r_i) + \sum_K A_K(r_i) \]  

(2.36)

\[ B^{\text{tot}}(r_i) = B_0(r_i) + \sum_K B_K(r_i). \]  

(2.37)

In calculations of NMR properties, the Coulomb gauge, where \( \nabla \cdot A = 0 \), is commonly used for vector potentials. \( A_0(r_i) \) corresponding to the external field can be written as

\[ A_0(r_i) = \frac{1}{2} B_0 \times r_{iO}, \]  

(2.38)

where \( r_{iO} \) denotes a vector from the gauge origin to electron \( i \). \( A_K(r_i) \), the vector potential corresponding to the magnetic field of the nuclear spins, may, in turn, be expressed as

\[ A_K(r_i) = \frac{\mu_0}{4\pi} \frac{m_K \times r_{iK}}{r_{iK}^3}, \]  

(2.39)

where \( r_{iK} \) is the vector from nucleus \( K \) to electron \( i \). Substituting the vector potential into Equation (2.33), one is left with a Hamiltonian consisting of, first, the zeroth-order Hamiltonian corresponding to the unperturbed situation and, secondly, terms that are linear and bilinear in \( B \) and \( m_K \). The first- and second-order perturbation operators that are relevant for the nuclear shielding, spin-spin coupling, and magneto-optic effects of interest in this thesis are the orbital Zeeman (OZ), orbital hyperfine (paramagnetic nuclear spin-electron orbit, PSO), diamagnetic shielding (DS), diamagnetic nuclear spin-electron orbit (DSO), spin-dipolar (SD), and Fermi-contact (FC)
interactions, which can be written as \[28\]

\[
H^{(1)}_{OZ} = \sum_\epsilon h^{OZ}_{\epsilon} B_{0,\epsilon}; \quad h^{OZ}_{\epsilon} = \frac{e}{2m_e} \sum_i l_{iO,\epsilon},
\]  

\[
H^{(1)}_{PSO,K} = \sum_\epsilon h^{PSO}_{K,\epsilon} I_{K,\epsilon}; \quad h^{PSO}_{K,\epsilon} = \frac{e\hbar \mu_0}{m_e 4\pi \gamma K} \sum_i \frac{l_{iK,\epsilon}}{r_{iK}},
\]  

\[
H^{(2)}_{DS,K} = \sum_{\epsilon\tau} h^{DS}_{K,\epsilon\tau} B_{0,\epsilon} I_{K,\tau};
\]  

\[
h^{DS}_{K,\epsilon\tau} = \frac{e^2 \hbar^2}{2m_e 4\pi \gamma K} \sum_i \left( r_{iO} \cdot r_{iK} \right) \delta_{\epsilon\tau} - \frac{r_{iK} r_{iO,\tau}}{r_{iK}^3},
\]  

\[
H^{(2)}_{DSO,KL} = \sum_{\epsilon\tau} h^{DSO}_{KL,\epsilon\tau} I_{K,\epsilon} I_{L,\tau};
\]  

\[
h^{DSO}_{KL,\epsilon\tau} = \frac{e^2 \hbar^2}{2m_e 4\pi} \sum_i \left( r_{iK} \cdot r_{iL} \right) \delta_{\epsilon\tau} - \frac{r_{iL} r_{iK,\tau}}{r_{iL}^3},
\]  

\[
H^{(2)}_{SD,K} = \sum_{\epsilon\tau} h^{SD}_{K,\epsilon\tau} I_{K,\epsilon};
\]  

\[
h^{SD}_{K,\epsilon\tau} = \frac{e^2 \hbar^2 \mu_0}{2m_e 4\pi \gamma K} \sum_i \sum_{s_i,\epsilon} \frac{3r_{iK,\epsilon} r_{iK,\tau} - \delta_{\epsilon\tau} r_{iK}^2}{r_{iK}^3},
\]  

\[
H^{(1)}_{FC,K} = \sum_\epsilon h^{FC}_{K,\epsilon} I_{K,\epsilon}; \quad h^{FC}_{K,\epsilon} = \frac{4\pi e^2 \hbar^2 \mu_0}{3m_e 4\pi \gamma K} \sum_i \delta(r_{iK}) s_{i,\epsilon}.
\]  

In these formulae, \(l_{iO}\) and \(l_{iK}\) are the angular momenta of \(i\) with respect to the gauge origin \(O\) and nucleus \(K\), respectively.

### 2.3.1 Nuclear Shielding

From Equation (2.6), terms in the molecular Hamiltonian that are linear in \(B_0\) and \(I_K\) contribute to the nuclear shielding tensor. \(\sigma\) can be expressed as the sum of diamagnetic and paramagnetic parts as

\[
\sigma = \sigma^d_K + \sigma^p_K.
\]  

The diamagnetic part \(\sigma^d_K\) arises from Equations (2.11) and (2.6) as the ground-state expectation value of the second-order operator \(h^{DS}\)

\[
\sigma^d_K = \frac{1}{\gamma K \hbar} \langle 0 | h^{DS}_K | 0 \rangle.
\]  

\(\sigma^p_K\) is obtained from the first-order operators as

\[
\sigma^p_K = \frac{1}{\gamma K \hbar} \langle h^{PSO}_K, h^{OZ} \rangle_0.
\]
2.3.2 Spin-Spin Coupling

The spin-spin coupling involves contributions in the Hamiltonian that are linear in both $I_K$ and $I_L$, resulting in five different terms [29]

$$J_{KL} = J_{KL}^{DSO} + J_{KL}^{PSO} + J_{KL}^{SD} + J_{KL}^{FC} + J_{KL}^{SD/FC},$$

given by

$$J_{KL}^{DSO} = \frac{1}{\hbar} \langle 0 | h_{KL}^{DSO} | 0 \rangle,$$

$$J_{KL}^{PSO} = \frac{1}{\hbar} \langle \langle h_{KL}^{PSO} \rangle \rangle_0,$$

$$J_{KL}^{SD} = \frac{1}{\hbar} \langle \langle h_{KL}^{SD} \rangle \rangle_0,$$

$$J_{KL}^{FC} = \frac{1}{\hbar} \langle \langle h_{KL}^{FC} \rangle \rangle_0,$$

$$J_{KL}^{SD/FC} = \frac{1}{\hbar} \left[ \langle \langle h_{KL}^{SD} \rangle \rangle_0 + \langle \langle h_{KL}^{FC} \rangle \rangle_0 \right],$$

For molecules that are very asymmetric, e.g., planar entities, the NMR interactions for different directions may vary significantly. Tensorial properties of a tensor $T$ with respect to the $z$ direction may be assessed through the anisotropy $\Delta T$ and asymmetry parameter $\eta_T$, defined through

$$\Delta T = T_{zz} = \frac{1}{2} (T_{xx} + T_{yy})$$

and

$$\eta_T = \frac{T_{xx} - T_{yy}}{T_{zz}}.$$

The FC term of the coupling is fully isotropic, while the other terms may contribute to the anisotropy and asymmetry parameters. The SD/FC term, on the other hand, is fully anisotropic and does not contribute to the isotropic spin-spin coupling.

2.3.3 Relativistic Theory

The Schrödinger equation does not take into account the effects of relativity. In heavy atoms, electrons close to the nuclei travel at relativistic speeds. The effects become substantial for NMR properties, as the core region of the atom is probed by the operators that are involved. The Dirac equation, in which the scalar nonrelativistic wave function is replaced by a four-component spinor, provides a relativistically nearly correct theory for electrons\(^\dagger\). The Dirac Hamiltonian is given by [30]

$$H_D = c \alpha \cdot \pi_4 + \beta m_e c^2 - e \phi,$$

where $\phi$ is the scalar potential and $\alpha$ refers here to the Dirac $4 \times 4$ matrix operators, through which $\beta$ is also defined. The matrix operators are obtained as $\alpha_i = \rho \otimes \sigma_i$,\(^\dagger\)

\(^\dagger\)Upon extending the Dirac one-particle theory to a many-body problem, the interactions between electrons cannot be expressed analytically. The NR Coulomb operator, which is not Lorentz covariant, is thus used, resulting in a small error [30].
where

\[ \rho = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \]  

(2.58)

and

\[ \alpha_0 = \beta = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \]  

(2.59)

The Pauli spin matrices \( \sigma \) are the observables related to the spin of spin-\( \frac{1}{2} \) particles and are written as

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} ; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} ; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]  

(2.60)

The four-spinor solutions of the Dirac equation are

\[ \Psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix} \]  

(2.61)

where \( L \) refers to the large-component wave function, which corresponds to positive-energy "electronic" states, and \( S \) to the small-component wave function, corresponding to negative-energy "positronic" states, which may be discarded in nonrelativistic theory. Relativistic four-component calculations are significantly more time-consuming than NR calculations, which limits their feasibility. Less expensive, exact two-component (X2C) methods \[31\] have also been formulated, in which the small components are eliminated but relativistic effects on the electronic wave function are nevertheless retained.

Expanding the relativistic Hamiltonian [Equation (2.57)] similarly to the NR Hamiltonian (2.33), leads to the relativistic forms of the operators, of which the Zeeman

\[ h^Z = \frac{e}{2} \sum_i (\alpha \times r_{iO})_z \]  

(2.62)

and hyperfine

\[ h^\text{hf}_{K,c} = \frac{e \mu_0 \hbar \gamma_K}{4\pi} \sum_i \frac{(\alpha \times r_{iK})_c}{r_{iK}^3} \]  

(2.63)

are relevant for the relativistic calculations discussed in the this thesis.
Chapter 3: Electronic Structure Calculations

The field of quantum chemistry is centered on solving the time-independent Schrödinger equation

\[ H\Psi = E\Psi \]  

for a given atomic, molecular, or solid-state system. The Schrödinger equation can, however, be solved exactly only for a system consisting of one proton and one electron. Hence, various ways of approximating the many-body problem have been developed, giving rise to different methods in computational chemistry and materials science [15, 17]. These methods usually utilize the Born-Oppenheimer approximation, in which the electrons move in a static potential created by the much heavier nuclei, which are considered as stationary. This allows the separation of the electronic and nuclear components of the wave function, making calculations substantially less complicated.

3.1 Methods

The different electronic structure calculation methods offer a variety of advantages regarding efficiency and accuracy. Hartree-Fock (HF) theory provides the simplest solution [15]. This method takes the Coulomb interaction between electrons into account only as an average repulsion. As a result, HF will only usually give \( \sim 99\% \) of the total energy, and can cause large errors in the calculation of other properties. The remaining \( \sim 1\% \) between the HF energy and the exact energy is called the electron correlation energy, which can be accounted for by electron correlation methods [15]. These include post-Hartree-Fock theories, which are based upon HF, as well as density functional theory (DFT) methods. In DFT, correlation is incorporated approximately through various exchange-correlation functionals, which in present-day calculations are mostly semi-empirical. Calibration with respect to experimental results or more accurate calculations is typically required.

3.1.1 Hartree-Fock Theory

In Hartree-Fock, an electron is depicted as moving in the static potential of the nuclei (from the Born-Oppenheimer approximation) and the average distribution of the other electrons. This is realized by taking a trial wave function that consists of one Slater
determinant [15]. A Slater determinant can be used to construct a fermionic wave function as an antisymmetrized product of single-electron wave functions. The Slater determinant for a system comprising of \(N\) electrons is given by

\[
\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\
\chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(N) & \chi_2(N) & \cdots & \chi_N(N)
\end{vmatrix},
\]

(3.2)

where the different one-electron functions \(\chi\) are given as products of a spatial function and a spin function [15]. In the linear combination of atomic orbitals (LCAO) model, the spatial functions \(\psi\), i.e., molecular orbitals, are created as linear combinations of basis functions \(\phi\) as [15]

\[
\psi_i = \sum_P c_{P,i} \phi_P.
\]

(3.3)

The variational method is used, which states that the energy calculated from an approximation of the wave function will always be higher than the true energy. Thus, a better wave function gives a smaller energy, and the best wave function allowed by the wave function ansatz and the basis set gives the minimum energy [16]. Through the requirement that the first variation of the energy \(E\) with respect to the wave function parameters vanishes \((\delta E = 0)\), from the wave function ansatz (equation 3.2) and using the Lagrange method to keep the one-electron wave functions orthonormal, one can acquire the HF equations:

\[
F\psi_i = \varepsilon_i \psi_i.
\]

(3.4)

Here, \(F\) is the Fock operator and \(\varepsilon_i\) is the MO energy, which is related to the Lagrange multipliers [16]. The Fock operator can be expressed through the one-electron operator \(h\), and the two-electron Coulomb and exchange operators \(J\) and \(K\), as [15]

\[
F = h + \frac{1}{2} \sum_j \left( J_j - K_j \right).
\]

(3.5)

The Coulomb operator describes the repulsion energy between electrons, while the exchange operator describes the electron exchange energy, which refers to the decrease in the energy for pairs of electrons with the same spin. \(J\) and \(K\) are both functions of all the solutions \(\{\psi_i\}\), which implies that iterative methods are called for. The solutions of each iteration are used in the operators, which is why the term self-consistent field (SCF) is used. Using the LCAO model, the HF equations may be written in matrix form as the Roothaan-Hall equations [32,33]

\[
FC = SC\epsilon,
\]

(3.6)

where

\[
F_{PQ} = \langle \phi_P | F | \phi_Q \rangle
\]

(3.7)
3.1. Methods

and

\[ S_{PQ} = \langle \phi_P | \phi_Q \rangle. \]  

(3.8)

Here, \( F \) is the Fock matrix, \( C \) is the MO coefficient matrix, \( S \) is the AO overlap matrix, and \( \epsilon \) is the orbital energy matrix. An initial guess for the AO coefficients is made, after which the Fock matrix is constructed, its eigenvalues giving new coefficients \( C \), and these are then used iteratively until specified convergence thresholds are reached.

3.1.2 Density-Functional Theory

DFT methods are based on the Hohenberg-Kohn theorem that states that the ground state energy of a system is a unique functional of its electron density [34]. Hence, in DFT, the electronic Schrödinger equation is solved for a system that is described through the electron density rather than the many-body wave function [17]. The wave function of a system with \( N \) electrons has \( 3N \) variables, while the electron density only has three (x, y and z). Through what is called the Kohn-Sham (KS) method [35], the many-body problem of interacting electrons in a static potential is reduced to the problem of hypothetical non-interacting electrons moving in an effective potential that includes Coulomb correlations. The KS method involves splitting the kinetic energy functional of a system into two parts, one of which is the kinetic energy for non-interacting electrons, and the other is included in an exchange-correlation term \( E_{xc}[\rho] \) that accounts for interactions between electrons [15]. The electron density is written in terms of one-electron KS orbitals \( \psi_i \) as

\[ \rho(r) = \sum_i |\psi_i(r)|^2. \]  

(3.9)

Minimization of the energy functional using the Lagrange method will lead to eigenvalue equations similarly as in the case of the HF equations. These are called the Kohn-Sham equations and can be formulated as [15]

\[ F_{KS} \psi_i = \epsilon_i \psi_i, \]  

(3.10)

where

\[ F_{KS} = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_K \frac{Z_K}{r_{1K}} + \int \frac{\rho(r_2)}{r_{12}} \, dr_2 + V_{xc}(r_1). \]  

(3.11)

\( V_{xc}(r_1) \) is the exchange-correlation potential, which is related to the exchange-correlation energy \( E_{xc}[\rho] \) through

\[ V_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}. \]  

(3.12)

The main problem in DFT is that the exact form of \( E_{xc}[\rho] \) is unknown. Different approximations of this term lead to different DFT methods. The local density approximation (LDA) is the simplest method [36]. In LDA, the electron density of the system is assumed to be a very slowly changing function, and thus \( E_{xc}[\rho] \) depends only
on the density at the location where it is evaluated. Usually the exchange-correlation energy is split into exchange energy $E_x[\rho]$ and correlation energy $E_c[\rho]$. In LDA, $E_x[\rho]$ is obtained for the uniform electron gas model and $E_c[\rho]$ stems from parametrizations of data from quantum Monte Carlo calculations for the uniform electron gas [36].

An improvement over LDA is to make $E_x[\rho]$ and $E_c[\rho]$ depend on the derivatives of the density as well as the density itself [17]. This approach is called generalized gradient approximation (GGA). $E_x[\rho]$ can also be given exactly by HF theory when the HF orbitals are replaced by KS orbitals. Hybrid DFT methods use suitable combinations of the exact exchange from HF and exchange and correlation functionals from LDA and GGA methods. More accurate results for molecular properties are usually obtained when a suitable amount of exact exchange is incorporated [37].

Both HF and DFT methods effectively lead to one-electron functions that characterize the many-body system. HF does not incorporate correlation, but does include exact exchange, while DFT includes both exchange and correlation approximately. The DFT approach leads to results that are usually more accurate than HF results, which is seen also for magnetic properties [38]. DFT methods have turned out to be successful, but it must be kept in mind that there is no practical way to systematically improve them, and comparison to either experiment or systematic many-body computations must be carried out to verify results.

### 3.1.3 Coupled Cluster Theory

Coupled cluster (CC) methods are based on the HF method, but differ from it by systematically incorporating electron correlation. To improve upon HF results, more than one Slater determinant is needed to construct the wave function. For a closed-shell system with $N$ electrons and $n$ basis functions, solution of the HF equations will give $N/2$ occupied orbitals and $n-N/2$ unoccupied orbitals. In CC, a cluster operator is used to generate modified Slater determinants from the HF determinant. These determinants are constructed by replacing occupied MOs by unoccupied MOs. The number of replaced MOs defines the type of correction that is added to the reference function. If one MO is replaced, the Slater determinant is singly excited as compared to the HF determinant, and if two MOs are replaced, it is doubly excited etc. If all possible determinants were included, the correlation treatment would be exact within a given basis [15]. The coupled cluster wave function can be written as

$$|\Psi_{CC}\rangle = e^T|\Psi_{HF}\rangle$$

$$e^T = 1 + T + \frac{1}{2}T^2 + \frac{1}{6}T^3 + \ldots = \sum_{k=0}^{\infty} \frac{1}{k!} T^k,$$

where $\Psi_{HF}$ is the HF wave function and the cluster operator $T$ is given by [15]

$$T = T_1 + T_2 + T_3 + \ldots + T_N.$$
The effect of applying $T$ on the HF wave function is given by \[ T_1 \Psi_{HF} = \sum_{ip} t^p_i \Psi^p_i \quad ; \quad T_2 \Psi_{HF} = \sum_{ijpq} t^{pq}_{ij} \Psi^{pq}_{ij} \quad ; \quad \ldots \] (3.16)

Here, $t^p_i$ and $t^{pq}_{ij}$ are single- and double-excitation amplitudes, etc. Equation (3.13) is inserted into the Schrödinger equation, and it is projected from the left by $\Psi_{HF}$ and the excited determinants $\Psi^{pq}_{ij \ldots}$, leading to

$$\langle \Psi_{HF} | H e^T | H_{HF} \rangle = E$$

and

$$\langle \Psi^{pq}_{ij \ldots} | H e^T | H_{HF} \rangle = E \langle \Psi^{pq}_{ij \ldots} | e^T | \Psi_{HF} \rangle,$$

where the former equation is used to evaluate the energy and the latter is used to iteratively solve for the excitation amplitudes. In many cases the CC method is the most accurate, albeit most time-consuming, currently available quantum chemical approach. In this thesis, the CC method is used where applicable, i.e., for small molecules, to judge the performance of DFT methods.

### 3.2 Basis Sets

Common basis functions used in LCAO expansions [Equation (3.3)] are Slater type orbitals (STOs) \[ \phi_S(r, \theta, \varphi) = Y_{lm}(\theta, \varphi) r^l e^{-\zeta r} \] (3.19) and Gaussian type orbitals (GTOs)

$$\phi_G(r, \theta, \varphi) = Y_{lm}(\theta, \varphi) r^l e^{-\zeta r^2},$$

(3.20)

where $r$ is the distance from the nucleus, $Y_{lm}(\theta, \varphi)$ are the spherical harmonics for angular momentum quantum number $l$ ($l = 0$ corresponds to $s$ orbitals, $l = 1$ to $p$ orbitals etc.), and $\zeta$ are the exponents that determine the spatial range of the orbital.

The GTOs are in principle inferior to STOs because STOs have the correct “cusp” at the nucleus, while GTOs have zero slope \[15\]. This causes problems with representing the correct behavior near the nucleus with GTOs. The GTO also has a shorter “tail”, i.e., falls off too rapidly at large $r$, and thus represents the wave function further from the nucleus poorly. Because of these disadvantages, a larger number GTOs are needed to achieve the same accuracy as with STOs. GTOs are, however, preferred because of the ease of calculating two-electron integrals with them due to the Gaussian product theorem \[16\].

The exponents of GTOs can be optimized to give a minimum atomic energy with reference to, e.g., SCF calculations (e.g., Huzinaga basis sets \[39\]) or correlated calculations, as in correlation consistent (cc) basis sets \[40\]. A minimal basis set refers to the minimum number of functions required to build all the occupied orbitals in the atoms of a system in their ground state. A double zeta (DZ) basis contains twice the
number of functions of a minimal basis, triple zeta (TZ) three times the number of functions, etc. With the above-mentioned traditional methods of creating basis sets, the basis is optimized for each element separately. Basis sets can also be optimized for specific properties, e.g., the Jensen pJ-n basis sets [41], which have been constructed for accurate calculations of indirect spin-spin coupling constants using DFT methods.

The quality of a basis set can be improved by increasing the number of basis functions. A complete basis set contains an infinite number of functions and its result in a calculation is called the basis-set limit. The main complication when working with basis sets is the computational time involved. For Hartree-Fock and DFT calculations, the time increases as \( n^4 \), where \( n \) is the number of basis functions, while for more accurate methods the power of \( n \) increases. This implies that for demanding properties or large molecules, calculations involving large basis sets may not be feasible.

### 3.2.1 Completeness Optimization

Completeness optimization was introduced by Manninen and Vaara [18] as a novel method of generating basis sets. Only a mathematical criterion is used, as opposed to optimization with regard to atomic energies, which is usually the case in traditional basis sets. Using this scheme, basis sets achieving the level of quality equal to that of traditional sets can be generated with a smaller number of functions. An important tool used in completeness-optimization is the concept of the completeness profile, defined as [42]

\[
Y(\zeta) = \sum_n \langle g(\zeta)|\chi_m \rangle^2,
\]

where \( \{\chi\} \) is a set of orthonormalized basis functions and \( g(\zeta) \) is a “test” GTO with the exponent \( \zeta \). \( g(\zeta) \) is used to analyze the completeness of \( \{\chi\} \), and the value of \( Y(\zeta) \) is 1 for all \( \zeta \) in a complete Gaussian basis set (a basis set that has an infinite number of functions). A measure for the deviation from completeness is [18]

\[
\tau = \int_{\log(\zeta_{\text{min}})}^{\log(\zeta_{\text{max}})} [1 - Y(\zeta)] d \log(\zeta).
\]

\( Y(\zeta) \) can be visualized on a \( \log(\zeta), Y(\zeta) \) plot, in which case the profile of a basis set that is complete for a certain range of \( \zeta \) will be 1 within this range, creating a plateau-type figure. Figure 3.1 shows the completeness profile of a traditional basis set, cc-pVTZ.

Completeness-optimized basis sets can be generated using the Kruunuhaka program [43]. With the completeness-optimization scheme in Kruunuhaka, one can specify the exponent range in which the basis set should be complete, i.e., the overlap with arbitrary GTOs with exponents in the same range should approach unity [18]. Once a basis set achieving this is created, the number of functions is reduced, which will increase \( \tau \) and cause ripples in the plateau region of a completeness profile. The adequate exponent range and “smoothness” of the plateau can be determined exper-
Figure 3.1: Completeness profile of the basis set cc-pVTZ for carbon. Profiles for the different $l$-values are shown separately.

imentally by carrying out trial calculations of the investigated property. The trial calculations may be done for a small model system that has chemical bonds that are similar to the system of interest. This results in a basis set that is as economic as possible for a given accuracy requirement, determined by the exponent interval $[\zeta_{\text{min}}, \zeta_{\text{max}}]$ and the allowed $\tau$. The completeness profiles of the four co basis sets (co-0, co-1, co-2, and co-3) that are used in this thesis for calculations of the laser-induced splitting and NSOR are shown in Figure 3.2.

The co basis set can in principle be used for any element because it is not constructed by using characteristics that are specific to a single atom. This universality does, however, have some limitations. The required exponent range becomes larger for increasingly heavy atoms, and the too large depth and/or an unsuitable location of the ripples in the completeness profile may have unwanted consequences. If a completeness-optimized basis set is generated for an atom for calculations of a specific property, the same basis set can also be used in calculations for any atom before it in the periodic table, as the required exponent range increases with atomic number. Nevertheless, when considering the computational cost, it is more efficient to optimize the exponent range for each element separately. In the work done in this thesis, the same basis set is used for atoms C–F close to each other in the periodic table.
Figure 3.2: Completeness profiles of the basis sets co-0, co-1, co-2 and co-3 for carbon.
4 Summary of Papers

4.1 Paper I – NMR Parameters in Graphene Fragments

The remarkable electron mobility, thermal conductivity, opacity, and breaking strength of graphene [44] give rise to countless potential applications. Experimental NMR is yet to be done on graphene, which makes theoretical evaluation of its magnetic properties of interest. The electronic structure of graphene has been studied using solid-state methods with periodic boundary conditions, in which a zero-gap semiconductor band structure is indicated [45]. Large planar hydrocarbons can be used to simulate portions of carbon nanosheets, i.e., graphene fragments or graphene nanoflakes, which are finite molecules with a finite band gap.

In Paper I, the nuclear shielding ($\sigma$) and spin-spin coupling ($J$) tensors, along with their anisotropies, were evaluated for $^{13}$C in increasingly large hydrocarbon molecules using the DFT functionals BLYP [46, 47] (0%), B3LYP [47–49] (20%), BHandHLYP [47, 50] (50%), PBE (0%), and PBE0 [51] (25%). The numbers in parentheses denote the percentage of the HF exact exchange incorporated in the DFT functional. The molecules are depicted in Figure 4.1. The nuclear shielding as well as one-bond ($^1J$), two-bond ($^2J$), and three-bond ($^3J$) spin-spin coupling were calculated for the innermost carbon nuclei. Ethene (C$_2$H$_4$) was used for testing of basis set convergence and calibration of the DFT methods with respect to the ab initio CCSD method (coupled cluster including single and double excitations). The nanosystems of interest here can be obtained from the benzene molecule (C$_6$H$_6$), by adding consecutive planar layers of benzene molecules, carbon hexagons, to the carbon rings to form coronene (C$_{24}$H$_{12}$), circumcoronene (C$_{54}$H$_{18}$), and circumcircumcoronene (C$_{96}$H$_{24}$).

It was hypothesized that the properties converge with system size to a limiting value, which could then be assigned to larger graphene fragments. Completeness optimization was used to generate basis sets that give near basis-set limit results.

Two co basis sets were compared to the traditional energy-optimized correlation consistent (cc) basis set families cc-pVXZ [40], cc-pCVXZ [52], aug-cc-pVXZ [53], aug-cc-pCVXZ [52], and Jensen’s pcJ-n sets. The basis-set convergence is seen in Figure 4.2, from which it can be concluded that the co basis sets give values closer to the basis-set limit than the other basis set families, with relatively few functions.

The performance of the DFT functionals for ethene can be seen in Table 4.1. The magnitude of $\sigma$ increases with the amount of exact exchange in the functional,
Figure 4.1: The studied molecules: ethene, benzene, coronene, circumcoronene, and circumcircumcoronene. The different color carbons indicate the atoms between which the spin-spin coupling tensor was calculated. The shielding tensors were calculated for the innermost carbon atoms.

while DFT results overall remain far below the experimental and CCSD values. This deshielding is, however, characteristic to DFT [54]. For $^1J$, the best agreement with experiment among the DFT functionals is obtained with BLYP and PBE. In all parameters, an overestimation that further increases along with the percentage of exact exchange in the functional occurs. On the basis of the calculations done for ethene (results given here) and benzene (not shown), the PBE/co-r level of theory was chosen to study the larger molecules.

As the co-r basis set is still too large for feasible calculations of the largest system (circumcircumcoronene), and, furthermore, the shielding and spin-spin coupling involve highly local hyperfine operators, the locally dense basis set concept was applied [56, 57]. Calculations were carried out with coronene, circumcoronene, and circumcircumcoronene with the innermost (co-r**) or two innermost benzene rings
Figure 4.2: $^{13}$C nuclear shielding constant in ethene as a function of the number of basis functions $n$ with co basis sets (co-b with C:18s11p7d and H:11s7p and co-r with C:15s8p5d and H:4s2p) and traditional basis-set families using the BLYP method.

Table 4.1: Nuclear shielding and spin-spin coupling constants and anisotropies (with reference to the plane normal direction) for ethene with the basis set co-b and different DFT functionals.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Shielding</th>
<th>Spin-spin coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma$</td>
<td>$\Delta \sigma$</td>
</tr>
<tr>
<td>BLYP</td>
<td>41.58</td>
<td>174.40</td>
</tr>
<tr>
<td>B3LYP</td>
<td>43.77</td>
<td>178.16</td>
</tr>
<tr>
<td>BHandHLYP</td>
<td>47.79</td>
<td>180.56</td>
</tr>
<tr>
<td>PBE</td>
<td>44.76</td>
<td>176.75</td>
</tr>
<tr>
<td>PBE0</td>
<td>47.72</td>
<td>180.14</td>
</tr>
<tr>
<td>CCSD</td>
<td>68.30</td>
<td>165.72</td>
</tr>
</tbody>
</table>

$^a$ SD contribution calculated with the co-r basis set. $^b$ The ACES-II program used for the CCSD calculations does not report the SD/FC cross-term contribution necessary for $\Delta^1J$. $^c$ Ref. [55], liquid crystal solution.

(co-r*) treated with the co-r basis, while the traditional basis def2-SVP [58] was used for the rest of the molecule. The results show that the performance of co-r** is sufficient for circumcircumcoronene. Figure 4.3 shows the nuclear shielding and spin-spin coupling constants for benzene and the larger molecules. All parameters excluding $\sigma$ and $^1J$ display an oscillatory convergence with system size. Also $\sigma$ and $^1J$ do, however, seem to level off with the larger systems, and similar results are expected for even larger molecules. Convergence of the parameters occurs despite the fact that there is no convergence in energetics (e.g., the HOMO-LUMO gap) at these system sizes, which is interpreted to follow from the locality of NMR properties. From Figure 4.3,
limiting values can be assigned to finite graphene fragments. These values, based on visual inspection, are $\sigma = 54 \pm 1$ ppm, corresponding to the chemical shift 134 ppm with CH$_4$ as a reference, $\Delta \sigma = 207 \pm 4$ ppm, and for the couplings: $^1J = 59.0 \pm 0.5$ Hz, $^1\Delta J = -1.5 \pm 0.5$ Hz, $^2J = 0.2 \pm 0.4$ Hz, $^2\Delta J = -4.6 \pm 0.2$ Hz, $^3J = 6 \pm 1$ Hz, and $^3\Delta J = 3 \pm 1$ Hz. The results are useful for future experimental work, as prediction of the NMR parameters for graphene nanoflakes is, thus, made. The methods used here may also be used for efficient studies of other carbon nanosystems.

4.2 Paper II – Laser-induced NMR splitting in hydrocarbons

In Refs. [3] and [4], it was proposed that circularly polarized light impinging onto an NMR sample induces a shift in the NMR frequency, and can thus lead to enhancements in molecular structure determination. Computational studies [8,9] using conventional
laser frequencies concluded that the effect was too small to be measured. It was, however, predicted that the magnitude of the shift would increase with the static polarizability of the system, and that massive amplification of the effect would occur around optical resonances.

In Paper II, the laser-induced NMR splitting, $2\Delta$, for $^{13}$C was computed at standard laser frequencies in the visible/near-infrared (VIS/NIR) region, as well as at frequencies approaching the optical resonances of the systems for ethene ($C_2H_4$), benzene ($C_6H_6$), coronene ($C_{24}H_{12}$), fullerene ($C_{60}$), and circumcoronene ($C_{54}H_{18}$) using the ab initio wave function methods HF, CC2 [59], and CCSD (which is the most accurate of the presently used methods), as well as the DFT functionals BLYP, B3LYP, and BHandHLYP. The nuclei for which the effect is studied are equivalent to those indicated in Figure 4.1. The selection of the molecules is based on decreasing excitation energies and increasing polarizability with the system size, in an attempt to find molecules for which the splitting would be of such magnitude that it could be detected experimentally.

The laser-induced shift is a computationally demanding property because the electronic structure must be described well both close to the nuclei due to the hyperfine operator involved, and also at the outer limits of the electron cloud, as this is where the interaction with the external electric field mainly occurs. In Paper II, the completeness-optimization scheme was applied for the first time to create compact basis sets that furnish basis-set-limiting values for magneto-optic properties. Due to the size of the larger studied molecules, calculations giving adequate results are unattainable using traditional basis sets. The laser-induced splitting for ethene using the HF method and three co basis sets as well as the correlation-consistent basis set families is shown in Figure 4.4. It is evident that the performance of the co sets exceeds that of the energy-optimized sets, even at under 100 functions for carbon. The co sets also give results that are close to each other, making the smaller co basis sets suitable for use in calculations involving larger molecules.

In addition to the basis-set testing, ethene was used also to analyze the accuracy of the DFT methods. Figure 4.5 shows $2\Delta/I_0$ for ethene at various laser frequencies using different ab initio and DFT methods with the co-2 basis. It is seen that the BHandHLYP functional performs very well in comparison to the correlated wave function methods. Consequently, the BHandHLYP method and co-2 and co-3 sets were used for the remaining calculations.

$2\Delta/I_0$ as a function of laser frequency at the BHandHLYP/co-2 level (BHandHLYP/co-3 for the two largest molecules) for all the studied systems at standard laser frequencies are seen in Figure 4.6. The splitting at frequencies approaching excitation energies are shown in Figure 4.7 for ethene and circumcoronene. From Figure 4.6, the magnitude of the splitting increases with frequency and with system size. The distinct behavior of circumcoronene is due to the fact that it is already approaching its lowest optical excitation energy. In Figure 4.7, the isotropic rotational average of the splitting is shown, as well as the splittings corresponding to the beam and induced field in the $x$, $y$, and $z$ directions (as seen in Figure 4.1), which could be attainable with experiments done on single crystals. Again, the splitting grows with system size and
Figure 4.4: Laser-induced $^{13}$C NMR splitting divided by beam intensity $2\Delta/I_0$ for ethene at 514.5 nm at the Hartree-Fock level using completeness-optimized sets (co-1 with C:13s11p4d2f and H:6s2p, co-2 with C:10s7p3d and H:3s1p, and co-3 with C:7s4p3d and H equivalent to co-2) and correlation consistent basis sets with different number of basis functions ($n$).

Figure 4.5: Laser-induced $^{13}$C NMR splitting divided by beam intensity $2|\Delta|/I_0$ as a function of laser frequency in ethene with various methods using the co-2 basis set.

frequency, and the regions where substantial enhancement of the effect are seen are in the vicinity of the excitation energies of the systems. It must be kept in mind, however, that perturbation theory currently in use breaks down at the resonances, making evaluation of the splitting at the exact locations of excitation energies impossible.

Dynamic polarizabilities of the systems near the resonances are studied as well, and they are found to be in accordance with Figure 4.7. Laser intensities required to
4.3 Paper III – NSOR and Chemical Distinction

Finding systems for which experimental detection of the laser-induced splitting is feasible appears possible but nevertheless problematic in Paper II. Hence, it is more enticing to continue investigations of magneto-optic effects through the opposite phenomenon arising from the Faraday effect, the NSOR, as it is easier to detect.

**Figure 4.6:** Laser-induced $^{13}$C NMR splitting divided by beam intensity $2|\Delta|/I_0$ as a function of laser frequency in different hydrocarbon systems using the co-2 basis and BHandHLYP functional (co-3 basis for fullerene and circumcoronene). A change of sign occurs in $2\Delta/I_0$ for circumcoronene after 0.0656245 a.u. (694.3 nm).

**Figure 4.7:** Laser-induced $^{13}$C NMR splitting divided by beam intensity, $2\Delta/I_0$, (a) C$_2$H$_4$ using BHandHLYP/co-2 and (b) C$_{54}$H$_{18}$ using BHandHLYP/co-3 at frequencies around optical resonances. The line corresponding to the induced field in the $x$ direction is not visible for coronene, as the effect of a beam in the plane of the molecule is minimal.
The NSOR has indeed been seen experimentally in $^1\text{H}$ in liquid water and $^{129}\text{Xe}$ in Ref. [10]. This phenomenon could be used as an alternative to traditional NMR methods, provided that chemical distinction is observed. Differing signals should thus be observed for nuclei in different chemical surroundings. In Paper III, the first-principles theory of the NSOR was formulated, and its magnitude was evaluated at standard VIS/NIR laser frequencies for isolated water (H$_2$O), nitromethane (CH$_3$NO$_2$), ethanol (C$_2$H$_5$OH), urea [(NH$_2$)$_2$CO], and 11-cis-retinal protonated Schiff base (PSB11), which is a light-sensitive molecule found in the eye. For all systems excluding PSB11, also the Verdet constants were computed. The molecules are shown in Figure 4.8.

$V_{\text{H}}$, given in Table 4.2, and $V$ were calculated for water at the different frequencies using the basis sets co-1 and co-2 that were developed in Paper II, and the \textit{ab initio} methods HF, CC2, and CCSD, as well as the DFT functionals BLYP, B3LYP, BHandHLYP, PBE, and PBE0. Comparison reveals that, as seen before, the
4.3. Paper III – NSOR and Chemical Distinction

Table 4.2: Calculated nuclear spin-induced optical rotation angle divided by unit concentration and sample length, \(V_H\), [in \(10^{-6}\) rad/(M cm)] in liquid water using different methods and the basis set co-2. \(^a\)

<table>
<thead>
<tr>
<th>(\omega) (a.u.)</th>
<th>(\lambda) (nm)</th>
<th>HF</th>
<th>BHandHLYP</th>
<th>B3LYP</th>
<th>BLYP</th>
<th>PBE0</th>
<th>PBE</th>
<th>CC2</th>
<th>CCSD</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0932147</td>
<td>488.8</td>
<td>0.30</td>
<td>0.41</td>
<td>0.55</td>
<td>0.74</td>
<td>0.51</td>
<td>0.71</td>
<td>0.58</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>0.0885858</td>
<td>514.5</td>
<td>0.27</td>
<td>0.36</td>
<td>0.49</td>
<td>0.66</td>
<td>0.45</td>
<td>0.63</td>
<td>0.52</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>0.0854545</td>
<td>532.0</td>
<td>0.25</td>
<td>0.33</td>
<td>0.46</td>
<td>0.61</td>
<td>0.42</td>
<td>0.59</td>
<td>0.48</td>
<td>0.39</td>
<td>0.40 ± 0.08 (^b)</td>
</tr>
<tr>
<td>0.0773571</td>
<td>589.0</td>
<td>0.20</td>
<td>0.27</td>
<td>0.37</td>
<td>0.49</td>
<td>0.33</td>
<td>0.47</td>
<td>0.39</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>0.0791732</td>
<td>770.0</td>
<td>0.12</td>
<td>0.16</td>
<td>0.21</td>
<td>0.27</td>
<td>0.26</td>
<td>0.22</td>
<td>0.18</td>
<td>0.20 ± 0.04 (^b)</td>
<td></td>
</tr>
<tr>
<td>0.0428226</td>
<td>1064.0</td>
<td>0.06</td>
<td>0.08</td>
<td>0.11</td>
<td>0.14</td>
<td>0.10</td>
<td>0.13</td>
<td>0.11</td>
<td>0.09</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Normalized to 1 M = 1 mol dm\(^{-3}\) concentration and full polarization of proton spins, \(\langle I_Z \rangle = 1/2\).

\(^b\) Ref. [10]. Liquid-state measurement.

hybrid DFT functionals with the largest amount of exact exchange, i.e., PBE0 and BHandHLYP in this case, give values closest to those with CCSD. For the NSOR, the experimental values from Ref. [10] are reproduced quantitatively with CCSD. The excellent agreement with experiment may, however, be partly coincidental, as solvation and medium effects such as bulk magnetization are not taken into account in these calculations. It was seen that co-1 and co-2 give results close to each other and, once again, the BHandHLYP/co-2 level was selected for further analyses, in which the co-2 exponents for carbon are used also for nitrogen and oxygen.

Figure 4.9 shows \(V_H\) as a function of laser frequency in water, nitromethane, ethanol, and urea. It is observed, expectedly, that the magnitude of the effect increases with frequency, as does the laser-induced splitting, which is calculated through the same response theory formula. In addition, it was seen that differing values are given by different molecules and also inequivalent nuclei in the same molecule, which can be considered as analogous to the chemical shift of traditional NMR. In order to be more beneficial, chemical distinction through NSOR would require selection of nuclear spins, instead of only the detection of the average signal from all the nuclei in the molecule. This could in principle be achieved through optical excitation. It was seen earlier in Paper II, that the antisymmetric polarizability \(\alpha^{(1k)}(\omega)\) increases considerably at near-resonant frequencies. Figure 4.10 illustrates \(^1\)HSOR in ethanol at frequencies approaching resonances. Significant amplification of the effect is seen as before, but also the nuclei in different chemical groups are excited at different resonances.

For excitations in the range of laser wavelengths that are experimentally attainable, the PSB11 molecule could be used. \(V_H\) in PSB11 was computed at the standard laser frequencies. Chemical distinction between different nuclei and different groups is again conveyed. Further experimental work to explore the possibilities of optical NMR is encouraged, as the existence of chemical distinction through NSOR is proved.
Figure 4.9: Calculated $V_H$ [in $10^{-5}$ rad/(M cm)] as a function of laser frequency in liquid ethanol, nitromethane, and water, as well as solid urea at the BHandHLYP/co-2 level. Equivalent nuclei in the same functional group are averaged.

Figure 4.10: $V_H$ [in rad/(M cm)] in liquid ethanol close to optical resonances (173.59, 148.72, 141.38, and 139.25 nm, dashed vertical lines) at the BHandHLYP/co-2 level of theory. Offsets of 0.002 rad/(M cm) are used to improve visibility.

4.4 Paper IV – Experimental and Theoretical NSOR in Organic Molecules

The results of Paper III indicate that the NSOR may in fact be a potential alternative to traditional NMR, and Paper IV continued with this phenomenon. Experimental and computational evaluation of the NSOR and Verdet constants was carried
Figure 4.11: The studied molecules in Paper IV: water, methanol, ethanol, propanol, isopropanol, hexene, hexane, cyclohexane, and perfluorohexane (H$_2$O, CH$_3$OH, C$_2$H$_5$OH, CH$_3$CH$_2$CH$_2$OH, C$_3$H$_6$O, C$_6$H$_{12}$O, C$_6$H$_{14}$, C$_6$H$_{12}$, and C$_6$F$_{14}$). Numbering of the nuclei used in the calculations is also given.

out for $^1$H in liquid water (H$_2$O), methanol (CH$_3$OH), ethanol (C$_2$H$_5$OH), propanol (CH$_3$CH$_2$CH$_2$OH), isopropanol (C$_3$H$_6$O$_2$), hexene (C$_6$H$_{12}$), hexane (C$_6$H$_{14}$), and cyclohexane (C$_9$H$_{12}$), and $^{19}$F in perfluorohexane (C$_6$F$_{14}$) at 405 nm. The molecules are depicted in Figure 4.11. In the theoretical part of the study, the wave function methods HF and CCSD (where feasible) were used, along with DFT functionals BLYP, B3LYP, and BHandHLYP. As it was realized in Ref. [19] that in an experimental sample, the bulk magnetization will provide an additional term [Equation (2.26)] to the NSOR angle, the bulk correction $V_b$ was also evaluated. The co-2 basis set was employed once again along with the co-0 basis set (with C-O: 12s8p4d1f and H: 8s8p5d), which was developed in Ref. [26] for basis-set converged NSOR for both $^1$H and first-row main-group systems through calibration with the hydrogen fluoride molecule.

Figure 4.12 shows the true NSOR ($V_K$) and bulk-corrected values ($V_K + V_b$) along with the experimental results. Of the DFT functionals, B3LYP and BHandHLYP...
are displayed, as they were seen to give results closest to experimental values. It is seen that the use of a larger basis set leads to larger values of NSOR in all cases excluding water, for which no significant changes are observed. For all molecules except hexene and perfluorohexane, $V_K$ is smaller than the experimental result. The bulk correction does, however, bring the theoretical result overall closer to experiment. In the case of water, the bulk correction leads to overestimation using the B3LYP method. For perfluorohexane, the total NSOR is overestimated. The experimental results reported here are among the first demonstrations of the optical chemical shift between molecules (in addition to Refs. [12] and [13]), and qualitative agreement is achieved through first-principles calculations. In most cases, the bulk magnetization correction brings theory and experiment closer to each other, but the other medium effects should also be taken into account for a more detailed analysis.

4.5 Paper V – Relativistic Effects in the Optical Rotation of Xenon

In Ref. [10] the experimental NSOR in liquid $^{129}$Xe was compared to the nonrelativistic theoretical results obtained in Ref. [9], leading to excellent agreement. This is surprising, as relativistic effects should play a role in calculations for heavy nuclei. It was, in fact, noticed in the course of the current work, that a factor of two is
missing from the theoretical analysis in Ref. [9], leaving their calculations in reality ~50% higher than the measured values in Ref. [10]. Paper V targeted at the evaluation of relativistic NSOR, Verdet constants, and nuclear shielding constants for $^{129}$Xe. Nonrelativistic HF, DFT, and CCSD, two-component (X2C) [31] HF, and fully relativistic four-component Dirac-Fock (DHF) and Dirac-DFT (DDFT) calculations were carried out. The DFT functionals employed here were BLYP, B3LYP, and BHandHLYP. Completeness optimization was used in a first application to fully relativistic calculations. Intermolecular interaction effects were also estimated through calculations involving a Xe dimer. The bulk correction is not computed here, as for xenon these effects are minimal.

The basis-set convergence of $\sigma$, $V$, and $V_{Xe}$ using the traditional Dyall basis sets vxz and cvxz [60–62] and the completeness-optimized basis set co (35s32p24d3f) was analyzed, and it was seen that the Dyall basis sets do not yet converge in the series with $x = 2, 3,$ and 4 for the NSOR, and the results move monotonously away from the co value. It was also demonstrated that the addition of diffuse $d$-type functions to the dyall.cv4z set does, however, bring the result much closer to the co value. For the other properties, the Dyall sets converge to values that are somewhat lower than those with the co set.

In Figure 4.13, the relativistic DHF and X2C results for both $V_{Xe}$ and $V$ are seen to be close to each other, as well as the experimental results. Comparing DHF to NR values, it is seen that the earlier discrepancy between NR theory [9] and experiment [10], can be accounted for through relativity. As in all the previous studies, the magnitude of the NSOR grows with frequency. Figure 4.14 gives $V_{Xe}$ and $V$ with various methods using the co basis set. As the percentage of exact exchange in the DFT functional increases, the results are lowered closer to the HF values. Despite this, DFT results remain significantly higher than HF or experimental values. For NR $^{129}$XeSOR, CCSD results are ~65–75% higher than HF, which implies that relativistic ab initio correlated results (methods for which are currently not available) would also increase $V_{Xe}$, rendering it further away from the experimental values. For $V$, the same trends are observed, but on a smaller scale.

As it seems as though $^{129}$XeSOR is overestimated, the approximations that are made should be considered. Our calculations involved an isolated $^{129}$Xe atom, while the experiment was conducted on liquid $^{129}$Xe. It was seen in Ref. [26], that for $^1$H and $^{17}$O in water, $V_K$ is lowered by 14% and 29%, respectively, upon going from a static molecule in vacuo to an interacting molecule in liquid phase. In Paper V, a decrease in the NSOR values of ~35–45% is also seen for DHF calculations on a $^{129}$Xe dimer at its equilibrium geometry [$r_{Xe-Xe} = 4.3627$ Å (Ref. [65])] with the co basis set, results for which are given in Table 4.3.

The calculations done in Paper V verify that relativistic treatment is necessary for $^{129}$Xe, and compatibility with experimental NSOR cannot be achieved nonrelativistically. DFT results for an isolated atom remain higher than experimental values, but agreement is improved if intermolecular interaction effects are accounted for.
Figure 4.13: (a) $^{129}$Xe nuclear spin-induced optical rotation angle divided by unit concentration and sample length, $V_{Xe}$, [in $10^{-5}$ rad/(M cm)] and (b) Verdet constant $V$ [rad/(T m)] for gaseous Xe at different laser wavelengths using the completeness-optimized basis set co and the fully relativistic four-component (DHF), exact two-component (X2C), and non-relativistic (NR) Hartree-Fock methods. The experimental data from Ref. [10] and Ref. [63] are also shown.

Table 4.3: Nuclear spin-induced optical rotation $\Phi_{NSOR}/(|\lambda|) [\text{in } 10^{-5} \text{ rad/(M cm)}]$ for $^{129}$Xe in an interacting Xe dimer (at the equilibrium interatomic distance $r_{Xe-Xe} = 4.3627$ Å) and a non-interacting Xe atom at different laser wavelengths using the completeness-optimized basis set co and the four-component DHF method. The difference between the interacting and non-interacting systems, $\delta$, is also given.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\omega$ (a.u.)</th>
<th>non-interacting</th>
<th>interacting</th>
<th>$\delta$</th>
</tr>
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<tr>
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</tr>
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</table>
Figure 4.14: (a-b) $^{129}$Xe Nuclear spin-induced optical rotation angle [in $10^{-5}$ rad/(M cm)] and (c-d) the Verdet constant [in rad/(T m)] for gaseous Xe at different laser wavelengths using the completeness-optimized basis set co and the Hartree-Fock (HF) method as well as density functional theory with BLYP, B3LYP, and BHandHLYP functionals. Nonrelativistic results are displayed on the left [(a) and (c)], while the relativistic results are given on the right [(b) and (d)]. Values obtained through both the default non-collinear and collinear spin density approaches [64] are shown for DFT, and they are seen to be nearly equivalent.
5 Conclusions

Magnetic properties, including traditional NMR parameters as well as magneto-optic phenomena, were studied in this thesis using electronic structure calculations for systems ranging from a xenon atom to large planar hydrocarbon molecules as large as 117 atoms. Results approaching the basis-set limit were attained through the use of completeness-optimization. In this recently developed method of generating basis sets, only mathematical criteria are used, which will lead to a basis set that is higher in quality than a traditional, energy-optimized basis set with the same number of functions. This outstanding performance was verified for all the co basis sets developed in the course of this work.

The \(^{13}\text{C}\) nuclear shielding and spin-spin constants, along with anisotropies with respect to the direction of the normal of the molecular plane, were evaluated for planar hydrocarbons that mimic graphene nanoflakes. Due to its remarkable properties, there is growing interest in the properties of graphene, but experimental NMR is yet to be done. The calculations done in Paper I of this thesis show that the NMR properties converge with system size, and limiting values can be assigned to large graphene fragments.

The use of circularly or linearly polarized light in NMR experiments leads to phenomena that can be useful in the detection of magnetic resonance. Through the Faraday effect, spin-polarized nuclei in a sample will rotate the plane of polarization of incident linearly polarized light, while through the inverse Faraday effect, a shift in the NMR lines occurs when circularly polarized light is shone onto the sample. This laser-induced NMR shift was calculated at both standard laser wavelengths and wavelengths approaching resonance energies for hydrocarbon molecules of increasing size in Paper II. It was observed that the magnitude of the shift grows with laser frequency and system size, with dramatic increase near wavelengths corresponding to excitation energies. Experimental detection of the shift, however, require laser beams of high intensity at small wavelengths.

The direct Faraday effect leads to nuclear spin-induced optical rotation, which is easier to detect and was, in fact, seen experimentally for the first time in \(^1\text{H}\) and \(^{129}\text{Xe}\) in Ref. [10]. In Paper III, the theory for NSOR was formulated, and the phenomenon was studied for small prototypical molecules as well as a retinal model, again at standard laser wavelengths as well as close to resonances. Similar observations were made regarding the size of the effect with respect to laser frequency as in Paper II. Also, differing signals were seen between different molecules and inequivalent nuclei in
the same molecule. The existence of such an optical chemical shift indicates that the phenomenon could indeed be used as an alternative to traditional NMR detection.

Paper IV combines theory and experiment for the NSOR in a series of molecular liquids, leading to qualitative agreement. It was seen that upon taking into account a correction term resulting from the bulk magnetization of the sample, the results are brought closer to the experimental values. An optical chemical shift between different molecules was experimentally verified.

In Ref. [10], excellent correspondence was noted between experiment and earlier nonrelativistic first-principles calculations [9] of the corresponding antisymmetric polarizability for the NSOR of $^{129}$Xe. This correspondence was, nevertheless, eradicated as it was noticed that a factor of two was missing from the earlier theoretical analysis. The NSOR for $^{129}$Xe was then calculated using relativistic four-component theory in Paper V. It was seen that the use of relativity leads to better results and, additionally, that electron correlation effects are significant. Through calculations involving a xenon dimer, it was observed that intermolecular interaction effects should be taken into account in order to acquire results that may be comparable to experiment.

This thesis presents a collection of studies involving computationally demanding molecular properties that are investigated using basis sets generated through completeness optimization. It was demonstrated that this recently developed, innovative method can be used to obtain basis sets that give results close to the basis-set limit with fewer functions than traditional, energy-optimized basis sets. Accurate calculations of NMR properties for nanosystems were made feasible for the first time using completeness optimization.

The investigations of NMR methods involving nuclear magneto-optic phenomena carried out in this thesis are among the first that propose systems that may be appealing to the experimentalist. The development of a first-principles theory for the nuclear spin-induced optical rotation allowed calculations that revealed the existence of an optical chemical shift, which implies that the NSOR could be used as an alternative to traditional NMR methods. The benefits of optical NMR can in the future include enhanced sensitivity and smaller sample volumes. Experimental studies, including Paper IV of this thesis, have already been conducted, showing promising results. Theoretical analysis is also being continued in, e.g., Ref. [26] with focus on detailed solvation effects.
Bibliography


