

Efficient methods for self-consistent field
calculation of molecules in finite
magnetic fields

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Preface

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Abstract

The LONDON program performs non-perturbative finite field calculations on molecules in strong magnetic fields. To make sure results are gauge-origin independent London orbitals are used. At the Hartree-Fock level, the two-electron contributions take the longest time to calculate. For Gaussian orbitals, charge density fitting and auxiliary density matrix method have been implemented with success in other quantum chemistry programs, to approximate the two-electron contributions. In this project, the performance of these methods are investigated for London orbitals in the LONDON program.

Abbreviations

AO	Atomic orbital
MO	Molecular orbital
RHF	Restricted Hartree-Fock
ROHF	Restricted open-shell Hartree-Fock
UHF	Unrestricted Hartree-Fock
SCF	Self-consistent field
LCAO	Linear combination of atomic orbitals
DFT	Density functional theory
KS DFT	Kohn-Sham DFT
GGA	Generalized gradient approximations
DF	Charge density fitting
RI	Resolution of the identity
RI-J	RI for coulomb
RI-K	RI for exchange
ADMM	Auxiliary density matrix method
ADMMX	ADMM with no DFT correction

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Introduction

Taking magnetic fields into account in quantum chemical calculations can be done through perturbation theory for weak magnetic fields. For strong magnetic fields, however, perturbation theory breaks down. A non-perturbative approach is needed. The LONDON [1] code is able to perform finite field calculations in strong magnetic fields. To make sure the calculations are gauge-origin independent, a gauge-origin dependent phase factor is included into the orbitals. With this code, non-perturbative phenomena such as paramagnetic to diamagnetic transitions [2] and a new chemical bonding mechanism have been predicted [3].

Strong magnetic fields, orders of magnitude stronger than any magnetic fields found on Earth, exist on stellar objects such as white dwarfs and neutron stars. Magnetic fields on some white dwarfs can be as strong as 10^5 T, and fields on neutron stars can be stronger than 10^7 T. In such strong magnetic fields, the magnetic interactions will be equally or more important than electronic interactions for the energy [4, 5]. Even if the temperatures on these objects are very high, hydrogen molecules have been found to exist on white dwarfs[6], although not yet for any of the highly magnetized white dwarfs.

In this project, the task is to study approximations to the Coulomb and exchange terms in Hartree-Fock calculations. The approximations implemented are the charge density fitting approximation and the auxiliary density matrix method, which have been found to work well in the absence of magnetic fields. This project tests their performance when hybrid basis sets are used and finite magnetic fields are included.

1 Theory

1.1 Ab initio methods

In computational chemistry, the task is to solve the Schrödinger equation for chemically relevant systems. However, for most of the systems a chemist may want to investigate, this equation cannot be solved exactly. To obtain meaningful information about chemical systems within a reasonable amount of computation time, it is therefore necessary to introduce approximations.

Ab initio methods are a class of methods performing calculations based on fundamental properties of a system, without using any experimental data beyond values of fundamental constants. In this project, primarily the Hartree-Fock method is considered. The Hartree-Fock method is an important ab initio method because it is a relatively fast method that yields usable results on its own, and because the solution of a Hartree-Fock calculation can be used as a starting point for other more accurate ab initio methods. Density functional theory (DFT) is a different quantum chemical method based on a theorem stating that the density of the electrons determines all the properties of a system in its ground state. For the energy there exists a functional that yields the energy of the system, given the electron density (a functional transforms a function into a value, as opposed to a function that transforms a value into a value). If the form of this functional had been known, DFT would have been an ab initio method. Instead there are approximate functionals that are suited for different systems and levels of accuracy. An important advantage to DFT is that the electron density only has three dimensions, while the wavefunction is a $3N$ -dimensional function, where N is the number of electrons. For situations where good functionals exist, DFT constitutes a good compromise between accuracy and cost.

1.2 Born-Oppenheimer approximation

The time-independent Schrödinger equation can be written in its most general form as

$$\hat{H}\Psi = E\Psi. \quad (1)$$

Here Ψ is the wavefunction, describing all electrons and nuclei, E is the energy and \hat{H} is the Hamiltonian. Postponing the effects of external magnetic fields to section 1.8, the Hamiltonian, in atomic units (where $\hbar = e = m_e = 1/4\pi\epsilon_0 = 1$), is given by

$$\hat{H} = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2} - \sum_{K=1}^{N_\mu} \frac{\nabla_K^2}{2} - \sum_{i=1}^{N_e} \sum_{K=1}^{N_\mu} \frac{Z_K}{r_{iK}} + \sum_{i=1}^{N_e} \sum_{j=i+1}^{N_e} \frac{1}{r_{ij}} + \sum_{K=1}^{N_\mu} \sum_{L=K+1}^{N_\mu} \frac{Z_K Z_L}{r_{KL}}. \quad (2)$$

Here the lower-case letters i and j are used for electrons, and the capital letters K and L are used for nuclei. The summations run up to N_e , the number of electrons, or N_ν , the number of nuclei. The two single sums describe the kinetic energy contribution of the electrons and the nuclei. The double sums describe Coulombic interactions between the particles in the system, with the Coulomb potential $\frac{1}{r_{ab}}$, where $r_{ab} = |\mathbf{r}_a - \mathbf{r}_b|$. The first double sum describes the interaction between electrons and nuclei, the second describes interactions between electrons and the third describes interactions between nuclei.

Solving the Schrödinger equation for this Hamiltonian is an example of a many-body problem. Many-body problems are difficult and time-consuming to solve, and the computational complexity quickly increases as the number of particles increases. As a first step to alleviate this problem, the Born-Oppenheimer approximation is introduced. The idea of this approximation is that the atomic nuclei are much heavier than the electrons, and the nuclei are therefore assumed to be at rest compared to the electrons. This leads to a wavefunction consisting of a product of two parts. One part is the wavefunction for the nuclei, which only depends on the coordinates of the nuclei. The other part is the electronic wavefunction, which depends on the coordinates of the electrons and parametrically depends on the coordinates of the nuclei. For a set of coordinates for the nuclei, it is therefore possible to solve the Schrödinger equation by only considering the coordinates of the electrons. Because the nuclei are assumed to be at rest when considering the electrons, the term describing the kinetic energy of the nuclei vanishes. The resulting Hamiltonian for obtaining the electronic wavefunction is given by

$$\hat{H}_{el} = - \sum_{i=1}^{N_e} \frac{\nabla_i^2}{2} - \sum_{i=1}^{N_e} \sum_{K=1}^{N_\nu} \frac{Z_j}{r_{iK}} + \sum_{i=1}^{N_e} \sum_{j=i+1}^{N_e} \frac{1}{r_{ij}} + \sum_{K=1}^{N_\nu} \sum_{L=K+1}^{N_\nu} \frac{Z_L Z_K}{r_{KL}}. \quad (3)$$

It is conventional to retain the Coulombic interaction between nuclei in the electronic Hamiltonian (\hat{H}_{el}). This term is easy to add because it only depends on the nuclear coordinates, which are already known when the calculation starts. The equation to solve is then given by

$$\hat{H}_{el}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (4)$$

where $\psi(\mathbf{r})$ is the electronic wavefunction.

1.3 The variational principle

The variational principle can be expressed as

$$E_0 \leq \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (5)$$

It states that the ground state energy (E_0) is always lower than, or equal to, the expectation value of the Hamiltonian for any wavefunction ψ . The energy is equal to the ground state energy when ψ is the exact wavefunction for that Hamiltonian. The variational method is based on the variational principle. It is used to find approximate wavefunctions by using a parametrized function (ansatz). All variations of the parameters yield a wavefunction with energy higher than or equal to the energy of the ground state according to the variational principle. It is therefore safe to choose the parametrization that minimizes the expectation value of the Hamiltonian. With respect to energy, the best wavefunction within the parametrization has then been found.

1.4 Slater determinants

The Pauli principle states that a wavefunction describing fermions must be antisymmetric with respect to interchange of identical fermions. Since electrons are fermions, this applies to electronic wavefunctions as well. One way to impose the antisymmetry condition is to use Slater determinants of the form

$$\psi(\mathbf{r}, \mathbf{s}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_{N_e}(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_{N_e}(2) \\ \vdots & \vdots & \dots & \vdots \\ \phi_1(N_e) & \phi_2(N_e) & \dots & \phi_{N_e}(N_e) \end{vmatrix}, \quad (6)$$

where each $\phi_m(n)$ is a one-electron spin orbital and the prefactor is a normalization constant. A spin orbital is a product of a space-dependent part, referred to as an orbital, and a spin-dependent part. For the theories considered in this project, spin is restricted to two possible values, $(\pm \frac{1}{2}\hbar)$. The antisymmetry condition is imposed by using a Slater determinant because interchanging two electrons corresponds to interchanging two rows in the determinant, which changes the sign of a determinant.

1.5 Linear combination of atomic orbitals

An atomic orbital (AO) is an orbital describing an electron in an atom. In the same way, a molecular orbital (MO) is an orbital describing an electron

in a molecule. One way to express MOs is to use a linear combination of AOs (LCAO) as in

$$\phi_i(\mathbf{r}) = \sum_a c_i^a \chi_a(\mathbf{r}). \quad (7)$$

Here χ_a denotes AOs and ϕ_i denotes MOs. The LCAO approach can be justified by assuming that the AOs of an atom are quite similar to the orbitals close to the same atom in a molecule. This is a simplification, but even when this does not hold, the LCAO approach is still a way to express a complicated function (a MO) using simpler ones.

To represent the AOs, two types of functions are commonly used: Gaussian orbitals and Slater orbitals. Gaussian orbitals can be written in Cartesian form as

$$G^{lnm}(\mathbf{r}, \mathbf{R}, a) = (x - R_x)^l (y - R_y)^n (z - R_z)^m e^{-a(\mathbf{r}-\mathbf{R})^2}. \quad (8)$$

Where $\mathbf{r} = (x, y, z)$ and $\mathbf{R} = (R_x, R_y, R_z)$. Here the sum of the exponents l , n and m is equal to the angular momentum of the AO. The exponential describes the radial electron distribution around some point \mathbf{R} in space, where a describes how local or diffuse the function is.

The exponential in a Slater orbital is of the form

$$\chi(\mathbf{r}) = e^{-\zeta|\mathbf{r}-\mathbf{R}|}. \quad (9)$$

Where ζ corresponds to a for Gaussian orbitals. For $\zeta = Z$, the nuclear charge, the Slater orbital will have the same cusp around the nucleus and the same decay with distance as an s-orbital. An important advantage of Gaussian orbitals over Slater orbitals is the computation time needed to evaluate integrals over the functions. Gaussians are separable, and efficient techniques for evaluating integrals exist. This means calculations using Gaussians are faster even if more functions have to be used.

The set of functions (Gaussian or Slater) available to express MOs is called a basis set. A basis set needs to contain at least enough AOs to match the AOs of all atoms in the molecule. Adding more functions beyond this gives a better description of the MOs, but the computation time will of course increase, so functions should be chosen carefully. To get a better description of the AOs, it is common to combine Gaussians in a linear combination. The coefficients are predetermined, and all the functions operate as one AO; these basis sets are said to be contracted. Another common function type to include are Gaussians corresponding to higher angular momentum atomic orbitals — so-called polarization functions. The basis set is then said to be polarized. It is also common to add diffuse Gaussian functions. Here the exponent a in the Gaussian orbital is smaller than usual, and therefore the

Gaussian will be spread out over a larger area than for other basis functions. Basis sets with diffuse basis functions are called diffuse basis sets. To get a better description of the valence electrons, it is common to use so-called split-valence basis sets, where there are two of each of the basis functions corresponding to the valence AOs in each atom. In the same manner there is also triple-valence, quadruple-valence etc. To increase the flexibility of the basis set, it is also possible to decontract the basis. This means that instead of using the predetermined coefficients in the contracted basis, each Gaussian, in the contracted AO, is instead used as an AO in the LCAO approach.

1.6 Notation

A linear operator acting on a space spanned by a basis set can be expressed using the basis functions. A general operator can be written

$$\hat{\Lambda} = \sum_{ab} |a\rangle \Lambda^{a\bar{b}} \langle b|. \quad (10)$$

Where $\Lambda^{a\bar{b}}$, is the matrix inverse of Λ_{ab} . Matrix elements over the operator can then be written as

$$\Lambda_{\alpha\beta} = \langle \alpha | \hat{\Lambda} | \beta \rangle = \sum_{ab} \langle \alpha | a \rangle \Lambda^{a\bar{b}} \langle b | \beta \rangle = \sum_{ab} S_{\alpha a} \Lambda^{a\bar{b}} S_{b\beta} \quad (11)$$

The identity operator can then be written as

$$\hat{I} = \sum_{ab} |a\rangle S^{a\bar{b}} \langle b| \quad (12)$$

for a non-orthogonal basis, where $S^{a\bar{b}}$ is the matrix inverse of $S_{a\bar{b}}$ defined as

$$S_{ab} = \int \chi_a(\mathbf{r}) \chi_b(\mathbf{r}) d\mathbf{r}. \quad (13)$$

For an orthogonal basis, S will be given by the Kronecker delta function and the identity operator is reduced to

$$\hat{I} = \sum_a |a\rangle \langle a| \quad (14)$$

1.7 Hartree-Fock theory

Hartree-Fock theory is based on the variational method and uses a single Slater determinant as an ansatz for the electronic wavefunction. Applying

the LCAO approach to the MOs in the Slater determinant gives an ansatz depending on the coefficients in the LCAO. Minimizing the expectation value of the Hamiltonian over these coefficients under the constraint that the MOs remain orthogonal, yields the Hartree-Fock equations given by

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}. \quad (15)$$

This is a matrix equation where the \mathbf{C} matrix contains the coefficients from the LCAO approach as columns. \mathbf{S} is a matrix with overlap integrals for all basis functions. The diagonal (canonical solution) matrix $\boldsymbol{\epsilon}$ contains the energy of the molecular orbitals. \mathbf{F} contains expectation values of the Fock operator for the basis functions as in

$$F_{ab} = \int \chi_a(\mathbf{r})\hat{F}\chi_b(\mathbf{r})d\mathbf{r}. \quad (16)$$

The Restricted Hartree Fock (RHF) operator is given by

$$\begin{aligned} \hat{F} &= H^{core}(1) + \sum_i (2\hat{J}_i(1) - \hat{K}_i(1)) \\ \hat{H}^{core}(1) &= -\frac{1}{2}\nabla^2 - \sum_{\mu} \frac{Z_{\mu}}{r_{1\mu}} \\ \hat{J}_i(1) &= \int \phi_i^*(2) \frac{1}{r_{12}} \phi_i(2) d\mathbf{r}_2 \\ \hat{K}_i(1)\phi_j(1) &= \phi_i(1) \int \phi_i^*(2) \frac{1}{r_{12}} \phi_j(2) d\mathbf{r}_2 \end{aligned} \quad (17)$$

In RHF theory, each orbital is shared by two electrons. Taking different spin into account for the two electrons yields one spin orbital for each electron. To handle systems with an odd number of electrons (radicals), the open-shell RHF (ROHF) method can be used. Here most of the spatial orbitals are doubly occupied as in the RHF case, but it is possible to have some singly occupied orbitals to accommodate unpaired electrons. UHF is a generalization of RHF that can handle any number of electrons. For UHF theory there are different spatial orbitals for different spins. Only RHF theory is considered for this project.

For the derivation of the equations for the auxiliary density matrix method, it is useful to note that the Fock matrix can also be considered as a derivative

$$F_{ab} = \frac{\partial E_{tot}}{\partial P^{b\bar{a}}}. \quad (18)$$

Where $P^{b\bar{a}} = \sum_i^{occ} C_i^b C_i^{*\bar{a}}$ is the density matrix. It is especially useful to note that the exchange matrix can be expressed as a derivative of the exchange

energy

$$K_{ab} = \frac{\partial E_K}{\partial P^{ba}}. \quad (19)$$

The solution of the Hartree-Fock equations are the molecular orbitals and their energies. These can be found if the \mathbf{S} and \mathbf{F} matrices are known. The \mathbf{F} matrix does, however, depend on the molecular orbitals. This means that the Hartree-Fock equations depend on their own solution. To be able to solve this equation, it is therefore necessary to use an iterative method called the self-consistent field (SCF) method to solve the equations. This method requires an initial guess of molecular orbitals. A possible starting solution is to diagonalize \hat{H}^{core} , this corresponds to non-interacting electrons. From this starting solution, a Fock operator is computed and the \mathbf{F} and \mathbf{S} matrices are calculated, making it possible to find a new \mathbf{C} . The new solution is then set as a starting solution for the next step. This procedure is repeated until there is no significant difference between the starting solution and the new solution in an iteration. At this point it is assumed that the correct solution has been found.

In Hartree-Fock theory, the electron-electron repulsion is treated in a mean-field way by letting each electron interact with average electrostatic field of the other electrons. The error introduced with this simplification is called correlation energy. Hartree-Fock theory typically estimates the energy of a system with an accuracy of 0.5-2%, so correlation has a small contribution to the energy, compared to Coulomb interactions and kinetic energy. However, compared to the total energy of a molecule, the energy changes involved for many chemical phenomena are small. To achieve the needed accuracy, it is therefore often necessary to also include correlation. For many methods that include correlation, the solution of a Hartree-Fock calculation can be used as a starting point.

1.8 Magnetic fields in the Hamiltonian

In the LONDON program, molecular calculations are performed in the presence of an external magnetic field. This introduces new terms in the Hamiltonian. Using atomic units (magnetic fields are given in units of $B_0 = \frac{m_e e}{4\pi\epsilon_0 \hbar} = 2.35 \times 10^5$ T), the canonical momentum operator

$$\mathbf{p} = -i\nabla \quad (20)$$

is replaced with the physical momentum operator

$$\boldsymbol{\pi} = \mathbf{p} + \mathbf{A}. \quad (21)$$

Here \mathbf{A} is a vector potential that relates to the magnetic field as

$$\mathbf{B} = \nabla \times \mathbf{A}. \quad (22)$$

A given vector potential can only correspond to one magnetic field, while the opposite is not necessarily true. Adding the gradient of any function to a vector potential, called a gauge transformation, as in

$$\mathbf{A}' = \mathbf{A} + \nabla f(\mathbf{r}) \quad (23)$$

with $'$ denoting gauge-transformed quantities, will not change the magnetic field described by that vector potential. This can be seen from

$$\nabla \times \mathbf{A}' = \nabla \times (\mathbf{A} + \nabla f(\mathbf{r})) = \nabla \times \mathbf{A} + \nabla \times \nabla f(\mathbf{r}) = \nabla \times \mathbf{A}. \quad (24)$$

In LONDON, only uniform magnetic fields \mathbf{B} and vector potentials of the form

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) \quad (25)$$

are considered; the only allowed gauge transformation is then given by

$$f(\mathbf{r}) = \frac{1}{2}(\mathbf{B} \times \mathbf{C}) \cdot \mathbf{r} \quad (26)$$

This transformation is called a gauge-origin transformation. With this transformation, the position \mathbf{O} can be chosen freely and is referred to as the gauge origin.

With the physical momentum operator, the kinetic energy will be given by

$$\frac{1}{2}\boldsymbol{\pi}^2 = \frac{1}{2}(\mathbf{p} + \mathbf{A})^2 = \frac{1}{2}(\mathbf{p}^2 + 2\mathbf{A} \cdot \mathbf{p} + \mathbf{A}^2) \quad (27)$$

With the \mathbf{A} in eq. (25)

$$\mathbf{A} \cdot \mathbf{p} = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) \cdot \mathbf{p} = \frac{1}{2}\mathbf{B} \cdot (\mathbf{r} - \mathbf{O}) \times \mathbf{p} = \frac{1}{2}\mathbf{B} \cdot \mathbf{L}, \quad (28)$$

where $\mathbf{L} = (\mathbf{r} - \mathbf{O}) \times \mathbf{p}$ is the canonical orbital angular momentum operator. This term is called the orbital Zeeman term. The kinetic energy will then be given by

$$\frac{1}{2}\boldsymbol{\pi}^2 = \frac{1}{2}(\mathbf{p}^2 + \mathbf{B} \cdot \mathbf{L} + \mathbf{A}^2) \quad (29)$$

In relativistic theory, spin as an intrinsic property of electrons follows naturally. For non-relativistic theory, it is postulated. The electron spin interacts with external magnetic fields through the spin-Zeeman effect. With

spin-Zeeman and the kinetic energy in eq. (29) the Hamiltonian will be given by

$$\hat{H}_{\text{mag}} = \hat{H}_{el} + \sum_{i=1}^{N_e} \mathbf{B} \cdot \mathbf{L}_i + \frac{1}{2} \sum_{i=1}^{N_e} \mathbf{A}_i^2 + \mathbf{B} \cdot \sum_{i=1}^{N_e} \mathbf{s}_i. \quad (30)$$

Where \mathbf{A}_i means \mathbf{A} evaluated at the position of electron i .

1.9 London orbitals

A gauge transformation should not change expectation values of observables; however, when the vector potential is changed, the Hamiltonian also changes. To get gauge-independent expectation values of observables, the wavefunction will have to change as well. For a given gauge transformation the wavefunction changes as

$$\psi'(\mathbf{r}) = e^{-if(\mathbf{r})}\psi(\mathbf{r}). \quad (31)$$

The kinetic energy operator ($\frac{1}{2}\boldsymbol{\pi}^2$) is the only operator that contributes to the Fock operator that changes under a gauge transformation. It is therefore sufficient to show that expectation values of this operator do not change. This is shown by considering the expectation value of the gauge-transformed operator and wavefunction as in

$$\boldsymbol{\pi}' |\psi'\rangle = (\mathbf{p} + \mathbf{A}')e^{-if(\mathbf{r})} |\psi\rangle = e^{-if(\mathbf{r})}(\mathbf{p} + \mathbf{A}' - \nabla f) |\psi\rangle = e^{-if(\mathbf{r})}\boldsymbol{\pi} |\psi\rangle. \quad (32)$$

Applying the operator again yields

$$\boldsymbol{\pi}' e^{-if(\mathbf{r})}\boldsymbol{\pi} |\psi\rangle = e^{-if(\mathbf{r})}\boldsymbol{\pi}^2 |\psi\rangle, \quad (33)$$

and multiplying the bra from the left cancels the phase factor

$$\langle \psi' | e^{-if(\mathbf{r})}\boldsymbol{\pi}^2 |\psi\rangle = \langle \psi | e^{if(\mathbf{r})} e^{-if(\mathbf{r})}\boldsymbol{\pi}^2 |\psi\rangle = \langle \psi | \boldsymbol{\pi}^2 |\psi\rangle. \quad (34)$$

Thus the gauge transformation does not change the expectation value of the kinetic energy since

$$\langle \psi' | \boldsymbol{\pi}'^2 |\psi'\rangle = \langle \psi | \boldsymbol{\pi}^2 |\psi\rangle \quad (35)$$

In a complete basis it is possible to represent both ψ' and ψ exactly, but in a finite basis there is no guarantee that both can be represented equally well. To resolve this problem for gauge-origin transformations, a gauge-origin dependent phase factor is added to the Gaussian orbitals as in

$$\begin{aligned} \chi(\mathbf{r}) &= G^{\text{lnm}}(\mathbf{r}, \mathbf{R})e^{-i\mathbf{k}_a \cdot \mathbf{r}} \\ \mathbf{k}_a &= \frac{1}{2}\mathbf{B} \times (\mathbf{R} - \mathbf{O}) \end{aligned} \quad (36)$$

where \mathbf{k}_a is the value of \mathbf{A} at the center of the Gaussian. With these new basis functions, called London orbitals [7], all contractions over operators representing observables are independent of the gauge origin.

1.10 Magnetic properties

The energy of a system can be expanded in a Taylor series in terms of the field strength B ,

$$E(B) = E_0 + \frac{1}{2} \sum_{\alpha} J_{\alpha} B_{\alpha} - \frac{1}{2!} \sum_{\alpha\beta} \chi_{\alpha\beta} B_{\alpha} B_{\beta} + \frac{1}{3!} \sum_{\alpha\beta\gamma} X_{\alpha\beta\gamma} B_{\alpha} B_{\beta} B_{\gamma} + \dots \quad (37)$$

The coefficients in the expansion represent different magnetic properties. The first-order coefficient is the magnetic dipole moment, which is analogous to the electric dipole moment. In the same way, the second-order coefficient is the magnetizability, which is analogous to the electric polarizability. With the Taylor expansion around $B = 0$ the first order coefficient $J_{\alpha} = L_{\alpha}$, the canonical angular momentum. For a Taylor expansion around a $B \neq 0$, J_{α} is the physical angular momentum. To obtain the coefficients, it is common to use perturbation theory to calculate derivatives of the energy evaluated at zero field [8]. With the finite field calculations in the LONDON code, the coefficients can then be obtained in a more general way through a polynomial fitting of the energy as a function of magnetic field. For closed-shell systems, $E(B) = E(-B)$, so terms with odd powers of magnetic field are therefore zero.

1.11 Density functional theory

The fundamental idea in density functional theory (DFT) is to express the energy (or other properties) of the ground state as a functional of the density. In Kohn-Sham (KS) DFT, a set of orbitals corresponding to the electron density is reintroduced. This makes it possible to calculate most of the kinetic energy at the cost of dealing with the higher dimensionality of the orbitals. With the orbitals introduced, the kinetic energy, the nuclear attraction, and the Coulomb electron repulsion will have the same formulas in KS DFT and Hartree-Fock theory. In KS DFT, correlation and exchange are treated in a separate term. The exact relation between the electron density and the exchange and correlation energy is not known, and many approximate relations exist. One class of functionals are called generalized gradient approximation (GGA) functionals. Here the functional uses not only the electron density, but also the gradients of the electron density to express the functional.

1.12 Two-electron integrals

The contributions to the Fock matrix can be divided into one-electron contributions and two-electron contributions, where the one-electron contributions

are kinetic energy and Coulomb attraction to the nuclei, and the two-electron contributions are Coulomb repulsion between electrons and exchange. By introducing the Mulliken notation

$$(ab|cd) = \int \chi_a^*(1)\chi_b(1)\frac{1}{r_{12}}\chi_c^*(2)\chi_d(2)d\mathbf{r}_1d\mathbf{r}_2 \quad (38)$$

the Coulomb and exchange contribution can be written as

$$J_{\bar{a}b} = \sum_{c,d} P^{d\bar{c}} (ab|cd) \quad (39)$$

and

$$K_{\bar{a}b} = \sum_{c,d} P^{d\bar{c}} (ad|cb) \quad (40)$$

respectively. The two-electron contributions involve four-centre integrals, which means the integral is over four basis functions located on potentially four different nuclei. Because all four basis functions are summed over to find the total contribution, the calculation of the two-electron contributions formally scales as N^4 . This makes the calculation of the Coulomb and exchange terms the most time-consuming part of a Hartree-Fock calculation.

1.13 Charge density fitting

The purpose of introducing charge density fitting (DF) is to reduce the calculation time of the Coulomb matrix. To achieve this, a new basis set, different from the AO basis set, is introduced. With this auxiliary basis set, the Coulomb matrix can be calculated using three-center integrals instead of four-centre integrals.

1.13.1 Approximate representation of the electron density

In the expression for the Coulomb contribution given in eq. (39), it is possible to factor out an expression for the electron density given by

$$\rho(\mathbf{r}) = \sum_{cd} P^{d\bar{c}} \chi_c^* \chi_d. \quad (41)$$

In DF, this density is approximated by a density expressed in an auxiliary basis set,

$$\tilde{\rho}(\mathbf{r}) = \sum_{\alpha} P^{\alpha} \chi_{\alpha}(\mathbf{r}). \quad (42)$$

With the approximate density replacing the exact density, the Coulomb contribution becomes

$$J_{ab} = \sum_{\alpha} P^{\alpha} (ab|\alpha), \quad (43)$$

with the following notation for three-center integrals

$$(ab|c) = \int \chi_a^*(1)\chi_b(1)\frac{1}{r_{12}}\chi_c(2)d\mathbf{r}_1d\mathbf{r}_2. \quad (44)$$

This reduces the formal scaling of calculating the Coulomb contribution from n^4 to Nn^2 , where n is the number of AO basis functions and N is the number of auxiliary basis functions.

1.13.2 Derivation of the fitting equations

Unless the auxiliary basis spans the entire space of products of the AO basis functions, there will be a difference between the expanded density and the exact density. To find the best fit of the auxiliary density, a residual is defined

$$R(\mathbf{r}) = \rho(\mathbf{r}) - \tilde{\rho}(\mathbf{r}). \quad (45)$$

Different approaches have been proposed to minimize this residual. One alternative is to minimize the self-overlap of the residual (S approximation) [9, 10], another is to minimize the self-repulsion of the residual (V approximation) [11, 12]. The V approximation has previously been shown to give the best results [13].

To write the derivation of the fitting coefficients, the following notation is used

$$(a|b) = \int \frac{\chi_a^*\chi_b}{r_{ab}}d\mathbf{r} \quad (46)$$

This integral can be viewed as an overlap with the Coulomb norm.

To derive the coefficients in the V approximation, the derivative of the self-repulsion with respect to the coefficients in the auxiliary basis is set to zero

$$\frac{\partial}{\partial P^{\beta}} (R|R) = 0 \quad (47)$$

which expands to

$$\frac{\partial}{\partial P^{\beta}} (\rho - \tilde{\rho}|\rho - \tilde{\rho}) = \frac{\partial}{\partial P^{\beta}} ((\rho|\rho) - 2(\tilde{\rho}|\rho) + (\tilde{\rho}|\tilde{\rho})) = 0 \quad (48)$$

yielding

$$0 - 2(\beta|\rho) + 2(\beta|\tilde{\rho}) = 0 \quad (49)$$

giving the following equation:

$$(\beta|\tilde{\rho}) = (\beta|\rho) \quad (50)$$

Because this holds for all basis functions β this will be a set of linear equations described by

$$\mathbf{VP} = \mathbf{R}, \quad (51)$$

where the elements of matrix \mathbf{V} and the elements of the vector \mathbf{R} are given by

$$V_{\beta\alpha} = (\beta|\alpha) \quad (52)$$

and

$$R_{\beta} = (\beta|\rho) \quad (53)$$

respectively. The vector \mathbf{P} contains the fitting coefficients. Solving for \mathbf{P} yields the coefficients

$$\mathbf{P} = \mathbf{V}^{-1}\mathbf{R} \quad (54)$$

where P^{α} can be written as

$$P^{\alpha} = \sum_{\beta} V^{\alpha\beta} (\beta|\rho) \quad (55)$$

DF is sometimes referred to as the resolution of the identity (RI) approximation. The auxiliary basis functions can be introduced through a resolution of the identity in the expression for the Coulomb contribution. Inserting the resolution of the identity from eq. (12), with the overlap calculated with a Coulomb norm as defined in eq. (46), yields

$$\begin{aligned} \sum_{cd} P^{d\bar{c}} (ab|cd) &\approx \sum_{cd} P^{d\bar{c}} \sum_{\alpha\beta} (ab|\alpha) V^{\alpha\beta} (\beta|cd) = \\ &\sum_{\alpha\beta} (ab|\alpha) V^{\alpha\beta} (\beta|\rho) = \sum_{\alpha} (ab|\alpha) P^{\alpha}. \end{aligned} \quad (56)$$

1.13.3 The auxiliary basis set

The auxiliary basis set should be able to describe the electron density given as products of AO basis functions. The product of two Gaussians is a sum of Gaussians as in

$$G^{lnm}(\mathbf{r}, \mathbf{R}, a) \cdot G^{l'n'm'}(\mathbf{r}, \mathbf{S}, b) = \sum_{i,j,k}^{l+l',n+n',m+m'} G^{i,j,k}(\mathbf{r}, \mathbf{T}, d) \quad (57)$$

where the center of the new Gaussians $T = \frac{aR+bS}{a+b}$ and the combined exponent $d = a + b$. For Gaussians with the same center ($R = S$) this will reduce to a single Gaussian. With London orbitals, there is also the phase factor to consider. The product of two phase factors is

$$(e^{-ik_a \cdot r})^* e^{-ik_b \cdot r} = e^{(ik_a - ik_b) \cdot r}, \quad (58)$$

where

$$ik_a - ik_b = iB \times (R_a - R_b). \quad (59)$$

The gauge origin cancels, and only the difference between two centers remains. In this project, we have tested Gaussian auxiliary basis sets specifically developed for the RI approximation (cc-pVTZdenfit [14] and df-def2 [15]). For basis functions located on the same center, the phase factor cancels and only a Gaussian remains. This is what the auxiliary basis set is designed to handle (as well as products of Gaussians on different centers). For a product of two London orbitals with two different centers, the product will contain a phase factor. An increasing distance between centers will yield a larger exponent in the phase factor, which is not necessarily handled as well by the auxiliary basis. However, as the distance increases, the Gaussian part of the product will eventually be very small and make the whole product irrelevant. Whether the Gaussian part dies out before the phase factor becomes important, depends on parameters in both the Gaussian and the phase factor part of the product, and is difficult to predict. The magnetic field strength has the same effect as an increasing distance and is equally important, as can be seen from eq. (59). It can therefore be expected that at some point, as the magnetic field increases the Gaussian auxiliary basis sets will not yield a sufficient performance, and the phase factors will have to be handled in some way. It is, however, difficult to predict at what field strength this problem will arise.

Both the df-def2 and the cc-pVTZdenfit basis, are optimised to be auxiliary basis sets for RI-K. However, basis sets optimized for RI-K can also be used for RI-J (DF). For RI-J, the auxiliary basis expresses a density, while in RI-K the auxiliary basis expresses the products of the basis functions. Representing the products is more challenging, therefore an RI-K auxiliary basis is flexible enough to function as an auxiliary basis for RI-J as well. Basis sets optimized for RI-K can therefore be used for RI-J, but not the other way around. It has also been found that basis sets used for RI-J can be used for several AO basis sets. In this project, df-def2 is used with success as an auxiliary basis for both cc-pVDZ and cc-pVTZ.

There is another example of DF in non-perturbative calculations for strong magnetic fields that use the same auxiliary basis set [16]. Here, calcu-

lation of the Coulomb term with DF avoids calculation of four-centre integrals over London orbitals.

1.13.4 Implementation

To implement DF, it is necessary to compute the coefficients for the auxiliary basis set, and be able to evaluate three-centre integrals. The existing integral evaluation code in LONDON is sufficiently general to evaluate two-, three- and four-center integrals. To find the auxiliary coefficients, \mathbf{V} and \mathbf{R} in eq. (51) need to be calculated, and the equation needs to be solved. \mathbf{V} and \mathbf{R} were calculated with existing methods as two- and three-center integrals respectively. To solve the linear system of equations, \mathbf{V} is inverted and multiplied on the right hand side of the equation. The inversion was done through an eigenvalue decomposition, and to prevent linear dependence, eigenvalues below 10^{-10} were projected out (set to zero). The threshold was optimized with NaCl by minimizing the error with respect to the threshold, with no threshold the DF error was two orders of magnitude higher. Inverting \mathbf{V} is a slow way of solving the system of equations, but it is possible to prevent linear dependence this way, and the time limiting step in DF is still the calculation of the Coulomb matrix.

1.14 Auxiliary density matrix method

There is an RI approximation for exchange as well [17, 18, 14] (RI-K), but it will not yield the same speed-up as for DF (RI-J). The prefactor will be reduced, but the formal scaling of the exchange contribution will still be N^4 for the RI-K approximation. In this project, the auxiliary density matrix method (ADMM) [19] approximation has been implemented to approximate exchange. ADMM, like DF, uses an auxiliary basis to achieve a speed-up.

1.14.1 The ADMM approximation

ADMM is based on a trivial rearrangement of the difference between the exchange contribution in two different basis sets as in

$$E_{ex}^{HF}(\text{AO}) = E_{ex}^{HF}(\text{AUX}) + E_{ex}^{HF}(\text{AO}) - E_{ex}^{HF}(\text{AUX}) \quad (60)$$

The approximation is to replace the difference between Hartree-Fock exchange in AO and auxiliary basis, with exchange calculated with a DFT exchange functional, which leads to

$$E_{ex}^{HF}(\text{AO}) \approx E_{ex}^{HF}(\text{AUX}) + E_{ex}^{DFT}(\text{AO}) - E_{ex}^{DFT}(\text{AUX}). \quad (61)$$

The assumption here is that the difference between exchange calculated in two different basis sets is similar for DFT and Hartree-Fock even if the values of exchange in DFT and Hartree-Fock are different. GGA functionals have been used to calculate the DFT exchange in previous works [19, 20]. It should be noted that ADMM is also applicable to DFT. One way to calculate the exchange contribution in DFT is to let a fraction of exchange come from Hartree-Fock exchange and the remaining fraction from a functional. This method is called hybrid DFT, and ADMM can be used to speed up the calculation of the Hartree-Fock exchange term here as well. Using ADMM in a hybrid DFT calculation yields a higher speed-up than in a Hartree-Fock calculation, because DFT exchange in the larger basis needs to be computed anyway, and this term can be considered free in the ADMM contribution.

Technical challenges in handling two different basis sets in the DFT code in LONDON prevented the implementation of the DFT correction for this project. In addition, the DFT code is still slow, so implementing the DFT correction now would probably not yield any speed-up, but only improve the accuracy. To distinguish this implementation from the full ADMM approximation, the current implementation will be called ADMMX. Without the DFT correction, the method will yield a poorer accuracy. However, in the variety of quantum chemical methods performing calculations in strong magnetic fields, ADMMX can be one more method to choose from in the trade-off between speed and accuracy. It can be considered as a model Hamiltonian, slightly poorer than Hartree-Fock, but still not as crude as other model Hamiltonians used to include magnetic fields [21].

1.14.2 Approximate representation of the density matrix

Because the auxiliary basis set is smaller than the AO basis set in eq. (61), there will be an error when the orbitals are transformed into the auxiliary basis. One way to minimize the difference between the MOs represented in the AO basis and the MOs represented in the auxiliary basis, is to do a least-squares fitting of the MOs to the auxiliary basis set, which is equivalent to minimizing

$$R_2 = \sum_n^{\text{occ}} \int (\psi_{n,AO} - \psi_{n,aux})^2 d\mathbf{r}. \quad (62)$$

This method is called ADMM2. Another way to transform the MOs is to enforce that the auxiliary MOs remain orthogonal. This method is called ADMM1. To achieve this, it is necessary to introduce Lagrange multipliers,

and the minimization problem changes to

$$R_1 = \sum_n^{occ} \int (\psi_{n,AO} - \psi_{n,aux})^2 d\mathbf{r} + \sum_{nm}^{occ} \int \lambda_{nm} (\psi_{n,AO} \psi_{m,AO} - \psi_{n,aux} \psi_{m,aux}) d\mathbf{r} \quad (63)$$

A valid density matrix should fulfill some mathematical requirements, however when the AO density matrix is transformed into the auxiliary density matrix these conditions may not be fulfilled any more. The three requirements for a valid density matrix are

$$\begin{aligned} \mathbf{P}^\dagger &= \mathbf{P} \\ 2Tr(\mathbf{P}\mathbf{S}) &= N_e \\ \mathbf{P}\mathbf{S}\mathbf{P} &= \mathbf{P}. \end{aligned} \quad (64)$$

The first requirement states that the density matrix should be symmetric for a real density matrix or hermitian for a complex density matrix. The second requirement states that the density matrix should represent the correct number of electrons, given as the trace of the density matrix. The third requirement is the idempotency condition, that can be interpreted as all MOs having an occupation number of exactly 1 or exactly 0. All these requirements are fulfilled with the ADMM1 procedure. For ADMM2, only the first is fulfilled. However, ADMM1 is more difficult to work with because there is no simple relationship between the density matrix in the AO and the auxiliary basis. For ADMM2 it is more straightforward to transform the density matrix between AO and auxiliary basis, making ADMM2 easier to implement. Other procedures for ADMM have been tried to make the auxiliary density matrix fulfill more of the conditions compared to ADMM2, and still keep a simple relation between the AO and auxiliary density matrix. With ADMMQ [20] the second condition in eq. (64) is forced to be fulfilled. Compared to ADMM2, ADMMQ is a scaling of the auxiliary density matrix. A scaling of the the density matrix yields a different scaling for Hartree-Fock exchange and exchange calculated with a DFT functional. The difference in scaling can yield energies with a large deviation from the ADMM2 energy. The ADMMS approximation changes the scaling of the DFT functional to solve this problem.

ADMM2 has been implemented for this project. It is equivalent to a projection from the AO basis to the auxiliary basis as in

$$\hat{P}^{aux} = \hat{Q} = \hat{I}^{aux} \hat{P}^{orb} \hat{I}^{aux} \quad (65)$$

With the identity defined in eq. (12), this writes out to

$$\begin{aligned}\hat{Q} &= \sum_{\alpha\beta} |\alpha\rangle S^{\alpha\bar{\beta}} \langle\beta| \sum_{ab} |b\rangle P^{b\bar{a}} \langle a| \sum_{\gamma\delta} |\gamma\rangle S^{\gamma\bar{\delta}} \langle\delta| \\ \hat{Q} &= \sum_{\alpha\beta ab\gamma\delta} |\alpha\rangle S^{\alpha\bar{\beta}} S_{\bar{\beta}b} P^{b\bar{a}} S_{\bar{a}\gamma} S^{\gamma\bar{\delta}} \langle\delta|\end{aligned}\quad (66)$$

From the definition of an operator in eq. (10) it follows that

$$Q^{\alpha\bar{\delta}} = \sum_{\beta ab\gamma} S^{\alpha\bar{\beta}} S_{\bar{\beta}b} P^{b\bar{a}} S_{\bar{a}\gamma} S^{\gamma\bar{\delta}} \quad (67)$$

for the density matrix in the auxiliary basis expressed by the density matrix in the AO basis.

1.14.3 Contribution to the Fock matrix

The contribution to the Fock matrix is calculated in the auxiliary basis and is then transformed back to the AO basis. The contribution of the exchange matrix to the Fock matrix is defined by

$$K_{\bar{a}b} = \frac{\partial E_K}{\partial P^{b\bar{a}}} = \frac{\partial E_K}{\partial Q^{\alpha\bar{\delta}}} \frac{\partial Q^{\alpha\bar{\delta}}}{\partial P^{b\bar{a}}} \quad (68)$$

Differentiating eq. (67) and inserting into eq. (68) yields

$$K_{\bar{a}b} = \sum_{\gamma\delta\alpha\beta} S_{\bar{a}\gamma} S^{\gamma\bar{\delta}} k_{\bar{\delta}\alpha} S^{\alpha\bar{\beta}} S_{\bar{\beta}b} \quad (69)$$

where $k_{\bar{\delta}\alpha} = \frac{\partial E_K}{\partial Q^{\delta\bar{\alpha}}}$ is the exchange contribution in the auxiliary basis.

1.14.4 Implementation

In ADMM, the MOs need to be transformed to a different basis. There was an existing method available in LONDON to project a density matrix to a different basis. With the new density matrix, the exchange contribution was calculated. Transforming the exchange matrix to the AO basis was done as described in eq. (69). The auxiliary overlap and the mixed overlap between AO and auxiliary basis were calculated and the auxiliary basis overlap was inverted. This was done through an eigenvalue decomposition and eigenvalues below 10^{-9} were projected out (set to zero) to avoid linear dependence.

2 Results

The implementation of DF and ADMMX has been tested for six different systems, with the cc-pVDZ and cc-pVTZ basis sets. The 3-21G basis has been used as an auxiliary basis for ADMM. For DF, cc-pVTZdenfit has been used as an auxiliary basis for cc-pVTZ, however, cc-pVTZdenfit is not available for all atoms in all systems. Df-def2 has therefore been used for the remaining systems for cc-pVTZ, and for all systems with cc-pVDZ. The DF auxiliary basis sets are Gaussian basis sets, developed as auxiliary basis sets.

2.1 Results with zero magnetic field

For zero magnetic field, the phase factors in the London orbitals are equal to one, and there is no difference between London orbitals and Gaussian orbitals. The implementation of DF in LONDON can therefore, at zero magnetic field, be compared to the implementation in LSDALTON [22]. Comparing ADMMX and the ADMM implementation in LSDALTON will show the effect of the DFT correction for calculations at zero magnetic field. However, in LONDON all basis sets are Cartesian basis sets, while LSDALTON uses solid harmonic basis sets as standard. The implementation of ADMM and DF is therefore only implemented for solid harmonic basis functions in LSDALTON. Without DF or ADMM, it is possible to use a Cartesian basis for LSDALTON. Table 1 compares Cartesian and solid harmonic basis in LSDALTON. The difference between solid harmonic basis and Cartesian basis is larger than the error introduced by ADMM or DF. It is therefore not possible to compare absolute energies, only errors, between LSDALTON and LONDON when the approximations are used.

Table 2 shows errors using ADMM and DF for LSDALTON and LONDON. The expression "plain Hartree-Fock" is used to for a Hartree-Fock calculation with no ADMM and no DF. The DFT correction is included in the implementation in LSDALTON and has no option to run the ADMM calculations without it. It will therefore be difficult to compare the results for ADMM in table 2 between LSDALTON and LONDON, but the effect of the DFT correction will be indicated. In LSDALTON, the KT3X GGA exchange functional has given the best results for the calculations performed in this project. With this functional, the errors in LSDALTON are reduced by roughly an order of magnitude compared to the ADMMX implementation in LONDON. In LSDALTON, several ADMM variants are implemented, and the ADMMS variant in general performs better than the ADMM2 variant.

For DF, the accuracy is comparable between LSDALTON and LONDON. Since there is no difference between DF in LSDALTON and LONDON at zero

Table 1: Energies for Cartesian and solid harmonic basis for all test systems with the cc-pVDZ and cc-pVTZ basis sets using LSDALTON.

Basis set	System	Cartesian	Solid harmonic	Difference
		E_h	E_h	mE_h
cc-pVDZ	LiH	-7.94973	-7.94972	0.00
	NaCl	-621.42091	-621.42065	0.27
	N ₂ O	-183.67767	-183.67687	0.81
	Benzene	-230.72255	-230.72180	0.75
	Naphthalene	-383.38559	-383.38412	1.47
	C ₂₀	-756.68823	-756.68498	3.26
cc-pVTZ	LiH	-7.95175	-7.95167	0.08
	NaCl	-621.44089	-621.44062	0.28
	N ₂ O	-183.73032	-183.72942	0.90
	Benzene	-230.78051	-230.77938	1.13
	Naphthalene	-383.47985	-383.47796	1.90

magnetic field, this is not surprising. DF in always underestimate the energy, as indicated by table 2. For ADMMX all calculations in table 2 overestimates the energy, and this is usually the case for ADMMX calculations. There is therefore an error cancellation when both methods are used. For most calculations this is not significant since the errors are of so different magnitudes.

2.2 Results with magnetic field

When there is a magnetic field present, the phase factors in the London orbitals will be non-trivial functions of position. Gaussian and London orbitals are no longer the same. Table 3 shows errors for ADMM and DF at $B = 0.1 B_0$. Different directions of the magnetic field are marked as perpendicular (\perp) to the bond or the plane or parallel (\parallel) to the bond or the plane in the molecule. The parallel orientation is showed in figure 1 for the molecules where parallel orientation is ambiguous.

At $B = 0.1 B_0$, the error in both DF and ADMM are of the same order of magnitude as for zero magnetic field. The phase factors in the London orbitals do not seem to pose any problems at this magnetic field strength.

Table 4 shows energies for even stronger magnetic fields. For most systems, the field strength is $B = 1.0 B_0$. However, for the systems with the longest distances between atoms, the combination of strong magnetic field

Table 2: Errors in energy (mE_h) compared to plain Hartree-Fock for DF and ADMM using LSDALTON and LONDON with *cc-pVDZ* (DZ) and *cc-pVTZ* (TZ) basis sets at zero magnetic field.

Program	Basis	System	no density fitting		with density fitting		
			ADMM2	ADMMS	ADMM2	-	
LSDALTON	DZ	LiH	-1.49	-1.13	-1.53	-0.04	
		NaCl	-37.77	-27.40	-37.81	-0.03	
		N ₂ O	2.59	14.04	2.56	-0.03	
		Benzene	-7.03	1.51	-7.15	-0.13	
		Naphthalene	-15.28	-1.16	-15.44	-0.19	
		C ₂₀	-110.29	-81.04	-110.41	-0.12	
	TZ	LiH	-6.06	-5.49	-6.08	-0.02	
		NaCl	-42.99	-32.52	-43.03	-0.04	
		N ₂ O	0.56	15.43	0.55	-0.01	
		Benzene	-34.66	-25.17	-34.72	-0.09	
		Naphthalene	-57.82	-42.32	-57.92	-0.14	
		C ₂₀	-185.18	-151.38	-185.25	-0.08	
	LONDON	DZ	LiH	2.71	-	2.70	-0.01
			NaCl	87.37	-	87.36	-0.01
N ₂ O			94.92	-	94.91	-0.02	
Benzene			112.90	-	112.87	-0.04	
Naphthalene			187.33	-	187.28	-0.07	
C ₂₀			298.24	-	298.17	-0.07	
TZ		LiH	2.74	-	2.73	-0.02	
		NaCl	85.22	-	85.21	-0.01	
		N ₂ O	110.13	-	110.13	-0.00	
		Benzene	132.24	-	132.21	-0.07	
		Naphthalene	220.71	-	220.65	-0.11	

Table 3: Errors in energy (mE_h) compared to plain Hartree-Fock for $B = 0.1 B_0$ with ADMM and DF using LONDON.

Basis set	System	ADMM	both	densfit
cc-pVDZ	LiH \perp	2.25	2.24	-0.01
	LiH \parallel	2.42	2.41	-0.01
	NaCl \perp	87.44	87.43	-0.01
	NaCl \parallel	87.29	87.28	-0.01
	N ₂ O \perp	94.51	94.49	-0.02
	N ₂ O \parallel	95.47	95.46	-0.02
	Benzene \perp	117.03	117.00	-0.04
	Benzene \parallel	114.19	114.16	-0.04
	Naphthalene \perp	193.77	193.71	-0.07
	Naphthalene \parallel 1	189.22	189.16	-0.07
	Naphthalene \parallel 2	189.30	189.24	-0.07
	C ₂₀ \perp	302.53	302.46	-0.07
	cc-pVTZ	LiH \perp	2.58	2.57
LiH \parallel		2.47	2.46	-0.02
NaCl \perp		85.30	85.29	-0.01
NaCl \parallel		85.24	85.23	-0.01
N ₂ O \perp		110.00	110.00	-0.00
N ₂ O \parallel		110.98	110.97	-0.00
Benzene \perp		136.62	136.59	-0.07
Benzene \parallel		134.11	134.08	-0.07
Naphthalene \perp		227.36	227.31	-0.12
Naphthalene \parallel 1		223.38	223.32	-0.11
Naphthalene \parallel 2		223.57	223.52	-0.11

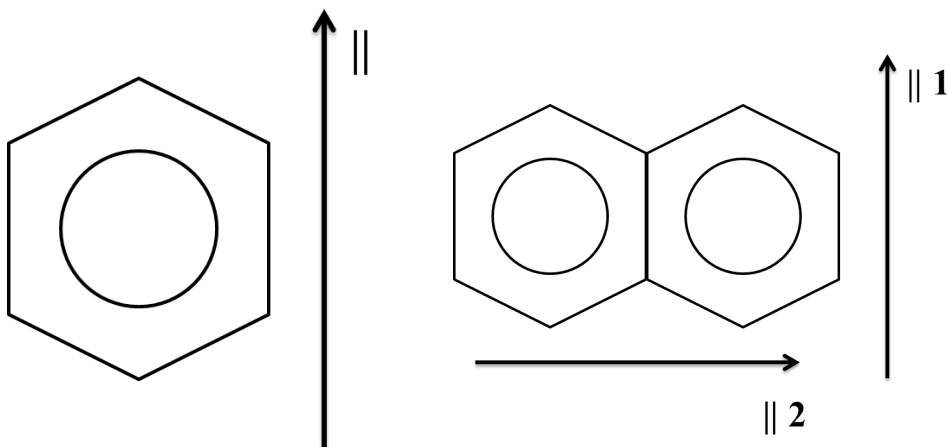


Figure 1: Orientation of field for planar molecules. Orientations denoted || 1 and || 2 for naphthalene, and the orientation denoted || for benzene is showed.

and long distances is not handled by the current version of LONDON. In LONDON, the integrals over basis functions are computed with the Boys function using complex valued arguments. The current implementation works best for arguments that are close to the real axis in the complex plane. With a combination of long distances and strong magnetic fields, the phase factor gives arguments to the Boys function with a large imaginary part. For naphthalene and C_{20} , the strongest magnetic field investigated is therefore $B = 0.5 B_0$. For C_{20} , there are convergence problems in the SCF procedure for $B = 0.5 B_0$ because of a small HOMO-LUMO gap. The results are therefore limited to $B = 0.4 B_0$ for C_{20} .

For the strongest field strengths, the DF error is still of the same order of magnitude as for zero field. For ADMM, the most notable increase in error is for NaCl. For perpendicular orientation of the field compared to the bond, the SCF optimization fails to converge for ADMM with the 3-21G auxiliary basis set for the strongest fields. Figure 2 shows error in energy for NaCl with cc-pVDZ and cc-pVTZ for perpendicular orientation and parallel orientation of the field. For cc-pVDZ, calculations with ADMM failed to converge at $B = 1.0 B_0$. For cc-pVTZ, the calculations failed to converge from $B = 0.7 B_0$ and up to $B = 1.0 B_0$. For parallel orientation, the error rises to almost $1 E_h$. With the 3-21G* basis set, calculations converged for all field strengths and the error remained at the same level as for other systems. The importance of polarization in the auxiliary basis can in part be understood by considering the slope in figure 2. One contribution to $\frac{\partial E}{\partial B}$ is the physical angular momentum; the difference in slope between ADMM/3-21G

Table 4: Errors in energy (mE_h) compared to plain Hartree-Fock at the B (B_0) given, with ADMM and DF using LONDON.

Basis set	System	B	ADMM	both	densfit
cc-pVDZ	LiH \perp	1.0	3.14	3.14	-0.01
	LiH \parallel	1.0	7.41	7.40	-0.01
	NaCl \perp	1.0	928.35	928.19	-0.04
	NaCl \parallel	0.9	843.19	843.12	-0.03
	N ₂ O \perp	1.0	102.44	102.24	-0.19
	N ₂ O \parallel	1.0	98.64	98.62	-0.02
	Benzene \perp	1.0	165.19	164.76	-0.36
	Benzene \parallel	1.0	385.19	385.13	-0.06
	Naphthalene \perp	0.5	268.33	268.26	-0.08
	Naphthalene \parallel 1	0.5	243.25	243.17	-0.09
	Naphthalene \parallel 2	0.5	277.89	277.81	-0.10
	C ₂₀ \perp	0.4	357.05	356.96	-0.09
cc-pVTZ	LiH \perp	1.0	13.76	13.61	-0.28
	LiH \parallel	1.0	19.61	19.53	-0.15
	NaCl \perp	1.0	942.32	942.05	-0.03
	NaCl \parallel	0.6	570.42	569.61	-0.03
	N ₂ O \perp	1.0	140.96	140.84	-0.11
	N ₂ O \parallel	1.0	346.34	346.33	-0.04
	Benzene \perp	1.0	305.67	305.86	-0.10
	Benzene \parallel	1.0	385.92	385.97	-0.09
	Naphthalene \perp	0.5	197.49	197.45	-0.25
	Naphthalene \parallel 1	0.5	295.25	295.19	-0.10
	Naphthalene \parallel 2	0.5	331.21	331.13	-0.11

and ADMM/3-21G* could therefore be explained by a more similar level of polarization in the AO and auxiliary basis for 3-21G* compared to 3-21G.

At the cc-pVTZ level, the convergence problems can be attributed to a small HOMO-LUMO gap. For all calculations that do not converge, the gap is smaller than $0.1 E_h$. For the cc-pVDZ calculation, the HOMO-LUMO gap varies more, but for some iterations the gap is as small as for cc-pVTZ calculations.

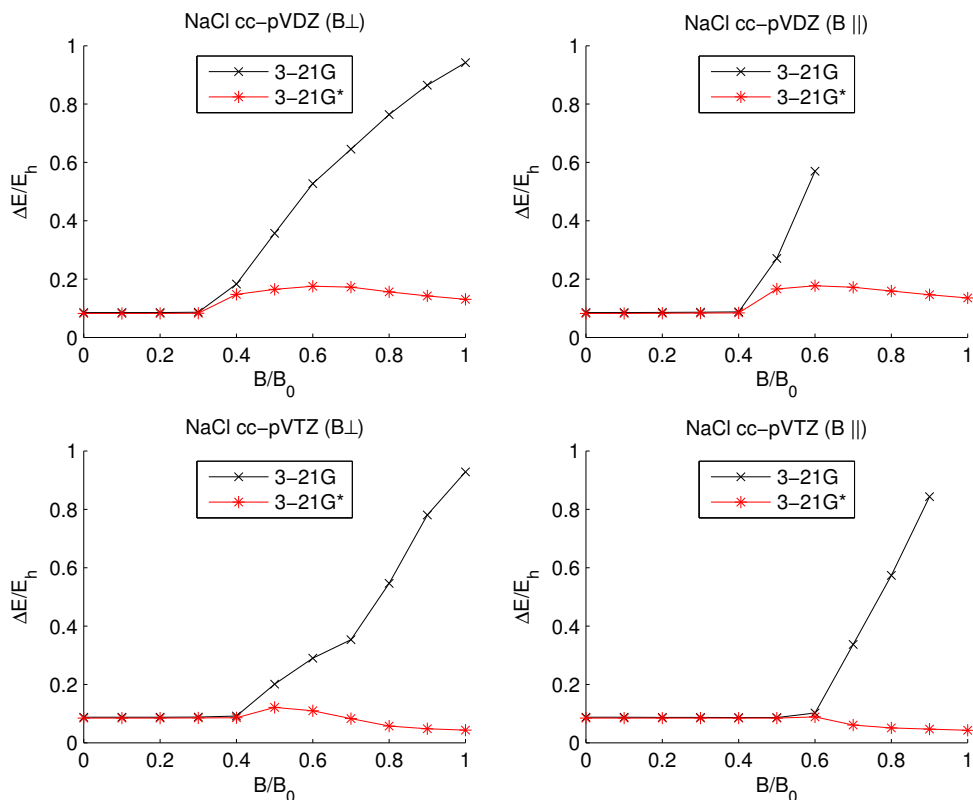


Figure 2: Error in energy with ADMM compared to plain Hartree-Fock for NaCl with cc-pVDZ and cc-pVTZ with perpendicular and parallel orientation of the field. The improvement of ADMM with 3-21G* as an auxiliary basis compared to 3-21G is clearly demonstrated.

2.3 Timings

Table 5 shows timings for the methods for the largest systems investigated in this project. The three smaller systems take less than one second for a SCF

iteration for most combinations of program and basis set, and have therefore been omitted. There are two factors that make comparisons between LSDALTON and LONDON difficult for timings. For LONDON, the DFT correction is not implemented; this is the largest time consumer for ADMM in LSDALTON. For DF in LSDALTON, J-engine [23, 24, 25] is also implemented. This speeds up DF in LSDALTON additionally. The speed-up with LONDON compared to LSDALTON is quite similar, with a larger ratio for the LONDON implementations with the two smallest systems and a smaller ratio for the largest system. The effect of J-engine and the DFT correction can be seen in the timings as LSDALTON takes the most time in ADMM, while it is the opposite for LONDON.

Table 5: Timings (s) for LSDALTON and LONDON with cc-pVDZ (DZ) and cc-pVTZ (TZ). Timings for calculating exchange and Coulomb with ADMM2 (A2) and DF are shown, with their total time given under "Both". "HF" shows the time needed to calculate exchange and Coulomb with plain Hartree-Fock, and the ratio between "HF" and "Both" is given under "Ratio".

Program	Basis	System	A2	DF	Both	HF	Ratio
LSDALTON	DZ	Benzene	3	0	4	4	1.0
		Naphthalene	10	1	10	24	2.4
		C ₂₀	13	2	15	46	3.1
	TZ	Benzene	9	1	10	62	6.2
		Naphthalene	25	2	27	334	12.4
		C ₂₀	28	5	33	507	15.4
LONDON	DZ	Benzene	5	38	44	143	3.3
		Naphthalene	28	153	182	705	3.9
		C ₂₀	68	727	795	1617	2.0
	TZ	Benzene	6	152	159	2576	16.2
		Naphthalene	30	579	609	11594	19.0
		C ₂₀	70	2328	2398	28892	12.1

2.4 Paramagnetic to diamagnetic transition of C₂₀

C₂₀ is a system with 20 carbon atoms organized in a ring. It is a paramagnetic system, which means the energy of the system decreases with an increasing

magnetic field. However, the paramagnetic behaviour is only present up to a critical value of magnetic field. For magnetic fields stronger than this critical value, the energy will start to increase with increasing magnetic field and the system is diamagnetic. This critical value will be given by a minimum in energy as a function of magnetic field. It is interesting to see if this limit changes by introducing DF or ADMM. Figure 3 shows energy as a function of magnetic field calculated with plain Hartree-Fock, DF, ADMM and both ADMM and DF. The critical value for paramagnetism appears at the same magnetic field strength for all four cases.

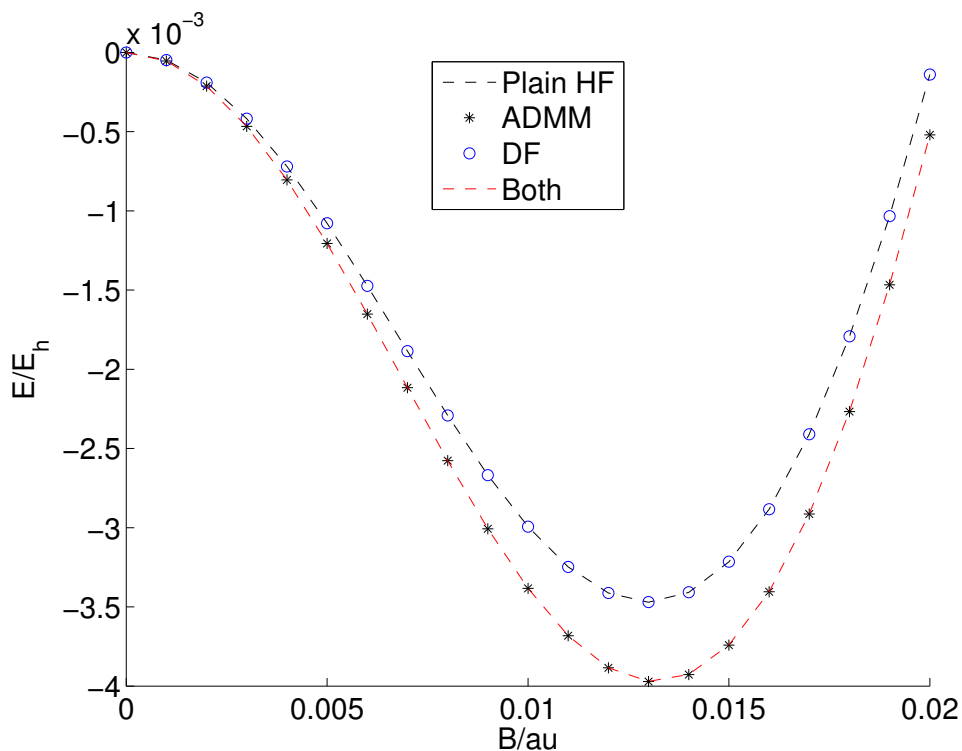


Figure 3: Energy as a function of magnetic field, showing the paramagnetic behaviour of C_{20} . Zero set to energy at zero field for each curve ($E(B) - E(0)$).

2.5 Dissociation of magnetically bound molecules

In strong magnetic fields, a new bonding mechanism has been predicted [3], by which anti-bonding orbitals are stabilized relative to the bonding orbitals. With this mechanism, molecules with bonds of zero bond order can be stable. He_2 , He_3 and larger clusters have been predicted [26], where He_3

is an equilateral triangle. Figure 4 shows the structure for clusters of helium where the triangle structure of He_3 seems to be repeated.

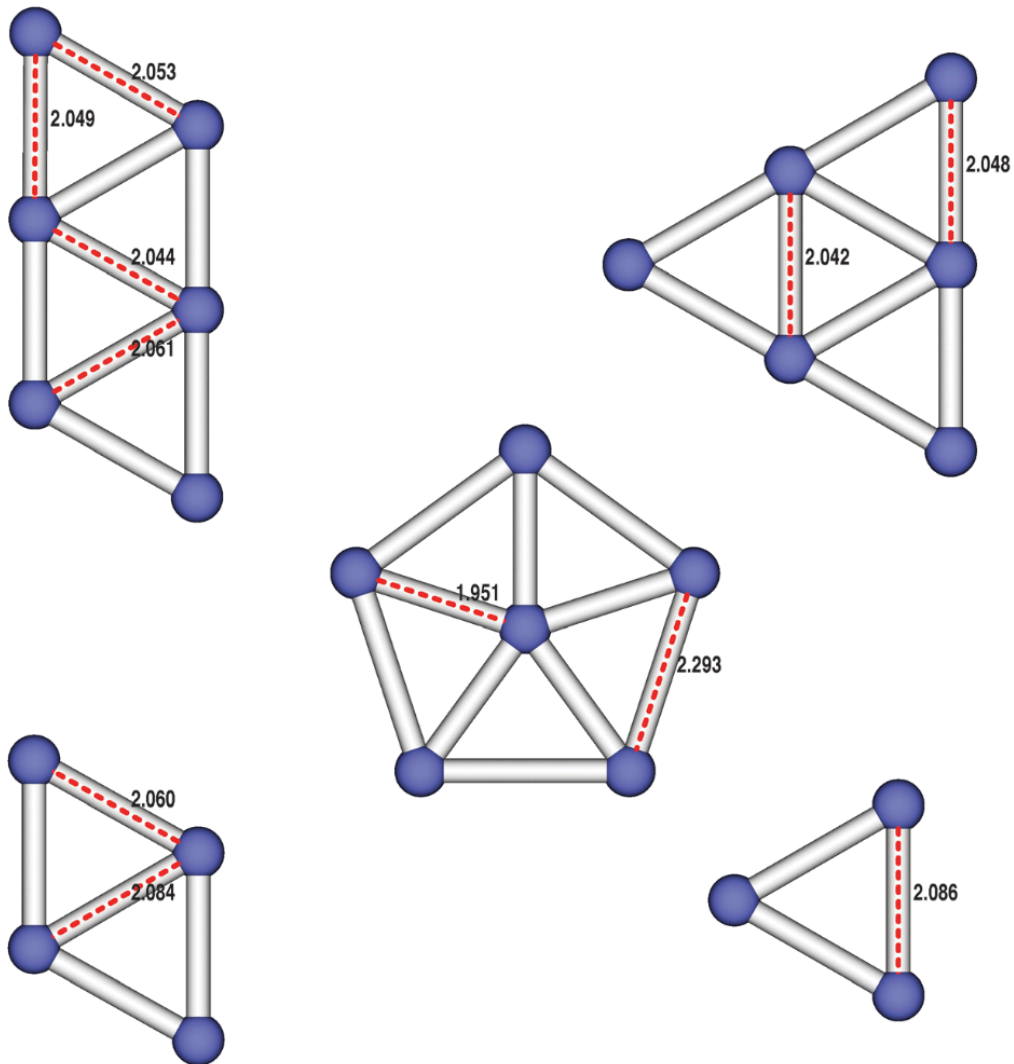


Figure 4: Structures for clusters of helium. Reproduced from Ref [26] with permission of The Royal Society of Chemistry.

To test the performance of the ADMMX approximation, dissociation curves for He_2 and He_3 have been calculated at $B = 1 B_0$. For He_3 , all bonds have been kept at the same relative length in the dissociation. Figures 5 and 6 show the dissociation curves and the error for the ADMM calculations, respectively. The basis functions for He with 3-21G* have been created by adding the polarization functions from 6-31G* to the 3-21G basis. For He

this means an additional p-function compared to 3-21G. ADMMX yields a minimum closer to plain Hartree-Fock with 3-21G* compared to 3-21G as an auxiliary basis, though the difference is not large. For the total energy, figure 6 shows that with 3-21G* the error is smaller and more constant along the curve compared to 3-21G. This indicates that polarization in the auxiliary basis for ADMMX is important to keep the error constant with respect to nuclear distances as well as for magnetic field. The dissociation curves are another example of the importance of including polarization in the auxiliary basis for ADMMX with strong fields. The dissociation curve named Hartree is a Hartree-Fock calculation with no exchange contribution. This curve has basically the same minimum as for the plain Hartree-Fock calculation, which means exchange does not move the minimum of the curve, and that this is handled by ADMMX.

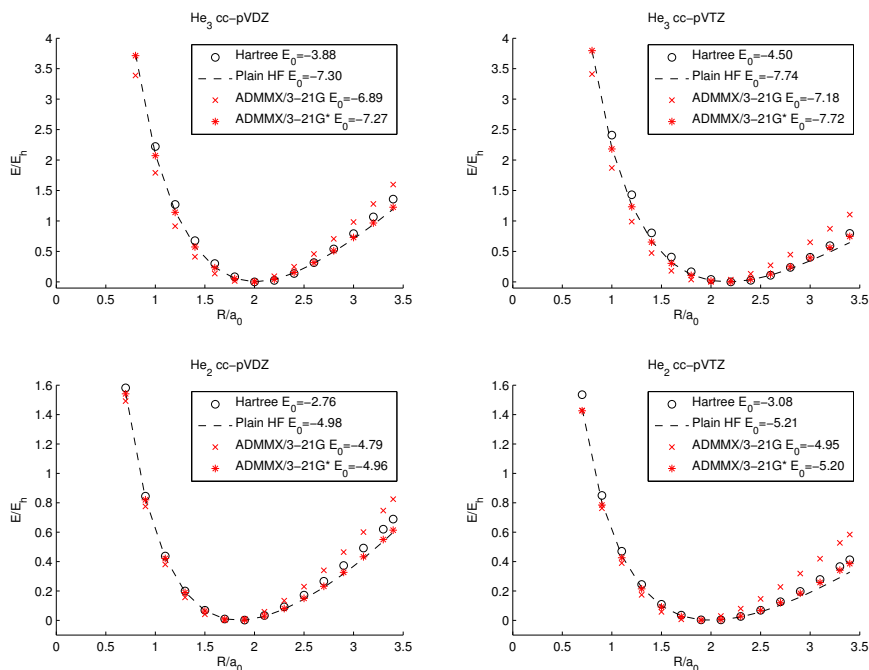


Figure 5: Dissociation curve at $B = 1.0 B_0$, showing the perpendicular paramagnetic bonding of He_2 and He_3 . Zero set to energy minimum for each curve ($E(r) - E(r_{min})$).

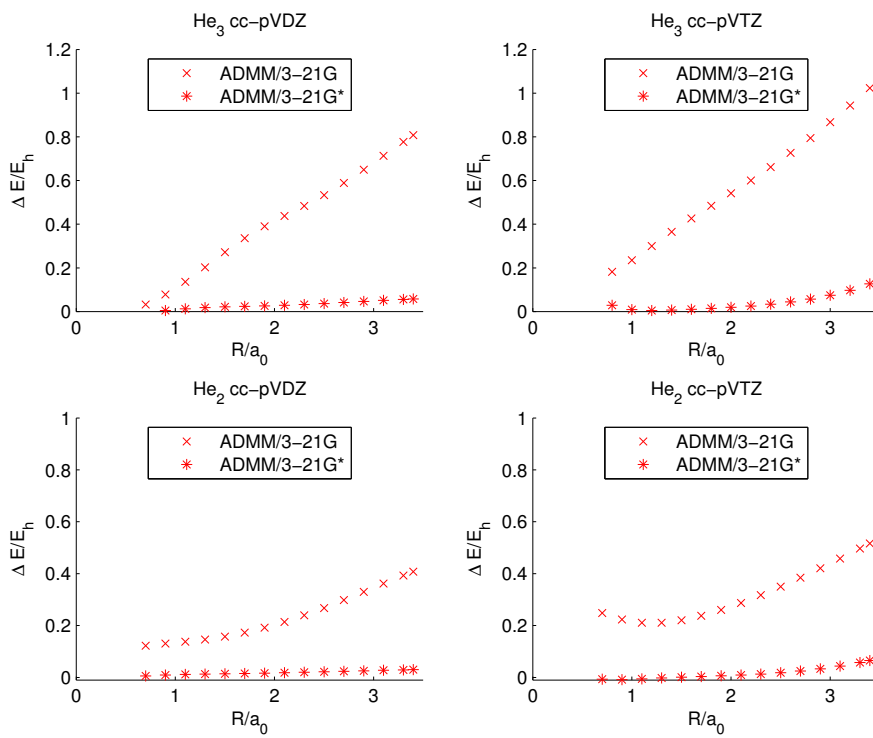


Figure 6: Error compared to plain Hartree-Fock for ADMMX in dissociation curve at $B = 1.0 B_0$, with a polarized and a non-polarized basis set.

3 Discussion

3.1 Conclusion

In this project, DF and ADMMX have been implemented and tested in the LONDON code with plane-wave hybrid basis sets. The implementations have been tested for 6 test systems with cc-pVDZ and cc-pVTZ as AO basis sets. The calculations have been performed at different magnetic field strengths to investigate how the error varies with magnetic field.

For DF, the basis sets df-def2 and cc-pVTZdenfit have been tested; these are basis sets developed for DF in field-free calculations. With these auxiliary basis sets, the DF error is below $1 mE_h$ for all systems and magnetic field strengths investigated. The phase factors in the London orbitals do not seem to pose any major problems.

The 3-21G and 3-21G* basis sets have been investigated as auxiliary basis sets for ADMMX. Since ADMMX does not have the DFT correction, the accuracy of the method is poorer than for other implementations of ADMM. However, with a polarized auxiliary basis for calculations involving strong fields, the error remains fairly constant with magnetic field. With a constant error, it is possible to describe properties depending on derivatives. ADMMX has been found to give an accurate description of phenomena such as the paramagnetic diamagnetic transition and the dissociation of magnetically bound molecules. Polarization in the auxiliary basis is important to make the errors fairly constant, with respect to both magnetic field and nuclear distances.

The speed-up for the systems investigated when using both ADMMX and DF range from a factor two to a factor four for cc-pVDZ calculations and from a factor 12 to a factor 19 for cc-pVTZ calculations.

3.2 Further work

ADMMX has been able to yield chemically relevant information. The investigation of paramagnetic to diamagnetic transitions was described well for C_{20} . With the speed-up from DF and ADMMX, larger systems can be investigated. Since the response of a molecule to magnetic fields is proportional to the flux of the magnetic field, larger systems will show effects of magnetic fields at lower field strengths. ADMMX can therefore be used to investigate systems that show the paramagnetic to diamagnetic transition at lower magnetic fields. This gets us one step closer to finding molecules that show this transition in experimentally attainable fields. For the helium molecules, the dissociation curves for these perpendicular paramagnetic

bound molecules was well described by the current implementation. This is another phenomenon that can be investigated further for larger molecules. It should be noted that the Hartree dissociation curve showed the same minimum as the plain Hartree-Fock and ADMMX calculations. This means that exchange does not move the minimum of the dissociation curve. It should be explored how ADMMX performs when exchange moves the minimum of the dissociation curve.

Auxiliary basis sets have been developed for DF, but this is not the case for ADMM. It can be expected that the errors in the ADMM method can be reduced by developing auxiliary basis sets specifically for this method. For calculations in strong magnetic fields, it seems a polarized version would be needed.

To reduce the errors of the ADMMX method it is natural to include a DFT correction. How a polarized auxiliary basis will effect the DFT correction should be investigated. A polarized auxiliary basis leads to a fairly constant error, with respect to magnetic field, between Hartree-Fock exchange in AO and auxiliary basis. To get accurate results the same has to be the case for the DFT exchange functional.

A different approach to reduce the computation time of exchange is the RI-K approximation. The speed-up of RI for exchange is given by the ratio between the number of occupied orbitals and the total number of orbitals. For small molecules with large basis sets, this ratio is the highest. However, in the RI-K approximation, the auxiliary basis represents products of basis functions. With London orbitals, the products could be complex. This adds a challenge to implementing RI-K for London orbitals.

The current implementations of ADMM and DF reduce the computation time for two electron contributions in Hartree-Fock calculations in the LONDON code. Speed has not been prioritized in the development of the code so far, it can therefore be expected that substantial reductions in computation time can be achieved in other parts of the code as well. At present the code is not parallelised, this can also be considered to speed up calculations.

4 Appendix

4.1 Geometries

LiH			
Li	0.000	-2.258	0.000
H	0.000	2.258	0.000

NaCl			
Na	0.000	-2.665	0.000
Cl	0.000	2.665	0.000

N ₂ O			
N	0.000	0.000	0.000
N	2.241	0.000	0.000
O	-2.128	0.000	0.000

Benzene

C	0.000	2.639	0.000
C	2.285	1.319	0.000
C	2.285	-1.319	0.000
C	0.000	-2.639	0.000
C	-2.285	-1.319	0.000
C	-2.285	1.319	0.000
H	0.000	4.671	0.000
H	4.045	2.336	0.000
H	4.045	-2.336	0.000
H	0.000	-4.671	0.000
H	-4.045	-2.336	0.000
H	-4.045	2.336	0.000

Naphthalene

C	2.239	-2.112	0.000
C	1.904	-4.762	0.000
C	-0.451	-5.764	0.000
C	0.207	-0.556	0.000
C	-7.131	-3.622	0.000
C	-6.796	-0.971	0.000
C	-5.099	-5.178	0.000
C	-2.612	-4.184	0.000
C	-2.280	-1.550	0.000
C	-4.441	0.031	0.000
H	0.458	1.458	0.000
H	4.115	-1.341	0.000
H	3.530	-5.975	0.000
H	-0.708	-7.777	0.000
H	-5.350	-7.191	0.000
H	-9.007	-4.392	0.000
H	-8.422	0.242	0.000
H	-4.184	2.044	0.000

	C_{20}		
C	6.3020277	-4.5786545	0.0
C	7.3873441	-2.4914432	0.0
C	-4.5119870	6.3578001	0.0
C	7.7898030	0.0000715	0.0
C	-2.4071314	7.4084887	0.0
C	7.4410660	2.3265989	0.0
C	6.3021990	4.5788452	0.0
C	0.0867960	7.7957112	0.0
C	4.6524803	6.2559836	0.0
C	2.4072518	7.4086186	0.0
C	-6.3020277	4.5786545	0.0
C	-7.3873441	2.4914432	0.0
C	4.5119870	-6.3578001	0.0
C	-7.7898030	-0.0000715	0.0
C	2.4071314	-7.4084887	0.0
C	-7.4410660	-2.3265989	0.0
C	-6.3021990	-4.5788452	0.0
C	-0.0867960	-7.7957112	0.0
C	-4.6524803	-6.2559836	0.0
C	-2.4072518	-7.4086186	0.0

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