Higher-Order Perturbative Relativistic Corrections to Energies and Properties

Dissertation zur Erlangung des Grades ,,Doktor der Naturwissenschaften" im Promotionsfach Chemie

am Fachbereich Chemie, Pharmazie und Geowissenschaften der Johannes Gutenberg-Universität in Mainz



von

Stella Stopkowicz geboren in Bad Ems

Mainz, 2011

Dekan:

- 1. Berichterstatter:
- 2. Berichterstatter:
- 3. Berichterstatter:

Tag der mündlichen Prüfung: 22. 02. 2012

Contents

Ι.	Introduction	6
١١.	Quantum-Chemical Methods in Non-relativistic and Relativistic Theories	11
	II.1. Basic equations in non-relativistic and relativistic theories	11
	II.2. Hartree-Fock theory	15
	II.3. Correlation methods	17
	II.3.1. Møller-Plesset perturbation theory	21
	II.3.2. Coupled-cluster theory	22
111	I. Derivative Theory	24
	III.1. Numerical versus analytical differentiation	24
	III.2. Analytic derivatives	25
	III.3. Numerical differentiation	29
IV	7. Direct Perturbation Theory	32
	IV.1. DPT expansion	32
	IV.2. DPT corrections at the Hartree-Fock level	34
	IV.2.1. Expansion of the perturbed wave function	37
	IV.2.2. Separation of scalar-relativistic and spin-orbit contribution \ldots \ldots	41
	IV.2.3. DPT from a non-relativistic Lagrangian	44
	IV.2.4. DPT6 corrections from a non-relativistic Lagrangian	50
	IV.3. DPT corrections at correlated levels of theory	53
	IV.3.1. Separation of scalar-relativistic and spin-orbit contribution \ldots \ldots	62
	IV.4. DPT4 for electrical properties	66
	IV.5. Further ideas for relativistic corrections	68
V.	. Calculation of Relativistic Integrals	71
	V.1. Cartesian Gaussians	71
	V.2. The McMurchie-Davidson scheme	73
	V.2.1. Expansion with respect to Hermite Gaussians	73
	V.2.2. Recursion relations for the coefficients	73

	V.2.3.	One-electron integrals with factorizable operators $\ldots \ldots \ldots \ldots$	74	
	V.2.4.	One-electron integrals with non-factorizable operators	77	
	V.2.5.	Two-electron integrals	79	
V	.3. One-	electron integrals for relativistic corrections	81	
	V.3.1.	Scalar-relativistic nuclear-electron potential integral	84	
	V.3.2.	Spin-orbit nuclear-electron potential integral	85	
	V.3.3.	Scalar-relativistic dipole-moment integral	86	
	V.3.4.	Spin-orbit dipole-moment integral	87	
	V.3.5.	Scalar-relativistic quadrupole-moment integral	89	
	V.3.6.	Spin-orbit quadrupole-moment integral $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	91	
	V.3.7.	Scalar-relativistic electric-field gradient integral $\ .\ .\ .\ .$.	93	
	V.3.8.	Spin-orbit electric-field gradient integral $\ldots \ldots \ldots \ldots \ldots \ldots$	96	
V	.4. Two-	-electron integrals for relativistic corrections	98	
	V.4.1.	Scalar-relativistic two-electron integrals	99	
	V.4.2.	Spin-orbit two-electron integrals	100	
VI.	Implemer	ntation	103	
V	I.1. DPT	4 energy corrections at the Hartree-Fock level	103	
V	I.2. DPT	4 energy corrections at correlated levels of theory	106	
V	I.3. DPT	4 corrections to electrical properties	108	
V	I.4. Valid	lation of the integrals	108	
V	I.5. Valid	lation of the HF-DPT4 energy	110	
V	I.6. Valid	lation of the MP2-DPT4 energy	111	
VII.	Application	ons	112	
V	II.1. Rela	tivistic corrections to total energies at the Hartree-Fock level	112	
	VII.1.1	.DPT4 energies at the HF level: Comparison to fully relativistic		
		calculations	113	
	VII.1.2	. Term analysis of the DPT4 correction at the HF level	117	
	VII.1.3	. Basis-set convergence of the DPT4 correction at the HF level	118	
VII.2. Relativistic corrections to total energies at correlated levels of theory				
VII.2.1. DPT4 energies at MP2 level: Comparison to fully relativistic cal				
		culations	120	
	VII.2.2	Analysis of the correlated SR-DPT4 correction	123	
V	II.3. Rela	tivistic corrections to electrical properties	125	

Contents

VII.3.1. DPT4 properties at the HF level: Comparison to fully relativistic							
calculations $\ldots \ldots 127$							
VII.4. Relativistic corrections to hyperfine parameters							
VII.4.1. Halogen quadrupole-coupling tensors of CH_2BrF and $CHBrF_2$ 132							
VII.4.2. Halogen quadrupole-coupling tensor of CH_2FI							
VIII. Conclusion 137							
IX. Appendix 140							
IX.1. Perturbative expansion of the Dirac-Hartree-Fock equations							
IX.2. CPHF equations for the relativistic perturbation							
IX.3. First derivative of the Lagrange multipliers							
IX.4. Spin orthogonality for the g_{12}^{SO} integrals $\ldots \ldots 145$							
IX.5. Spin integration for the $f_{pq}^{(SO)}$ matrix elements $\ldots \ldots \ldots$							
IX.6. Spin-integrated quantities for SR-DPT4 at the MP2 level \ldots \ldots \ldots 149							
IX.7. Accuracy of the numerical SR-DPT4 and SO-DPT4 results							
IX.8. Basis-set dependence of DPT4							
References 157							
List of publications							

I. Introduction

The importance of quantum chemistry in the field of chemical research is nowadays continuously increasing due to the advances in computer science and the resulting increase of computing power as well as the improvements in quantum-chemical methods and algorithms.¹ Quantum chemistry is able to provide information about energies and properties of molecules within a purely theoretical framework. Therefore, in many cases, theoretical predictions concerning the properties of unknown molecules or systems that are difficult to handle experimentally become feasible. Furthermore, a fruitful field lies in the interplay between theory and experiment.² Results from quantum-chemical calculations may help in the evaluation, interpretation, as well as confirmation of experimental findings and can even guide experiments.

The basis for the description of atoms and molecules in quantum-chemical calculations is usually given by the Schrödinger equation. As an analytic solution to this equation is only possible for up to two particles, in quantum chemistry a variety of methods to solve the Schrödinger equation in an approximate manner has been developed.¹ These methods differ in both the accuracy that can be obtained as well as the required computational effort. Which method can be used for a specific system depends mostly on the system size N as the computing time for a given method scales with some power of N. In solid-state chemistry and for large molecules mostly density-functional theory (DFT),³⁻⁵ which scales with $N-N^4$, depending on the actual implementation, as well as semiempirical methods⁶ are employed. For small and medium-sized systems, however, computationally more demanding yet also more accurate methods like Møller-Plesset (MP) perturbation theory,^{7,8} which scales with N^5 , and highly accurate coupled-cluster (CC) methods⁹⁻¹⁴ are applicable. Both are so called 'post-Hartree-Fock' theories, as they are based on the Hartree-Fock (HF) wave function as a starting point, and include electron-correlation effects, i.e., the explicit dependence of the movement of one electron on those of the others, missing in the HF treatment. Using, for example, the CC singles and doubles $(CCSD)^{15}$ method with a perturbative correction for the triples excitations $(CCSD(T)^{16})$, which scales with N^7 , energies can be obtained within an accuracy of a few kcal/mol.¹

However, when based on the Schrödinger equation, none of these methods account for relativistic effects, i.e., all effects that arise due to the fact that the speed of light c is

finite. The formalism that combines quantum theory with special relativity is referred to as relativistic quantum mechanics^{17,18} with the Dirac equation as a starting point to treat relativistic effects in atoms and molecules. Prominent examples for relativistic effects in chemistry are the color of gold, which, in a non-relativistic world, would be silver-colored,^{19,20} as well as the liquid state of elemental mercury at room temperature, which should be solid from a non-relativistic perspective.^{19,20}

When dealing with heavy elements, it is nowadays common to account for relativistic effects in quantum-chemical calculations while for systems containing lighter elements, i.e., such from the first four rows (H-Kr) of the periodic table, these effects are often ignored. Although, for example, relativistic effects on energies for elements of the second row of the periodic table are already of the same order of magnitude as correlation effects, the reason why they are often not considered is the fact that for chemical reactions only energy differences instead of absolute energies are relevant. Chemical reactions are accompanied by changes in the valence shells, so that electron correlation is essential. Relativistic effects, however, affect mostly the inner shells and thus cancel for a large part when taking energy differences. Nevertheless, to achieve a quantitative agreement with experiment, relativistic effects need to be accounted for even for very light elements (see, for example, Ref. 21).

The most rigorous, yet computationally most demanding, way to treat relativistic effects is to base the well-known methods from non-relativistic quantum chemistry directly on the Dirac rather than the Schrödinger equation.¹⁷ As the one-electron Dirac equation is of a four-component form, i.e., the operators are 4×4 matrices and the wave function is a four-component spinor consisting of the so-called large component (upper two parts of the spinor) and the small component (lower two parts of the spinor), these approaches are referred to as 'four-component' methods.^{22,23} For most methods in nonrelativistic quantum chemistry, a four-component variant has been developed. To mention are here the HF^{24–26} approach, DFT,^{27–29} second-order MP (MP2),^{30,31} configuration interaction (CI),^{32–36} CCSD,³⁷ CCSD(T),³⁸ and even general CC methods with arbitrary excitations.^{39,40} However, the computational costs compared to the non-relativistic counterparts are much higher^{23,41} due to several reasons such as the use of complex algebra, the increased basis-set size, and less symmetries that can be exploited. A four-component CCSD calculation, for example, is at least 32 times more expensive than its non-relativistic variant.⁴¹

In order to reduce the computational costs, approximate schemes to treat relativistic effects have been developed. To mention are here especially the 'two-component' or

I. Introduction

'quasi-relativistic' approaches.⁴² The full four-component Hamiltonian gives rise to both a positive-energy (electronic states) as well as a negative-energy spectrum (positronic states). For chemistry, only the electronic states are of interest where in the wave function the upper two components are, in fact, significantly larger (roughly by a factor of 2c) than the lower two. Accordingly, schemes have been suggested in which the small component is eliminated either by expressing it in terms of the large component or via a suitable unitary transformation. Both variants yield a two-component problem with an effective Hamiltonian which should (approximately) reproduce the positive-energy spectrum. The detailed procedures how this reduction to two-component form is achieved define the different quasi-relativistic methods, as, for example, the Douglas-Kroll-Hess^{42,43} scheme, the regular approximation,^{44–48} and the more recent 'exact two-component' (X2c) approach.^{49–57} In these schemes, both the scalar-relativistic (SR) contributions, i.e., those which are independent of the spin, as well as the spin-orbit (SO) contributions can be accounted for.

In addition to the two-component schemes, one-component approaches have been developed.^{58–62} They carry the advantage that the implementation into an existing nonrelativistic computer program is much more straightforward compared to the methods mentioned before. One possibility is to split SR and SO effects within the two-component schemes and to treat SR effects only. Afterwards, the SO effects can be dealt with in a non-variational, i.e., perturbative manner. If, as it is the case in this work, inclusion of relativistic effects is needed in order to reach high-accuracy for chemical applications involving rather light elements, perturbative techniques¹⁷ are well suited, since relativistic effects are rather small. Perturbative schemes in these cases appear as a cost-effective alternative to the rather expensive rigorous four-component methods, in particular when electron correlation is considered as well.

However, the formulation of a satisfactory perturbative scheme for the treatment of relativistic effects is not straightforward. When starting from the Schrödinger equation, the proper definition of the perturbed operators appears to be an issue, while, when starting from the Dirac equation, it is not obvious at first sight how to define the proper nonrelativistic limit. In this context, the often used scheme involving the Pauli-Hamiltonian with mass-velocity, Darwin, and SO terms as perturbations proves to be unsatisfactory, as it is only applicable within lowest-order perturbation theory due to singularities in the Hamiltonian.⁶³

An elegant solution to the above mentioned problems is offered by Direct Perturbation Theory (DPT).^{63–71} Here, perturbation theory is applied to the Dirac equation after changing the metric⁶⁸ and the proper non-relativistic limit for electronic states is obtained in form of the Lévy-Leblond equation,^{68,72} i.e., a four-component equation that is equivalent to the Schrödinger equation. There is no restriction to lowest-order perturbation theory and DPT can be in principle applied in any order. Expressions for up to DPT6 have been reported in the literature.^{70,71} It should be noted that orders are counted with respect to c^{-1} , with c being the speed of light, and thus DPT6 corresponds to third-order perturbation theory.

DPT was first suggested by Rutkowski in the 1980s^{64–66} and later pursued in more detail by Kutzelnigg^{68–71,73,74} thus presenting itself to be an attractive scheme for the treatment of relativistic effects. The lowest-order treatment at the DPT2 level is nowadays routinely available and efficiently implemented in terms of energy gradients.⁷⁵ However, for higher orders, no general implementation has been presented so far. Promising results nevertheless have been reported for one-electron systems⁷⁶ and for the series of the noble-gas atoms⁷³ which render a general implementation worthwhile. The development of such an implementation has been hampered by the fact that the detailed expressions for higher orders of DPT are rather involved and that, unlike for DPT2,⁷⁵ it has not been clear how existing analytic-derivative techniques^{77,78} could be exploited to facilitate such an implementation.

The investigation of DPT4, i.e., the second-order perturbation theory treatment of relativistic effects, seems of particular interest, since it allows a judgement of the accuracy and convergence of the DPT series. Additionally, it is the lowest order for which SO contributions appear in the relativistic treatment of closed-shell systems.

In this work DPT4 is formulated in terms of energy derivatives for both the HF as well as correlated methods in order to exploit the existing analytic second-derivative techniques^{78,79} in the program package CFOUR⁸⁰ which is used for the implementation of DPT4. Beside the modifications required to make the analytic second-derivative code work for the DPT4 corrections, additional, so-called relativistic integrals needed in the DPT4 treatment had to be implemented into CFOUR. Furthermore, in order to calculate DPT4 corrections to electrical properties such as dipole moment, quadrupole moment and electric-field gradient (efg), further integrals to account for the SO contributions in DPT4 were included to CFOUR and the framework for calculating these DPT4 corrections numerically was set up.

The resulting procedure is used for a study concerning the convergence behaviour of the DPT corrections, for both the SR and SO contributions, to energies and properties at the HF level as well as for correlated levels of theories in the case of energies. For the

I. Introduction

DPT4 energies at the HF level furthermore the basis set-convergence is investigated. In addition, a joint experimental and theoretical study in rotational spectroscopy concerning the importance of relativistic effects to the bromine and iodine quadrupole-coupling tensors of selected molecules is discussed, thereby exploiting the methods which have been developed in the present work.

Chapters II and III review the theoretical background of derivative theory as well as quantum-chemical methods in relativistic in non-relativistic theories. In chapter IV the underlying theory of DPT is discussed which has been developed in this work. The evaluation of the necessary integrals is presented in chapter V while the implementation of the DPT4 corrections into CFOUR is found in chapter VI. In chapter VII the calculations for the relativistic corrections to energies and properties are discussed and in chapter VIII a summary is given.

II. Quantum-Chemical Methods in Non-relativistic and Relativistic Theories

In this chapter the quantum-chemical methods that are relevant for this work are discussed. In principle, for all methods used in non-relativistic quantum chemistry a relativistic counterpart exists as well. While in non-relativistic theories the starting point is the Schrödinger equation, for a relativistic description one has to start from the Dirac equation. This requires modifications compared to the non-relativistic treatment and leads to increased computational costs. In the following, the Hartree-Fock (HF) method, Møller-Plesset (MP) perturbation theory, as well as the coupled-cluster (CC) approach are discussed from both the non-relativistic and the relativistic perspective.

II.1. Basic equations in non-relativistic and relativistic theories

The basis for describing atoms and molecules in the framework of non-relativistic quantum chemistry is given by the time-independent Schrödinger equation

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

This equation corresponds to an eigenvalue problem with the wave function Ψ which completely describes the state of the atom or molecule, the total energy E of the system and the Hamiltonian \hat{H} which for a molecule in atomic units (a.u.) is given by

$$\hat{H} = \underbrace{\sum_{A} \left(-\frac{1}{2M_A} \nabla_A^2 \right)}_{\hat{T}_{n}} + \underbrace{\sum_{a} \left(-\frac{1}{2} \nabla_a^2 \right)}_{\hat{T}_{e}} + \underbrace{\sum_{A < B} \frac{Z_A Z_B}{r_{AB}}}_{\hat{V}_{nn}} + \underbrace{\sum_{A,a} \left(-\frac{Z_A}{r_{Aa}} \right)}_{\hat{V}_{ne}} + \underbrace{\sum_{a < b} \frac{1}{r_{ab}}}_{\hat{V}_{ee}}.$$
 (II.2)

In (II.2) the appearing quantities are the distances r, the nuclear mass M_A , the atomic number Z_A , and the nabla operator

$$\nabla = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}.$$
 (II.3)

The \hat{T} operators describe the kinetic energy of electrons and nuclei and the \hat{V} operators account for the Coulomb interactions between charged particles. Within the Born-Oppenheimer approximation⁸¹ the movement of electrons and nuclei is separated. As electrons move about 2000 times faster than the nuclei (due to the difference in the masses) this is a reasonable approximation. This separation leads to the electronic Schrödinger equation which no longer includes the kinetic energy of the nuclei and the potential V_{nn}

$$\underbrace{(\hat{T}_{\rm e} + \hat{V}_{\rm ne} + \hat{V}_{\rm ee})}_{\hat{H}_{\rm el}} \Psi_{\rm el} = E_{\rm el} \Psi_{\rm el} \tag{II.4}$$

$$\left[\sum_{a}\underbrace{\left(-\frac{1}{2}\nabla_{a}^{2}+\sum_{A}\left(-\frac{Z_{A}}{R_{Aa}}\right)\right)}_{\hat{h}(a)}+\sum_{a(II.5)$$

In non-relativistic quantum-chemical calculations this equation is solved using a variety of different approximations.

For relativistic quantum chemistry, the starting point within the Born-Oppenheimer approximation is given by the time-independent Dirac equation.^{17,18} In the one-electron case it is given as

$$\underbrace{\begin{pmatrix} V & c\boldsymbol{\sigma}\hat{\mathbf{p}} \\ c\boldsymbol{\sigma}\hat{\mathbf{p}} & V - 2mc^2 \end{pmatrix}}_{\mathbf{h}_{\mathrm{D}}'} \underbrace{\begin{pmatrix} \overline{\varphi} \\ \overline{\chi} \\ \overline{\psi} \end{pmatrix}}_{\overline{\Psi}} = E \begin{pmatrix} \overline{\varphi} \\ \overline{\chi} \end{pmatrix}, \qquad (\mathrm{II.6})$$

where c is the speed of light, V is the electron-nucleus potential, $\hat{\mathbf{p}}$ is the momentum operator, m is the electron mass, and $\boldsymbol{\sigma}$ is the vector of the Pauli matrices σ_x, σ_y , and σ_z ,

which are given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$
 (II.7)

The wave function in (II.6) is a four-component spinor consisting of the so-called large and small components ($\overline{\varphi}$ and $\overline{\chi}$) which are both two-component functions.¹⁷ An important property that distinguishes the Dirac equation from the Schrödinger equation is given by its behaviour with respect to Lorentz transformations. These transformations connect time and space coordinates and are consistent with Einstein's principle of relativity. Invariance with respect to Lorentz transformations is essential for a relativistic theory and it can be shown¹⁷ that (II.6) is in fact Lorentz invariant.

For the many-electron case, the Dirac Hamiltonian is given by

$$\hat{H}'_{\rm D} = \sum_{a} \hat{\mathbf{h}}'_{\rm D}(a) + \sum_{a < b} \hat{g}_{ab} \mathbf{I}_{(4)}$$
(II.8)

with the two-electron interaction term \hat{g}_{ab} and the four-component unity matrix $\mathbf{I}_{(4)}$. The easiest and commonly used choice for \hat{g}_{ab} is to work with the potential V_{ee} leading to the so-called Dirac-Coulomb Hamiltonian

$$\hat{H}_{\rm DC} = \sum_{a} \hat{\mathbf{h}}'_{\rm D}(a) + \sum_{a < b} \frac{1}{r_{ab}} \mathbf{I}_{(4)}$$
(II.9)

Due to the instantaneous interaction in V_{ee} this Hamiltonian is not Lorentz invariant. To make it Lorentz invariant up to the order of $\mathcal{O}(c^{-2})$, the Breit interaction is used

$$\hat{g}_{ab} = \frac{1}{r_{ab}} - \frac{1}{2r_{ab}} \left[\boldsymbol{\alpha}_a \boldsymbol{\alpha}_b + \frac{(\boldsymbol{\alpha}_a r_{ab})(\boldsymbol{\alpha}_b r_{ab})}{r_{ab}^2} \right]$$
(II.10)

with

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_x \\ \alpha_y \\ \alpha_z \end{pmatrix}, \quad \alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad i = x, y, z$$
(II.11)



Figure II.1.: Energy spectrum of the Schrödinger equation (left) and the Dirac equation (right). In the relativistic spectrum E is defined without the rest energy of the electron, i.e., mc^2 .

which yields the Dirac-Coulomb-Breit Hamiltonian

$$\hat{H}_{\text{DCB}} = \sum_{a} \hat{\mathbf{h}}'_{\text{D}}(a) + \sum_{a < b} \left(\frac{1}{r_{ab}} - \frac{1}{2r_{ab}} \left[\boldsymbol{\alpha}_{a} \boldsymbol{\alpha}_{b} + \frac{(\boldsymbol{\alpha}_{a} r_{ab})(\boldsymbol{\alpha}_{b} r_{ab})}{r_{ab}^{2}} \right] \right) \mathbf{I}_{(4)}.$$
 (II.12)

As the Breit correction terms are small and their evaluation is quite laborious, the Dirac-Coulomb Hamiltonian is used in this work.

In the Schrödinger equation the state with the lowest energy is the ground state. Therefore, when determining the energy using the variation principle with a trial wave function on the basis of the Schrödinger equation an upper bound for the ground-state energy is obtained. The Dirac equation yields a negative and positive energy spectrum (see figure II.1). While the positive energy solutions are associated with electronic states, the negative-energy solutions correspond to positronic states. Applying the variation principle to the Dirac equation in a naive manner will result in a variational collapse and special care needs to be taken, i.e., in restricting the variation to bound states only, in order to get an approximate solution for the ground-state.¹⁷

It can be shown (see chapter IV.1) that the non-relativistic limit of the Dirac equation is given by the so-called Lévy-Leblond equation⁷² which yields the same energy as the

Schrödinger equation (for electronic states) but includes spin and is of a four-component form. When eliminating the small component from the Lévy-Leblond equation, the Pauli equation is obtained which is in fact a two-component variant of the Schrödinger equation. Therefore, the Dirac equation can be considered as a relativistic generalization of the Schrödinger equation.

II.2. Hartree-Fock theory

The simplest choice for the wave function of an N-electron system that can be used to solve the Schrödinger or Dirac equation is given by a Slater determinant, i.e., an antisymmetrized and normalized product of N one-electron wave functions which accounts for the indistinguishability and the fermionic character of the electrons. In the case of the Dirac equation the Slater determinant is constructed from four-component spinors $\overline{\Psi}_i$

$$\overline{\Psi}_{i} = \begin{pmatrix} \Psi_{1} \\ \Psi_{2} \\ \Psi_{3} \\ \Psi_{4} \end{pmatrix} = \begin{pmatrix} \overline{\varphi} \\ \overline{\chi} \end{pmatrix}$$
(II.13)

while in the non-relativistic case the spin orbitals φ_i ,

$$\varphi_i = \phi_i \cdot s_i, \quad s_i = \alpha, \beta, \tag{II.14}$$

which are composed of a spatial orbital ϕ_i and the spin function s_i , are used.

The one-electron spinors or spin orbitals are optimized variationally using the orthonormality of the one-electron functions

$$\langle \overline{\Psi}_i \mid \overline{\Psi}_j \rangle = \delta_{ij} \tag{II.15}$$

as a constraint. Following this procedure, the canonical Dirac-Hartree-Fock (DHF) or Hartree-Fock (HF) equations (in the non-relativistic case)

$$\hat{\mathbf{f}}_{\mathrm{D}}' \overline{\mathbf{\Psi}}_i = \varepsilon_i \overline{\mathbf{\psi}_i}$$
 (II.16)

15

are obtained. These are effective one-electron equations with the Lagrange multiplier ε_i and the Fock operator $\hat{\mathbf{f}}'_{\mathrm{D}}$ which is given by

$$\hat{\mathbf{f}}_{\mathrm{D}}' = \hat{\mathbf{h}}_{\mathrm{D}}' + \sum_{j} (\hat{\mathbf{J}}_{\mathrm{D}j} - \hat{\mathbf{K}}_{\mathrm{D}j}).$$
(II.17)

In (II.17) the Coulomb operator $\hat{\mathbf{J}}_{Dj}$ and the exchange operator $\hat{\mathbf{K}}_{Dj}$ act in the following manner

$$\hat{\mathbf{J}}_{\mathrm{D}j}\overline{\mathbf{\Psi}}_{i}(\mathbf{r}_{1}) = \int \mathrm{d}^{3}\mathbf{r}_{2}\overline{\mathbf{\Psi}}_{j}^{\dagger}(\mathbf{r}_{2})\hat{g}_{12}\mathbf{I}_{(4)}\overline{\mathbf{\Psi}}_{i}(\mathbf{r}_{1})\overline{\mathbf{\Psi}}_{j}(\mathbf{r}_{2})$$
(II.18)

and

$$\hat{\mathbf{K}}_{\mathrm{D}j}\overline{\mathbf{\Psi}}_{i}(\mathbf{r}_{1}) = \int \mathrm{d}^{3}\mathbf{r}_{2}\overline{\mathbf{\Psi}}_{j}^{\dagger}(\mathbf{r}_{2})\hat{g}_{12}\mathbf{I}_{(4)}\overline{\mathbf{\Psi}}_{j}(\mathbf{r}_{1})\overline{\mathbf{\Psi}}_{i}(\mathbf{r}_{2}).$$
(II.19)

The HF energy is given as the expectation value

$$E_{\rm HF} = \sum_{i} \langle \overline{\Psi}_{i} \mid \hat{\mathbf{h}}_{\rm D}' \mid \overline{\Psi}_{i} \rangle + \frac{1}{2} \sum_{ij} \left(\langle \overline{\Psi}_{i} \overline{\Psi}_{j} \mid \hat{g}_{12} \mathbf{I}_{(4)} \mid \overline{\Psi}_{i} \overline{\Psi}_{j} \rangle - \langle \overline{\Psi}_{i} \overline{\Psi}_{j} \mid \hat{g}_{12} \mathbf{I}_{(4)} \mid \overline{\Psi}_{j} \overline{\Psi}_{i} \rangle \right).$$
(II.20)

In the non-relativistic case, the basic equations are the same except that the spinors are replaced by spin orbitals, the one-electron operator $\hat{\mathbf{h}}'_{\mathrm{D}}$ by its non-relativistic counterpart \hat{h} , and the general two-electron interaction term $\hat{g}_{12}\mathbf{I}_{(4)}$ by $1/r_{12}$.

Usually, the one-electron functions are expanded in a finite basis of Gaussian functions centered at the atomic positions as

$$\overline{\Psi}_{i} = \begin{pmatrix} \overline{\varphi} \\ \overline{\chi} \end{pmatrix} = \sum_{\mu=1}^{M_{\rm L}} c_{\mu i}^{\rm L} \begin{pmatrix} \omega_{\mu}^{\rm L} \\ 0 \end{pmatrix} + \sum_{\mu=1}^{M_{\rm S}} c_{\mu i}^{\rm S} \begin{pmatrix} 0 \\ \omega_{\mu}^{\rm S} \end{pmatrix}$$
(II.21)

with ω as basis functions for the different components, M as their number, and the coefficients c. To avoid a variational collapse, it is reasonable to restrict the choice for the small-component basis set using the so-called kinetic-balance condition⁸² (see also chapter IV.2.1)

$$\left\{\boldsymbol{\sigma}\hat{\mathbf{p}}\omega_{\mu}^{\mathrm{L}}\right\} \in \left\{\omega_{\mu}^{\mathrm{S}}\right\}.$$
 (II.22)

In the non-relativistic case the basis-set expansion is less problematic and given for the spatial orbitals by

$$\phi_i = \sum_{\mu=1}^M c_{\mu i} \omega_\mu. \tag{II.23}$$

Inserting the basis-set expansion into the working equations allows to significantly simplify the calculations as the evaluation of the resulting integrals is rather straightforward. However, the choice of an incomplete finite basis introduces an error which is usually referred to as basis-set error. Therefore, care has to be taken in order to make the chosen basis set large enough and to represent the one-electron functions in an adequate manner.

Due to the choice of the wave function as Slater determinant in HF theory the electronelectron interaction is described in a mean-field manner, i.e., one electron is only affected in its movement by the mean field created by all other electrons. In reality, however, the movement of one electron depends explicitly on the position of all others. This dependence is referred to as electron correlation. Accordingly, the exact energy of a system may be expressed as

$$E_{\text{exact}} = E_{\text{HF}} + E_{\text{corr}} \tag{II.24}$$

with the correlation energy E_{corr} . In the next section methods are discussed which account for the correlation energy.

II.3. Correlation methods

In the Dirac equation for many-electron systems a problem arises concerning the separation of electronic and positronic states. If, for example, a non-interacting two-particle system is given (see figure II.2) pure electronic or positronic states may be easily identified via their total energy. However, mixed states can appear as intruders into the energy region of the electronic states as indicated in figure II.2. This problem is usually referred to as continuum dissolution or the Brown-Ravenhall disease^{83,84} and can be avoided via a proper definition of the vacuum as will be discussed in the following within a secondquantization formulation.





Figure II.2.: Schematic representation of the Brown-Ravenhall disease: Mixed states can appear in the energetic region of electronic states.

In second quantization the Dirac Hamiltonian is given as

$$\hat{H}_{\rm D} = \sum_{pq} \underbrace{\langle \overline{\Psi}_p \mid \hat{\mathbf{h}}'_{\rm D} \mid \overline{\Psi}_q \rangle}_{h_{\rm Dpq}} \hat{a}_p^{\dagger} \hat{a}_q + \frac{1}{2} \sum_{pqrs} \underbrace{\langle \overline{\Psi}_p \overline{\Psi}_q \mid \hat{g}_{12} \mid \overline{\Psi}_r \overline{\Psi}_s \rangle}_{g_{\rm Dpqrs}} \hat{a}_p^{\dagger} \hat{a}_q^{\dagger} \hat{a}_s \hat{a}_r \tag{II.25}$$

with the particle creation operators \hat{a}_p^{\dagger} and the annihilation operators \hat{a}_p which fulfill the following anti-commutator relations

$$[\hat{a}_{p}^{\dagger}, \hat{a}_{q}^{\dagger}]_{+} = 0$$
 (II.26)

$$[\hat{a}_p, \hat{a}_q]_+ = 0$$
 (II.27)

$$[\hat{a}_p^{\dagger}, \hat{a}_q]_+ = \delta_{pq}. \tag{II.28}$$

Considering in the following only the one-electron terms

$$\hat{H}_{\mathrm{D}}^{0} = \sum_{pq} h_{\mathrm{D}pq} \hat{a}_{p}^{\dagger} \hat{a}_{q}, \qquad (\mathrm{II.29})$$

the sum which runs over all spinors, i.e., both electronic and positronic states, can be split up

$$\{\overline{\Psi}_p\} \to \{\overline{\Psi}_p, p = 1, \dots, m_e\}$$
 electronic states (II.30)

$$\{\Psi_a, a = 1, \dots, m_a\}$$
 positronic states (II.31)

leading to

$$\hat{H}_{D}^{0} = \underbrace{\sum_{pq}^{m_{e}} h_{Dpq} \hat{a}_{p}^{\dagger} \hat{a}_{q}}_{\hat{H}_{D}^{++}} + \underbrace{\sum_{ab}^{m_{p}} h_{Dab} \hat{a}_{a}^{\dagger} \hat{a}_{b}}_{\hat{H}_{D}^{--}} + \underbrace{\sum_{p}^{m_{e}} \sum_{a}^{m_{p}} h_{Dpa} \hat{a}_{p}^{\dagger} \hat{a}_{a}}_{\hat{H}_{D}^{+-}} + \underbrace{\sum_{a}^{m_{p}} \sum_{p}^{m_{e}} h_{Dap} \hat{a}_{a}^{\dagger} \hat{a}_{p}}_{\hat{H}_{D}^{-+}} + \underbrace{\sum_{a}^{m_{p}} \sum_{p}^{m_{p}} h_{Dap} \hat{a}_{a}^{\dagger} \hat{a}_{p}}_{\hat{H}_{D}^{-+}} + \underbrace{\sum_{a}^{m_{p}} \sum_{p}^{m_{p}} h_{Da} \hat{a}_{p}}_{\hat{H}_{D}^{-+}} + \underbrace{\sum_{a}^{m_{p}} \sum_{p}^{m_{p}} h_{D} \hat{a}_{p}}_{\hat{H}_{D}^{-+}} + \underbrace{\sum_{a}^{m_{p}} \sum_{p} \sum_{p}^{m_{p}} h_{D} \hat{b}_{p}}_{\hat{H}_{D}^{-+}} + \underbrace{$$

The Brown-Ravenhall disease cannot appear if all positronic states are occupied. However, such a description (Dirac picture)¹⁷ is not consistent with the usual definition of a vacuum state, as the latter is defined by the absence of particles. A consistent picture can yet be obtained by interchanging the role of creation and annihilation operators for the positronic states (particle-hole formalism¹⁷) as

$$\hat{b}_a^{\dagger} = \hat{a}_a, \quad \hat{b}_a = \hat{a}_a^{\dagger}. \tag{II.33}$$

In this way, originally occupied/unoccupied positronic states are considered unoccupied/occupied with respect to a new particle, the positron. The vacuum state of the Dirac picture is now characterized by the absence of electrons in the electronic states and positrons in the positronic states, respectively.

The Hamiltonian $\hat{H}_{\rm D}^0$ is then given as

$$\hat{H}_{D}^{0} = \underbrace{\sum_{pq}^{m_{e}} h_{Dpq} \hat{a}_{p}^{\dagger} \hat{a}_{q}}_{\hat{H}_{D}^{++}} + \underbrace{\sum_{ab}^{m_{p}} h_{Dab} \hat{b}_{a} \hat{b}_{b}^{\dagger}}_{\hat{H}_{D}^{--}} + \underbrace{\sum_{p}^{m_{e}} \sum_{a}^{m_{p}} h_{Dpa} \hat{a}_{p}^{\dagger} \hat{b}_{a}^{\dagger}}_{\hat{H}_{D}^{+-}} + \underbrace{\sum_{a}^{m_{p}} \sum_{p}^{m_{e}} h_{Dap} \hat{b}_{a} \hat{a}_{p}}_{\hat{H}_{D}^{-+}} \qquad (\text{II.34})$$

and it is easily seen that the vacuum expectation value of this operator

$$\langle 0 \mid \hat{H}_{\mathrm{D}}^{0} \mid 0 \rangle = \sum_{ab} h_{\mathrm{D}ab} \langle 0 \mid \hat{b}_{a} \hat{b}_{b}^{\dagger} \mid 0 \rangle = \sum_{ab} h_{\mathrm{D}ab} \delta_{ab} = \sum_{a} h_{\mathrm{D}aa}.$$
 (II.35)

is non-zero but given as the sum of the energies of all positronic states which yields $-\infty$. In order to avoid the negative infinite vacuum energy the normal-ordered Hamiltonian $H_{\rm D,N}^0$ is introduced as

$$H_{\mathrm{D,N}}^{0} = H_{\mathrm{D}}^{0} - \langle 0 \mid H_{\mathrm{D}}^{0} \mid 0 \rangle \tag{II.36}$$
$$m_{e} \qquad m_{p} \qquad m_{e} \qquad m_{p} \qquad m_{p} \qquad m_{e} \qquad m_{p} \qquad m_{p} \qquad m_{e} \qquad m_{p} \qquad m$$

$$=\sum_{pq}^{m_e} h_{\mathrm{D}pq} \hat{a}_p^{\dagger} \hat{a}_q - \sum_{ab}^{m_p} h_{\mathrm{D}ab} \hat{b}_a^{\dagger} \hat{b}_b + \sum_p^{m_e} \sum_{a}^{m_p} h_{\mathrm{D}pa} \hat{a}_p^{\dagger} \hat{b}_a^{\dagger} + \sum_a^{m_e} \sum_p^{m_e} h_{\mathrm{D}ap} \hat{b}_a \hat{a}_p \qquad (\text{II.37})$$

leading to a vacuum energy that is zero by constructionⁱ.

For application to quantum-chemical problems only electronic states are of interest. Therefore, in a further step, all terms with operators that create or annihilate positrons are dropped leading to the 'no-pair' approximation¹⁷ in which the (full) Hamiltonian is given as

$$\hat{H}_{D}^{\text{no-pair}} = \sum_{pq}^{m_{e}} h_{Dpq} \hat{a}_{p}^{\dagger} \hat{a}_{q} + \frac{1}{2} \sum_{pqrs}^{m_{e}} g_{Dpqrs} \hat{a}_{p}^{\dagger} \hat{a}_{q}^{\dagger} \hat{a}_{s} \hat{a}_{r} = \sum_{pq}^{m_{e}} h_{Dpq} \hat{a}_{p}^{\dagger} \hat{a}_{q} + \frac{1}{4} \sum_{pqrs}^{m_{e}} (g_{Dpqrs} - g_{Dpqsr}) \hat{a}_{p}^{\dagger} \hat{a}_{q}^{\dagger} \hat{a}_{s} \hat{a}_{r}.$$
(II.38)

This operator may be used in the correlation treatment which then is analogous to nonrelativistic theory. In practice one starts from a DHF calculation and drops the part of the matrices that corresponds to the negative-energy states in the subsequent correlation treatment.

Remaining differences to the non-relativistic treatment are, for example, that the matrix elements are complex, that the usual spin adaptation cannot be appliedⁱⁱ and that for the integral transformation more integrals need to be processed due to the small component basis.

$$\langle a \mid H_{\mathrm{D,N}}^0 \mid a \rangle = -h_{\mathrm{D}aa} > 0$$

ⁱA convenient feature of this Hamiltonian is that the positronic states now have a positive energy

which means that the electronic ground state may be obtained by using the variation principle. ⁱⁱNote that instead of spin adaptation time-reversal symmetry can be exploited.

II.3.1. Møller-Plesset perturbation theory

In perturbation theory, the Hamiltonian is partitioned in an unperturbed part $\hat{H}^{(0)}$ which can be solved exactly and a (small) perturbation part \hat{H}' , i.e.,

$$\hat{H}^{\text{exact}} = \hat{H}^{(0)} + \hat{H}'$$
 (II.39)

defining the perturbation part as the difference between the exact and the unperturbed Hamiltonian. In Møller-Plesset perturbation theory,⁷ the idea is that the HF potential already is a good approximation and is used as unperturbed problem. Starting from the no-pair Hamiltonian in (II.38) as \hat{H}^{exact} , the perturbed Hamiltonian \hat{H}' is given by

$$\hat{H}' = H_{\rm D}^{\rm no-pair} - \sum_{pq} \left(h_{{\rm D}pq} + \sum_{j} (g_{{\rm D}pjqj} - g_{{\rm D}pjjq}) \right) \hat{a}_p^{\dagger} \hat{a}_q \tag{II.40}$$

$$= \frac{1}{4} \sum_{pqrs} (g_{\text{D}pqrs} - g_{\text{D}pqsr}) \hat{a}_{p}^{\dagger} \hat{a}_{q}^{\dagger} \hat{a}_{s} \hat{a}_{r} - \sum_{pq} \sum_{j} (g_{\text{D}pjqj} - g_{\text{D}pjjq}) \hat{a}_{p}^{\dagger} \hat{a}_{q}.$$
(II.41)

The first and second-order energy expressions are then

$$E^{(1)} = \langle 0 \mid \hat{H}' \mid 0 \rangle \tag{II.42}$$

$$= \frac{1}{4} \sum_{pqrs} (g_{\text{D}pqrs} - g_{\text{D}pqsr}) \langle 0 \mid \hat{a}_{p}^{\dagger} \hat{a}_{q}^{\dagger} \hat{a}_{s} \hat{a}_{r} \mid 0 \rangle$$
$$= \sum \sum (a_{\text{D}} \mid \dots \mid a_{\text{D}} \mid \dots \mid a_{\text{D}} \mid \dots \mid a_{\text{D}} \mid 0) \langle 0 \mid \hat{a}^{\dagger} \hat{a} \mid 0 \rangle \qquad (\text{II} 43)$$

$$-\sum_{pq}\sum_{j}(g_{\mathrm{D}pjqj} - g_{\mathrm{D}pjjq})\langle 0 \mid \hat{a}_{p}^{\dagger}\hat{a}_{q} \mid 0\rangle \tag{11.43}$$

$$= -\frac{1}{2} \sum_{ij} (g_{\mathrm{D}ijij} - g_{\mathrm{D}ijji})$$
(II.44)

$$E^{(2)} = \sum_{\mu} \frac{|\langle \mu \mid \hat{H}' \mid 0 \rangle|^2}{\langle 0 \mid \hat{H}^{(0)} \mid 0 \rangle - \langle \mu \mid \hat{H}^{(0)} \mid \mu \rangle}$$
(II.45)

$$= \frac{1}{4} \sum_{ij} \sum_{ab} \frac{|(g_{\text{D}abij} - g_{\text{D}abji})|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}.$$
 (II.46)

Note that the correlation correction is given by the second-order energy, as the zerothand first-order correction terms only recover the HF energy.

II.3.2. Coupled-cluster theory

In CC theory, the wave function is generated using an exponential ansatz

$$\Psi_{\rm CC} = \exp(\hat{T})\Psi_{\rm HF} \tag{II.47}$$

with the reference wave function usually given by the HF determinant. The cluster operator \hat{T} is defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N$$
 (II.48)

$$=\sum_{n=1}^{N} \left(\frac{1}{n!}\right)^{2} \sum_{ij..ab} t_{ij..}^{ab..} \hat{a}_{a}^{\dagger} \hat{a}_{i} \hat{a}_{b}^{\dagger} \hat{a}_{j}$$
(II.49)

with T_1 for single excitations, \hat{T}_2 for double excitations, etc., and the amplitudes $t_{ij..}^{ab..}$ as the wave-function parameters that need to be determined. If the untruncated excitation range is used, the result is equal to the full configuration-interaction (FCI) method which provides the exact solution to the electron-correlation problem in the given basis set. However, usually the series needs to be truncated due to limited computational resources. The truncated CC methods are referred to as

$$\begin{split} \hat{T} &= \hat{T}_1 & \text{CC singles (CCS)} \\ \hat{T} &= \hat{T}_1 + \hat{T}_2 & \text{CC singles doubles (CCSD)}^{15} \\ \hat{T} &= \hat{T}_1 + \hat{T}_2 + \hat{T}_3 & \text{CC singles doubles triples (CCSDT)}^{85-87} \\ \hat{T} &= \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 & \text{CC singles doubles triples quadruples (CCSDTQ)}^{88,89} \\ &\vdots \\ \hat{T} &= \sum_n^N \hat{T}_n & \text{FCI.} \end{split}$$

The CC wave function is inserted into the Dirac or Schrödinger equation. Subtraction of the HF energy

$$(\underbrace{\hat{H} - E_{\rm HF}}_{\hat{H}_{\rm N}}) \exp(\hat{T}) \Psi_{\rm HF} = (\underbrace{E - E_{\rm HF}}_{E_{\rm CC}}) \exp(\hat{T}) \Psi_{\rm HF}, \qquad (\text{II.50})$$

multiplication from the left with $\exp(-\hat{T})$ as well as projection onto the reference determinant yields the CC energy

$$\langle \Psi_{\rm HF} \mid \exp(-\hat{T})\hat{H}_{\rm N}\exp(\hat{T}) \mid \Psi_{\rm HF} \rangle = E_{\rm CC}$$
 (II.51)

while projection onto excited determinants Φ_I leads to the CC equations

$$\langle \Phi_I \mid \exp(-\hat{T})\hat{H}_{\rm N} \exp(\hat{T}) \mid \Psi_{\rm HF} \rangle = 0 \tag{II.52}$$

which represent a system of non-linear equations.

At this point another often used CC scheme needs to be mentioned, the CCSD(T) method.^{16,90,91} In this approach, triple excitations are treated in a perturbative manner on top of a CCSD calculation. The advantage is that the cost scales only with M^7 (instead of M^8 for CCSDT), with M as the basis-set size, while a similar and sometimes even superior accuracy is provided compared to a full treatment of triple excitations.

In relativistic CC theory, the DHF wave function is used as reference determinant and the no-pair Hamiltonian $\hat{H}_{\rm D}^{\rm no-pair}$ is employed. Details can be found, for example, in Ref. 23.

III. Derivative Theory

Derivative theory plays a key role in the determination of molecular properties, i.e., those which are specific for a given electronic state. The property is then given as a response of the system to a perturbation. In this case, the energy depends on the corresponding perturbation parameter x with which the property is associated. If the perturbation is sufficiently weak, a Taylor expansion around the point x = 0, i.e.,

$$E(x) = E(x=0) + x \left(\frac{\mathrm{d}E}{\mathrm{d}x}\right)_{x=0} + x^2 \left(\frac{\mathrm{d}^2 E}{\mathrm{d}x^2}\right)_{x=0} + \dots, \qquad (\text{III.1})$$

is suitable and the desired property is obtained as the corresponding derivative.

The idea that a property may be defined as a response of the system to an applied perturbation is employed in this work to obtain relativistic corrections as energy derivatives using a suitable relativistic perturbation parameter.

III.1. Numerical versus analytical differentiation

In principle, the derivatives in (III.1) may be calculated either analytically or using numerical differentiation techniques. Both schemes have their advantages and disadvantages. When calculating first derivatives numerically, using, for example, a two-point formula

$$\left(\frac{\mathrm{d}E}{\mathrm{d}x}\right)_{x=0} = \frac{E(\Delta x) - E(-\Delta x)}{2\Delta x} \tag{III.2}$$

with a step size Δx , the obvious advantage is that only two energy calculations (determined in the presence of $\pm \Delta x$) are required. This is easily implemented, however, the accuracy of such schemes, especially for higher derivatives, is limited and it is often necessary to experiment with the step size to get reliable results. Furthermore, the computational cost may become very high. For example, if nuclear gradients are to be calculated, the computational cost is $2 \cdot 3N$ times higher than for an energy calculation itself, with N as the number of atoms.

On the other hand, if the derivative is to be calculated analytically, this requires a theoretical expression for the derivative and a more involved implementation (unlike to only

Unconstrained variation	Constrained variation Non-variation	
CI parameters	MO coefficients in HF	MO coefficients in CC, CI, MP t -amplitudes in CC and MP

 Table III.1.: Examples for different types of wave-function parameters

including a perturbation in an energy calculation). However, once this is accomplished, the calculation is more convenient and yields higher accuracy with often less computational cost. For first derivatives, for example, the cost is lower as the analytic expression is independent of the number of perturbations.

In this work, both techniques, i.e., numerical and analytical differentiation, as well as the mixed approach have been used to calculate relativistic corrections to energies and molecular properties.

III.2. Analytic derivatives

In order to calculate a first analytic derivative the energy needs to be differentiated with respect to the perturbation parameter x at the point x = 0, i.e.,

$$\left(\frac{\mathrm{d}E}{\mathrm{d}x}\right)_{x=0} = \left(\frac{\partial E}{\partial x}\right)_{x=0} + \left(\frac{\partial E}{\partial c}\right)_{x=0} \left(\frac{\partial c}{\partial x}\right)_{x=0}.$$
 (III.3)

In (III.3), c are the wave-function parameters which depend on the perturbation. Such parameters are, for example, the molecular-orbital (MO) coefficients, the configurationinteraction (CI) coefficients or the *t*-amplitudes in CC and MP theories as discussed in chapter II. In (III.3), the first term stems from the explicit dependence of E on the perturbation through the Hamiltonian and in some cases also the basis functions, whereas the second contribution accounts for the implicit dependence on x via the wave-function parameters c due to the chain rule.

For all parameters c that are determined in an unconstrained variation it follows that the partial derivative of the energy with respect to c vanishes and therefore only the first term in (III.3) needs to be evaluated. An example for this type of parameters is given by the CI coefficients (see table III.1).

There are two other types of wave-function parameters, i.e., those which are determined in a constrained variation and those which are obtained in a non-variational manner. For both types the above mentioned derivative is non-zero and, thus, the partial derivative of

III. Derivative Theory

the parameter with respect to the perturbation needs in principle to be calculated. This is possible, yet computationally not efficient.

An elegant solution to this issue is to enforce the stationarity of the energy expression with respect to all perturbation-dependent parameters c. This can be achieved using the method of Lagrange multipliers where side conditions are included in an energy functional. This is done in such a way that if those side conditions are fulfilled, the functional (the so-called Lagrangian) is equal to the energy itself.^{92,93}

For parameters that are determined by means of a constrained variation, the side conditions are given by the constraints of the variation. The side conditions may be written in a general form as

$$f(x, c(x)) = 0 \tag{III.4}$$

and are then used to construct the Lagrangian \tilde{E}

$$\tilde{E}(x,c(x),\lambda(x)) = E(x,c(x)) + \lambda(x)\underbrace{f(x,c(x))}_{=0}$$
(III.5)

with the so-called Lagrange multipliers $\lambda(x)$. The variation

$$\frac{\mathrm{d}\tilde{E}}{\mathrm{d}c} = 0 \tag{III.6}$$

then leads to the equations which determine the wave-function parameters for the given method. In HF theory, for example, the orthonormality condition of the orbitals is added as side condition to the Lagrangian and variation according to (III.6) leads to the HF equations. Solving these equations yields the MO coefficients as well as the Lagrange multipliers (which in the canonical HF case are given by the orbital energies ε_i). Furthermore, as the Lagrangian leads to the same energy as the energy expression itself, it is achieved that for its first derivative with respect to a perturbation x, analog to the unconstrained variation, only the term with the explicit dependence of \tilde{E} on x needs to be evaluated.

For non-variational procedures as in CC and MP theories, the Lagrangian approach can be employed to avoid the calculation of $\partial c/\partial x$ as well. Here, the side conditions f(x, c(x)) are given as the conditional equations that determine the wave-function parameters. They are included directly in the Lagrangian, again in such a way that if they are fulfilled, the Lagrangian is equal to the energy (see equation (III.5)). After its construction, the

Method	Parameter	Side condition	$L.m.^a$	$c.v.^b$	$n.v.^c$
HF	MO coefficients	orthonormality	ε_{ji}	\checkmark	
$\mathrm{MP}\ \&\ \mathrm{CC}$	MO coefficients	orthonormality	I_{pq}		\checkmark
	MO coefficients	Brillouin condition	Z_{ai}		\checkmark
	t-amplitudes	amplitude equations	λ^{ij}_{ab}		\checkmark

Table III.2.: Side conditions for wave-function parameters in HF, CC, and MP theories

^a Lagrange multiplier

 b constrained variation

 c non-variational

Lagrangian is then made stationary with respect to c and λ , i.e.,

$$\frac{\mathrm{d}\tilde{E}}{\mathrm{d}c} = 0 \tag{III.7}$$

$$\frac{\mathrm{d}E}{\mathrm{d}\lambda} = 0. \tag{III.8}$$

Equation (III.7) leads to perturbation-independent conditional equations for the Lagrange multipliers λ which need to be solved. Equation (III.8) leads back to the side conditions that are determined anyways to solve for the non-variational parameters.

For correlated methods such as MP2 and CC, the side conditions that are included in the Lagrangian are the orthonormality condition of the molecular orbitals, the Brillouin condition, and the amplitude equations. The wave-function parameters, both non-variational, are given by the MO coefficients as well as the amplitudes t (see table III.2 for an overview).

Using the method of Lagrange multipliers, the first derivative takes the form

$$\left(\frac{\mathrm{d}\tilde{E}}{\mathrm{d}x}\right)_{x=0} = \left(\frac{\partial E}{\partial x}\right)_{x=0} + \lambda \left(\frac{\partial f}{\partial x}\right)_{x=0} \tag{III.9}$$

for methods where the wave-function parameters are evaluated via a constrained variation or in a non-variational manner. The advantage is that calculation of $\partial c/\partial x$ is avoided but unlike a direct evaluation as in (III.3) for every non-variational parameter ca perturbation-independent equation needs to be solved to determine the corresponding Lagrange multiplier λ .

For higher derivatives (III.5) is differentiated with respect to all involved perturbations.

It can be shown that knowledge of the *n*th derivative of the parameters with respect to the perturbation suffices for the (2n + 1)th derivative of the energy. A similar rule exists for the Lagrange multipliers which states that the knowledge of the *n*th derivative suffices to calculate the (2n + 2)th energy derivative. These rules are commonly referred to as (2n + 1) and (2n + 2) rules.⁹²⁻⁹⁴

Therefore, for a second derivative of the energy with respect to the perturbations x and y only the first derivatives of the parameters are needed while the sum of all terms involving derivatives of the Lagrange mutipliers vanishes and the resulting functional derivative is given as

$$\left(\frac{\mathrm{d}^{2}\tilde{E}}{\mathrm{d}x\mathrm{d}y}\right)_{x,y=0} = \left(\frac{\partial^{2}E}{\partial x\partial y}\right)_{x,y=0} + \left(\frac{\partial^{2}E}{\partial x\partial c}\right)_{x=0} \left(\frac{\partial c}{\partial y}\right)_{y=0} + \left(\frac{\partial^{2}E}{\partial y\partial c}\right)_{y=0} \left(\frac{\partial c}{\partial x}\right)_{x=0} + \left(\frac{\partial^{2}E}{\partial c\partial c}\right) \left(\frac{\partial c}{\partial x}\right)_{x=0} \left(\frac{\partial c}{\partial y}\right)_{y=0} + \lambda \left(\frac{\partial^{2}f}{\partial x\partial y}\right)_{x,y=0} + \lambda \left(\frac{\partial^{2}f}{\partial x\partial c}\right)_{x=0} \left(\frac{\partial c}{\partial y}\right)_{y=0} + \lambda \left(\frac{\partial^{2}f}{\partial y\partial c}\right)_{y=0} \left(\frac{\partial c}{\partial x}\right)_{x=0} + \lambda \left(\frac{\partial^{2}f}{\partial c^{2}}\right) \left(\frac{\partial c}{\partial x}\right)_{x=0} \left(\frac{\partial c}{\partial y}\right)_{y=0}.$$
(III.10)

This means that for the second derivative of the energy in HF theory the so-called coupledperturbed HF (CPHF) equations^{79,95} need to be solved for the perturbation parameter xas well as y. For MP2 or CC additionally the perturbed amplitude equations have to be determined.

In some cases it turns out to be beneficial to take the second derivative starting from (III.9). If the derivative is evaluated in this manner, the (2n + 1) and (2n + 2) rules do not hold any longer for the second differentiation. Accordingly, derivatives of the Lagrange multipliers with respect to the second perturbation y also appear in the resulting expression

$$\begin{pmatrix} \frac{\mathrm{d}^{2}\tilde{E}}{\mathrm{d}x\mathrm{d}y} \end{pmatrix}_{x,y=0} = \left(\frac{\partial^{2}E}{\partial x\partial y}\right)_{x,y=0} + \left(\frac{\partial^{2}E}{\partial x\partial c}\right)_{x=0} \left(\frac{\partial c}{\partial y}\right)_{y=0} + \lambda \left(\frac{\partial^{2}f}{\partial x\partial y}\right)_{x,y=0} + \lambda \left(\frac{\partial^{2}f}{\partial x\partial c}\right)_{x=0} \left(\frac{\partial c}{\partial y}\right)_{y=0} + \left(\frac{\partial \lambda}{\partial y}\right)_{y=0} \left(\frac{\partial f}{\partial x}\right)_{x=0}.$$
(III.11)

Even though in this equation the derivative of the Lagrange multipliers is needed, the number of equations to be solved may be less than in (III.10). This is due to the fact that in (III.11) the derivatives of the wave-function parameters and Lagrange multipliers are needed only for the second perturbation y.⁹⁶

In this work, this variant of taking the second derivative (which is often referred to as asymmetric expression) has been used to calculate higher-order relativistic corrections.

III.3. Numerical differentiation

As already shown in (III.2) a simple possibility to calculate energy derivatives numerically consists in using a two-point formula. The equation given there approximates the derivative linearly using two displacements and is derived from

$$f(x) = a + bx$$

$$f(-x) = a - bx$$

$$\rightarrow b = \frac{f(x) - f(-x)}{2x}.$$
(III.12)

If higher accuracy is needed, the derivative may be calculated using more displacements. In this work four-, six-, and eight-point formulas have been used which correspond to a third-, fifth-, and seventh-grade polynomial. The four-point formula may be derived from

$$f(x) = a + bx + cx^{2} + dx^{3}$$

$$f(-x) = a - bx + cx^{2} - dx^{3}$$

$$f(2x) = a + 2bx + 4cx^{2} + 8dx^{3}$$

$$f(-2x) = a - 2bx + 4cx^{2} - 8dx^{3}$$

$$\rightarrow b = \frac{8[f(x) - f(-x)] - [f(2x) - f(-2x)]}{12x}$$
(III.13)

after elimination of c and d. For the six-point formula it follows

$$f(x) = a + bx + cx^{2} + dx^{3} + ex^{4} + fx^{5}$$

$$f(-x) = a - bx + cx^{2} - dx^{3} + ex^{4} - fx^{5}$$

$$f(2x) = a + 2bx + 4cx^{2} + 8dx^{3} + 16ex^{4} + 32fx^{5}$$

$$f(-2x) = a - 2bx + 4cx^{2} - 8dx^{3} + 16ex^{4} - 32fx^{5}$$

$$f(3x) = a + 3bx + 9cx^{2} + 27dx^{3} + 81ex^{4} + 243fx^{5}$$

$$f(-3x) = a - 3bx + 9cx^{2} - 27dx^{3} + 81ex^{4} - 243fx^{5}$$

$$\rightarrow b = \frac{45[f(x) - f(-x)] - 9[f(2x) - f(-2x)] + [f(3x) - f(-3x)]}{60x}.$$
(III.14)

More generally, with n points a polynomial of the order (n-1) can be fitted. This corresponds to a Taylor expansion and the coefficients correspond to the derivative of the same order

$$f(k) = \underbrace{f(k_0)}_{a} + \underbrace{\left(\frac{\partial f(k)}{\partial k}\right)_{k=k_0}}_{b} \underbrace{(k-k_0)}_{x} + \underbrace{\frac{1}{2}\left(\frac{\partial^2 f(k)}{\partial k^2}\right)_{k=k_0}}_{c} \underbrace{(k-k_0)^2}_{x^2} + \dots$$
(III.15)

To determine the coefficients, a linear system of equations is needed:

$$\begin{pmatrix} 1 & x & x^2 & x^3 & \dots \\ 1 & 2x & (2x)^2 & (2x)^3 & \dots \\ 1 & 3x & (3x)^2 & (3x)^3 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ \vdots \end{pmatrix} = \begin{pmatrix} f(x) \\ f(2x) \\ f(3x) \\ \vdots \end{pmatrix}$$
(III.16)

$$\mathbf{Ac} = \mathbf{f}$$
 (III.17)

which is solved by inverting the matrix **A** as

$$\mathbf{c} = \mathbf{A}^{-1}\mathbf{f}.\tag{III.18}$$

Naturally, if the derivatives are calculated using higher polynomials as approximation, the accuracy increases. In return, however, the computational cost rises as well because more energy calculations using different perturbation strengths have to be carried out. Yet, one has to pay attention as using a many-point formula will not necessarily give a reliable result. First of all, the step size x of the displacements may be too large to approximate

the derivative. In principle, one would choose very small step sizes but this can lead to numerical difficulties likewise. Furthermore, if the numerical values of the derivatives are small, it may be the case that the numerical accuracy of the underlying energy calculation is not sufficient. This may be estimated using the two-point formula. If the energy is, for example, accurate up to a value of $1 \cdot 10^{-10}$ and the step size is $5 \cdot 10^{-6}$ then using the two-point formula

$$\frac{2 \cdot 1 \cdot 10^{-6}}{2 \cdot 5 \cdot 10^{-6}} = 2 \cdot 10^{-5}$$
(III.19)

it is seen that the resulting derivative cannot be more accurate than to the fourth decimal place.

IV. Direct Perturbation Theory

In Direct Perturbation Theory (DPT), the goal is to account for relativistic effects in a perturbative manner without the high computational cost of a four-component treatment. Therefore, a relativistic perturbation parameter $\lambda_{\rm rel} = c^{-2}$ with c as the speed of light is introduced. In this work, the fourth-order DPT corrections (second order in $\lambda_{\rm rel}$) at the HF level as well as at correlated levels of theory, i.e., CC and MP2, are evaluated in terms of energy derivatives starting from relativistic and non-relativistic Lagrangians. Furthermore, some aspects concerning the derivation of DPT6 in the framework of HF theory starting from a non-relativistic Lagrangian are discussed. Finally, DPT4 corrections for electrical properties as well as further routes on the calculation of relativistic corrections are examined.

IV.1. DPT expansion

Starting from the one-electron Dirac equation as given in (II.6), it is found that for electronic solutions $\overline{\chi}$ is smaller than $\overline{\varphi}$ by roughly a factor of c. For a perturbative expansion both components should be of the same order of magnitude and accordingly a new metric is introduced as⁶³

$$\chi = c\overline{\chi}, \quad \varphi = \overline{\varphi}. \tag{IV.1}$$

Inserting (IV.1) into the one-electron Dirac equation (see equation (II.6)) and dividing the lower part of (II.6) by c, the modified Dirac equation is obtained

$$\begin{pmatrix} V & \boldsymbol{\sigma}\hat{\mathbf{p}} \\ \boldsymbol{\sigma}\hat{\mathbf{p}} & \frac{V}{c^2} - 2m \end{pmatrix} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = E \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{c^2} \end{pmatrix} \begin{pmatrix} \varphi \\ \chi \end{pmatrix}, \quad (IV.2)$$

$$\hat{\mathbf{h}}_{\mathrm{D}} \boldsymbol{\Psi} = E \; \hat{\mathbf{S}}_{\mathrm{D}} \boldsymbol{\Psi}. \tag{IV.3}$$

When (IV.3) is decomposed into

$$\left(\hat{\mathbf{h}}_{\mathrm{D}}^{(0)} + \lambda_{\mathrm{rel}}\hat{\mathbf{h}}_{\mathrm{D}}^{(2)}\right)\boldsymbol{\Psi} = E\left(\hat{\mathbf{S}}_{\mathrm{D}}^{(0)} + \lambda_{\mathrm{rel}}\hat{\mathbf{S}}_{\mathrm{D}}^{(2)}\right)\boldsymbol{\Psi},\tag{IV.4}$$

32

DPT can be obtained in a straightforward manner using a standard perturbative expansion. Relativistic effects are here introduced by terms containing the index 2 with $\lambda_{\rm rel} = c^{-2}$ as perturbation parameter, while all non-relativistic (nrl) terms appear with index 0 and define the unperturbed problem in form of the Lévy-Leblond equation.⁷² The operators and the wave function in (IV.4) are given by

$$\hat{\mathbf{h}}_{\mathrm{D}}^{(0)} = \begin{pmatrix} V & \boldsymbol{\sigma}\hat{\mathbf{p}} \\ \boldsymbol{\sigma}\hat{\mathbf{p}} & -2m \end{pmatrix}, \quad \hat{\mathbf{h}}_{\mathrm{D}}^{(2)} = \begin{pmatrix} 0 & 0 \\ 0 & V \end{pmatrix}, \quad \hat{\mathbf{S}}_{\mathrm{D}}^{(0)} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \hat{\mathbf{S}}_{\mathrm{D}}^{(2)} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \quad (\mathrm{IV.5})$$

$$\Psi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix}. \tag{IV.6}$$

After expanding both wave function and energy in terms of $\lambda_{\rm rel}$,

$$\Psi = \Psi^{(0)} + \lambda_{\rm rel} \Psi^{(2)} + \lambda_{\rm rel}^2 \Psi^{(4)} + \dots = \begin{pmatrix} \varphi^{(0)} + \lambda_{\rm rel} \varphi^{(2)} + \lambda_{\rm rel}^2 \varphi^{(4)} + \dots \\ \chi^{(0)} + \lambda_{\rm rel} \chi^{(2)} + \lambda_{\rm rel}^2 \chi^{(4)} + \dots \end{pmatrix}$$
(IV.7)

$$E = E^{(0)} + \lambda_{\rm rel} E^{(2)} + \lambda_{\rm rel}^2 E^{(4)} + \dots$$

= $E_{\rm nrl} + \Delta E_{\rm DPT2} + \Delta E_{\rm DPT4} + \dots,$ (IV.8)

thereby exploiting the unitary normalization condition 63

$$\langle \boldsymbol{\Psi} \mid \hat{\mathbf{S}}_{\mathrm{D}} \mid \boldsymbol{\Psi} \rangle = 1,$$
 (IV.9)

the DPT energy corrections are obtained 63 as

$$E^{(2)} = \langle \chi^{(0)} \mid V \mid \chi^{(0)} \rangle - E^{(0)} \langle \chi^{(0)} \mid \chi^{(0)} \rangle$$
(IV.10)

$$E^{(4)} = \operatorname{Re}\langle\chi^{(2)} \mid V \mid \chi^{(0)}\rangle - E^{(0)}\operatorname{Re}\langle\chi^{(2)} \mid \chi^{(0)}\rangle - \frac{1}{2}E^{(2)}\langle\chi^{(0)} \mid \chi^{(0)}\rangle.$$
(IV.11)

Alternatively, these corrections can be expressed in terms of energy derivatives, as shown in chapter III.2, using a Taylor expansion

$$E = E_0 + \lambda_{\rm rel} \left(\frac{dE}{d\lambda_{\rm rel}}\right)_{\lambda_{\rm rel}=0} + \frac{1}{2}\lambda_{\rm rel}^2 \left(\frac{d^2E}{d\lambda_{\rm rel}^2}\right)_{\lambda_{\rm rel}=0} + \dots$$
$$= E^{(0)} + \lambda_{\rm rel}E^{(2)} + \lambda_{\rm rel}^2E^{(4)} + \dots$$
(IV.12)

Along this route, it is more convenient to use a Lagrangian⁹²⁻⁹⁴ (see chapter III.2) for the differentiation instead of the energy since it allows to include all constraints straight from

the beginning. In the present case, the Lagrangian is given as

$$\tilde{E} = \langle \boldsymbol{\Psi} \mid \hat{\mathbf{h}}_{\mathrm{D}} \mid \boldsymbol{\Psi} \rangle - \varepsilon \left[\langle \boldsymbol{\Psi} \mid \hat{\mathbf{S}}_{\mathrm{D}} \mid \boldsymbol{\Psi} \rangle - 1 \right]$$
(IV.13)

with the Lagrange multiplier ε accounting for the normalization as side condition. To obtain the DPT2 energy correction, the Lagrangian is differentiated with respect to $\lambda_{\rm rel}$ thereby exploiting Wigner's (2n + 1) and (2n + 2) rules^{92–94}

$$E^{(2)} = \left(\frac{\partial \tilde{E}}{\partial \lambda_{\rm rel}}\right)_{\lambda_{\rm rel}=0}$$
(IV.14)

$$= \left\{ \langle \boldsymbol{\Psi} \mid \frac{\partial \hat{\mathbf{h}}_{\mathrm{D}}}{\partial \lambda_{\mathrm{rel}}} \mid \boldsymbol{\Psi} \rangle - \varepsilon \langle \boldsymbol{\Psi} \mid \frac{\partial \hat{\mathbf{S}}_{\mathrm{D}}}{\partial \lambda_{\mathrm{rel}}} \mid \boldsymbol{\Psi} \rangle \right\}_{\lambda_{\mathrm{rel}}=0}.$$
 (IV.15)

For the next higher order (DPT4), the Lagrangian is differentiated a second time with respect to λ_{rel} , leading to the asymmetric variant for the second derivative as discussed in chapter III.2

$$E^{(4)} = \frac{1}{2} \left(\frac{\partial^2 \tilde{E}}{\partial \lambda_{\rm rel}^2} \right)_{\lambda_{\rm rel}=0}$$
(IV.16)
$$= \left\{ \operatorname{Re} \left\langle \frac{\partial \Psi}{\partial \lambda_{\rm rel}} \middle| \frac{\partial \hat{\mathbf{h}}_{\rm D}}{\partial \lambda_{\rm rel}} \middle| \Psi \right\rangle - \varepsilon \operatorname{Re} \left\langle \frac{\partial \Psi}{\partial \lambda_{\rm rel}} \middle| \frac{\partial \hat{\mathbf{S}}_{\rm D}}{\partial \lambda_{\rm rel}} \middle| \Psi \right\rangle - \frac{1}{2} \frac{\partial \varepsilon}{\partial \lambda_{\rm rel}} \left\langle \Psi \middle| \frac{\partial \hat{\mathbf{S}}_{\rm D}}{\partial \lambda_{\rm rel}} \middle| \Psi \right\rangle \right\}_{\lambda_{\rm rel}=0}.$$
(IV.17)

The unperturbed and perturbed Lagrange multipliers $\varepsilon^{(0)}$ and $\varepsilon^{(2)}$ turn out to be given as the zeroth- and second-order energies as defined in (IV.8). Inserting the operators from (IV.5) and taking their derivatives yields the same corrections as in (IV.10) and (IV.11).

IV.2. DPT corrections at the Hartree-Fock level

For the many-electron case treated using HF theory, the occupied spinors

$$\Psi_i = \begin{pmatrix} \varphi_i \\ \chi_i \end{pmatrix} \tag{IV.18}$$

are labeled by indices i, j, k, l, \ldots and the wave function is given by a Slater determinant of four-component spinors $\Psi_i, i = 1, \ldots, N$. The Lagrangian then takes the form

$$\tilde{E} = \sum_{i} \langle \Psi_{i} \mid \hat{\mathbf{h}}_{\mathrm{D}} \mid \Psi_{i} \rangle + \frac{1}{2} \sum_{ij} \left(\langle \Psi_{i} \Psi_{j} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{i} \Psi_{j} \rangle - \langle \Psi_{i} \Psi_{j} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{j} \Psi_{i} \rangle \right) - \sum_{ij} \varepsilon_{ji} \left(\langle \Psi_{i} \mid \hat{\mathbf{S}}_{\mathrm{D}} \mid \Psi_{j} \rangle - \delta_{ij} \right)$$
(IV.19)

with $\hat{\mathbf{h}}_D$ and $\hat{\mathbf{S}}_D$ given in (IV.2) and the two-electron interaction operator $\hat{\mathbf{g}}_D$ defined by

$$\hat{\mathbf{g}}_{\mathrm{D}} = \begin{pmatrix} r_{12}^{-1} & 0 & 0 & 0\\ 0 & \lambda_{\mathrm{rel}} r_{12}^{-1} & 0 & 0\\ 0 & 0 & \lambda_{\mathrm{rel}} r_{12}^{-1} & 0\\ 0 & 0 & 0 & \lambda_{\mathrm{rel}}^2 r_{12}^{-1} \end{pmatrix}.$$
 (IV.20)

The Lagrange multipliers ε_{ji} turn out to be given as

$$\varepsilon_{ji} = \langle \Psi_j \mid \hat{\mathbf{f}}_{\mathrm{D}} \mid \Psi_i \rangle, \quad \text{with } \hat{\mathbf{f}}_{\mathrm{D}} = \hat{\mathbf{h}}_{\mathrm{D}} + \sum_k \left(\hat{\mathbf{J}}_{\mathrm{D}k} - \hat{\mathbf{K}}_{\mathrm{D}k} \right)$$
(IV.21)

$$= \langle \Psi_j \mid \hat{\mathbf{h}}_{\mathrm{D}} \mid \Psi_i \rangle + \sum_k \left(\langle \Psi_j \Psi_k \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_i \Psi_k \rangle - \langle \Psi_j \Psi_k \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_k \Psi_i \rangle \right).$$
(IV.22)

To obtain the DPT4 energy correction, the Lagrangian is first differentiated with respect to λ_{rel} thereby exploiting Wigner's rules

$$E^{(2)} = \left(\frac{\partial \tilde{E}}{\partial \lambda_{\rm rel}}\right)_{\lambda_{\rm rel}=0}$$
(IV.23)
$$= \left\{ \sum_{i} \langle \boldsymbol{\Psi}_{i}^{(0)} \mid \frac{\partial \hat{\mathbf{h}}_{\rm D}}{\partial \lambda_{\rm rel}} \mid \boldsymbol{\Psi}_{i}^{(0)} \rangle + \frac{1}{2} \sum_{ij} \left(\langle \boldsymbol{\Psi}_{i}^{(0)} \boldsymbol{\Psi}_{j}^{(0)} \mid \frac{\partial \hat{\mathbf{g}}_{\rm D}}{\partial \lambda_{\rm rel}} \mid \boldsymbol{\Psi}_{i}^{(0)} \boldsymbol{\Psi}_{j}^{(0)} \rangle - \langle \boldsymbol{\Psi}_{i}^{(0)} \boldsymbol{\Psi}_{j}^{(0)} \mid \frac{\partial \hat{\mathbf{g}}_{\rm D}}{\partial \lambda_{\rm rel}} \mid \boldsymbol{\Psi}_{j}^{(0)} \boldsymbol{\Psi}_{i}^{(0)} \rangle \right) - \sum_{ij} \varepsilon_{ji}^{(0)} \langle \boldsymbol{\Psi}_{i}^{(0)} \mid \frac{\partial \hat{\mathbf{S}}_{\rm D}}{\partial \lambda_{\rm rel}} \mid \boldsymbol{\Psi}_{j}^{(0)} \rangle \right\}_{\lambda_{\rm rel}=0}$$
(IV.24)

and then differentiated a second time with respect to $\lambda_{\rm rel},$ leading to

$$E^{(4)} = \frac{1}{2} \left(\frac{\partial^2 \tilde{E}}{\partial \lambda_{\rm rel}^2} \right)_{\lambda_{\rm rel}=0}$$
(IV.25)
$$= \left\{ \sum_i \operatorname{Re} \langle \boldsymbol{\Psi}_i^{(2)} \mid \frac{\partial \hat{\mathbf{h}}_{\rm D}}{\partial \lambda_{\rm rel}} \mid \boldsymbol{\Psi}_i^{(0)} \rangle + \sum_{ij} \operatorname{Re} \left(\langle \boldsymbol{\Psi}_i^{(2)} \boldsymbol{\Psi}_j^{(0)} \mid \frac{\partial \hat{\mathbf{g}}_{\rm D}}{\partial \lambda_{\rm rel}} \mid \boldsymbol{\Psi}_i^{(0)} \boldsymbol{\Psi}_j^{(0)} \rangle - \langle \boldsymbol{\Psi}_i^{(2)} \boldsymbol{\Psi}_j^{(0)} \mid \frac{\partial \hat{\mathbf{g}}_{\rm D}}{\partial \lambda_{\rm rel}} \mid \boldsymbol{\Psi}_j^{(0)} \boldsymbol{\Psi}_j^{(0)} \rangle \right) \right. \\ \left. + \frac{1}{4} \sum_{ij} \left(\langle \boldsymbol{\Psi}_i^{(0)} \boldsymbol{\Psi}_j^{(0)} \mid \frac{\partial^2 \hat{\mathbf{g}}_{\rm D}}{\partial \lambda_{\rm rel}^2} \mid \boldsymbol{\Psi}_i^{(0)} \boldsymbol{\Psi}_j^{(0)} \rangle - \langle \boldsymbol{\Psi}_i^{(0)} \boldsymbol{\Psi}_j^{(0)} \mid \frac{\partial^2 \hat{\mathbf{g}}_{\rm D}}{\partial \lambda_{\rm rel}^2} \mid \boldsymbol{\Psi}_j^{(0)} \boldsymbol{\Psi}_j^{(0)} \rangle \right) \\ \left. - \frac{1}{2} \sum_{ij} \varepsilon_{ji}^{(2)} \langle \boldsymbol{\Psi}_i^{(0)} \mid \frac{\partial \hat{\mathbf{S}}_{\rm D}}{\partial \lambda_{\rm rel}} \mid \boldsymbol{\Psi}_j^{(0)} \rangle \\ \left. - \sum_{ij} \operatorname{Re} \left(\varepsilon_{ji}^{(0)} \langle \boldsymbol{\Psi}_i^{(2)} \mid \frac{\partial \hat{\mathbf{S}}_{\rm D}}{\partial \lambda_{\rm rel}} \mid \boldsymbol{\Psi}_j^{(0)} \rangle \right) \right\}_{\lambda_{\rm rel}=0}.$$
(IV.26)

Inserting the operators from (IV.5) and (IV.20) and taking their derivatives yields

$$E^{(2)} = \sum_{i} \langle \chi_{i}^{(0)} | V | \chi_{i}^{(0)} \rangle + \sum_{ij} \left(\langle \varphi_{i}^{(0)} \chi_{j}^{(0)} || \varphi_{i}^{(0)} \chi_{j}^{(0)} \rangle + \langle \chi_{i}^{(0)} \varphi_{j}^{(0)} || \chi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \right) - \sum_{i} \varepsilon_{i}^{(0)} \langle \chi_{i}^{(0)} | \chi_{i}^{(0)} \rangle$$
(IV.27)

$$E^{(4)} = \sum_{i} \operatorname{Re} \langle \chi_{i}^{(2)} | V | \chi_{i}^{(0)} \rangle$$

+
$$\sum_{ij} \operatorname{Re} \left(\langle \varphi_{i}^{(2)} \chi_{j}^{(0)} || \varphi_{i}^{(0)} \chi_{j}^{(0)} \rangle + \langle \chi_{i}^{(2)} \varphi_{j}^{(0)} || \chi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \right)$$

+
$$\frac{1}{2} \sum_{ij} \langle \chi_{i}^{(0)} \chi_{j}^{(0)} || \chi_{i}^{(0)} \chi_{j}^{(0)} \rangle$$

-
$$\frac{1}{2} \sum_{ij} \varepsilon_{ji}^{(2)} \langle \chi_{i}^{(0)} | \chi_{j}^{(0)} \rangle$$

-
$$\sum_{i} \operatorname{Re} \left(\varepsilon_{i}^{(0)} \langle \chi_{i}^{(2)} | \chi_{i}^{(0)} \rangle \right), \qquad (IV.28)$$
where it is exploited in the last term that the zeroth-order ε matrix is diagonal in the canonical HF case. Note that the antisymmetrized integrals in (IV.28) are given as

$$\langle \chi_i \varphi_j \mid\mid \chi_i \varphi_j \rangle = \langle \chi_i \varphi_j \mid \chi_i \varphi_j \rangle - \langle \chi_i \varphi_j \mid \chi_j \varphi_i \rangle.$$
 (IV.29)

IV.2.1. Expansion of the perturbed wave function

In (IV.28), only the unperturbed large components $\varphi_i^{(0)}$ are so far known and are given via the usual non-relativistic HF spin orbitals. Therefore, it is necessary to determine in the following the unperturbed small component $\chi_i^{(0)}$ as well as the perturbed components $\varphi_i^{(2)}$ and $\chi_i^{(2)}$. This is achieved by expanding the Dirac-Hartree-Fock (DHF) equations formulated within the modified metric⁶³ in powers of $\lambda_{\rm rel}$ (see Appendix IX.1 for details). The zeroth-order equation leads to

$$\chi_p^{(0)} = \frac{1}{2m} \boldsymbol{\sigma} \hat{\mathbf{p}} \,\varphi_p^{(0)},\tag{IV.30}$$

which is equivalent to the result obtained from the Lévy-Leblond equation in the oneelectron case.⁶³ Using (IV.30), the DPT2 energy may be written as

$$E^{(2)} = \sum_{i} h_{ii}^{\lambda_{\rm rel}} - \sum_{i} \varepsilon_{i}^{(0)} S_{ii}^{\lambda_{\rm rel}} + \sum_{ij} \left(\langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \mid \hat{g}_{1}^{\lambda_{\rm rel}} + \hat{g}_{2}^{\lambda_{\rm rel}} \mid \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle - \langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \mid \hat{g}_{1}^{\lambda_{\rm rel}} + \hat{g}_{2}^{\lambda_{\rm rel}} \mid \varphi_{j}^{(0)} \varphi_{i}^{(0)} \rangle \right).$$
(IV.31)

In the above equation, the integrals and operators are given by

$$S_{pq}^{\lambda_{\rm rel}} = \langle \varphi_p^{(0)} \mid \frac{1}{4m^2} \hat{\mathbf{p}}^2 \mid \varphi_q^{(0)} \rangle, \qquad (\text{IV.32})$$

$$h_{pq}^{\lambda_{\rm rel}} = \langle \varphi_p^{(0)} \mid \frac{1}{4m^2} \boldsymbol{\sigma} \hat{\mathbf{p}} V \boldsymbol{\sigma} \hat{\mathbf{p}} \mid \varphi_q^{(0)} \rangle, \qquad (\text{IV.33})$$

$$\hat{g}_{n}^{\lambda_{\text{rel}}} = \frac{1}{4m^{2}} \boldsymbol{\sigma}_{n} \hat{\mathbf{p}}_{n} \frac{1}{r_{12}} \boldsymbol{\sigma}_{n} \hat{\mathbf{p}}_{n}, \quad n = 1 \text{ or } 2.$$
(IV.34)

The perturbed large component $\varphi_i^{(2)}$ is expanded in terms of the unperturbed functions

$$\varphi_i^{(2)} = \sum_p U_{pi}^{\lambda_{\rm rel}} \varphi_p^{(0)} \tag{IV.35}$$

with the generic indices p, q, r, s, \ldots denoting occupied and virtual orbitals. The coefficients $U_{pi}^{\lambda_{\text{rel}}}$ are obtained by solving the Coupled-Perturbed Hartree-Fock (CPHF) equa-

tions^{79,95,97,98} for the relativistic perturbation $\lambda_{\rm rel}$ (see Appendix IX.2 for details).

The perturbed small component $\chi_i^{(2)}$ may be determined via the second-order terms of the DHF equations

$$\chi_i^{(2)} = \frac{1}{2m} \left\{ \boldsymbol{\sigma} \hat{\mathbf{p}} \varphi_i^{(2)} + \left(V - \varepsilon_i^{(0)} + \sum_k \left[\hat{J}_k^{(0)} - \hat{K}_k^{(0)} \right] \right) \chi_i^{(0)} \right\},$$
(IV.36)

with

$$\langle \chi_j^{(0)} \mid \left[\hat{J}_k^{(0)} - \hat{K}_k^{(0)} \right] \mid \chi_i^{(0)} \rangle = \langle \chi_j^{(0)} \varphi_k^{(0)} \mid \chi_i^{(0)} \varphi_k^{(0)} \rangle - \langle \chi_j^{(0)} \varphi_k^{(0)} \mid \chi_k^{(0)} \varphi_i^{(0)} \rangle.$$
(IV.37)

However, a direct evaluation of $\chi_i^{(2)}$ via (IV.36) is not recommended, as it leads to divergences in the evaluation of the DPT corrections.^{64,65,71}

Consequently, in order to treat the perturbed small component $\chi_i^{(2)}$ on the same footing as $\varphi_i^{(2)}$, the following expansion is chosen,^{70,73,99} consistent with the kinetic-balance condition⁸²

$$\chi_i^{(2)} = \sum_p u_{pi}^{\lambda_{\text{rel}}} \chi_p^{(0)} = \sum_p u_{pi}^{\lambda_{\text{rel}}} \frac{1}{2m} \boldsymbol{\sigma} \hat{\mathbf{p}} \varphi_p^{(0)}.$$
 (IV.38)

To determine the expansion coefficients $u_{pi}^{\lambda_{\text{rel}}}$, the above expansion is inserted into (IV.36) followed by a projection on $\langle \chi_q^{(0)} | = \langle \varphi_q^{(0)} \frac{1}{2m} \boldsymbol{\sigma} \hat{\mathbf{p}} |$

$$\sum_{p} S_{qp}^{\lambda_{\text{rel}}} u_{pi}^{\lambda_{\text{rel}}} = \sum_{p} S_{qp}^{\lambda_{\text{rel}}} U_{pi}^{\lambda_{\text{rel}}} + \frac{1}{2m} \Big\{ h_{qi}^{\lambda_{\text{rel}}} - S_{qi}^{\lambda_{\text{rel}}} \varepsilon_{i} \\ + \sum_{k} (\langle \varphi_{q} \varphi_{k} \mid \hat{g}_{1}^{\lambda_{\text{rel}}} \mid \varphi_{i} \varphi_{k} \rangle - \langle \varphi_{q} \varphi_{k} \mid \hat{g}_{1}^{\lambda_{\text{rel}}} \mid \varphi_{k} \varphi_{i} \rangle) \Big\}.$$
(IV.39)

Note that the superscripts for the order of the perturbation are here dropped. Multiplication from the left with $(S^{\lambda_{\rm rel}})_{rq}^{-1}$ and summation over q finally leads to the expansion coefficients $u_{pi}^{\lambda_{\rm rel}}$

$$u_{pi}^{\lambda_{\rm rel}} = U_{pi}^{\lambda_{\rm rel}} + \frac{1}{2m} \sum_{q} (S^{\lambda_{\rm rel}})_{pq}^{-1} \left[h_{qi}^{\lambda_{\rm rel}} - S_{qi}^{\lambda_{\rm rel}} \varepsilon_i + \sum_{k} \langle \varphi_q \varphi_k \mid \mid \hat{g}_1^{\lambda_{\rm rel}} \mid \mid \varphi_i \varphi_k \rangle \right] \qquad (\text{IV.40})$$

with the antisymmetrized integral

$$\langle \varphi_q \varphi_k \mid\mid \hat{g}_1^{\lambda_{\text{rel}}} \mid\mid \varphi_i \varphi_k \rangle = \langle \varphi_q \varphi_k \mid \hat{g}_1^{\lambda_{\text{rel}}} \mid \varphi_i \varphi_k \rangle - \langle \varphi_q \varphi_k \mid \hat{g}_1^{\lambda_{\text{rel}}} \mid \varphi_k \varphi_i \rangle.$$
(IV.41)

Accordingly, in a short-hand notation, $u_{pi}^{\lambda_{\mathrm{rel}}}$ can be expressed as

$$u_{pi}^{\lambda_{\rm rel}} = U_{pi}^{\lambda_{\rm rel}} + A_{pi}^{\lambda_{\rm rel}} \tag{IV.42}$$

with

$$A_{pi}^{\lambda_{\rm rel}} = \frac{1}{2m} \sum_{q} (S^{\lambda_{\rm rel}})_{pq}^{-1} \left[h_{qi}^{\lambda_{\rm rel}} - S_{qi}^{\lambda_{\rm rel}} \varepsilon_i + \sum_{k} \langle \varphi_q \varphi_k \mid \mid \hat{g}_1^{\lambda_{\rm rel}} \mid \mid \varphi_i \varphi_k \rangle \right]$$
(IV.43)

thereby stating that the expansion coefficients for the perturbed small component only differ from those of the perturbed large component by the additional $A_{pi}^{\lambda_{\text{rel}}}$ terms. Therefore, alterations in the large component affect the small component as well. Furthermore, the relation between both components changes in every order.

Using the relations for $\chi_i^{(0)}$, $\chi_i^{(2)}$, and $\varphi_i^{(2)}$ as given in (IV.30), (IV.38), and (IV.35), the DPT4 energy expression (IV.28) is rewritten in the following manner

$$E^{(4)} = \sum_{i} \operatorname{Re} \left(\sum_{p} u_{pi}^{\lambda_{\mathrm{rel}}} \left(h_{pi}^{\lambda_{\mathrm{rel}}} - \varepsilon_{i} S_{ip}^{\lambda_{\mathrm{rel}}} \right) \right) - \frac{1}{2} \sum_{ij} \varepsilon_{ij}^{(2)} S_{ij}^{\lambda_{\mathrm{rel}}} + \sum_{ij} \operatorname{Re} \left(\sum_{p} u_{pi}^{\lambda_{\mathrm{rel}}} \langle \varphi_{p} \varphi_{j} \parallel \hat{g}_{1}^{\lambda_{\mathrm{rel}}} \parallel \varphi_{i} \varphi_{j} \rangle + \sum_{p} U_{pi}^{\lambda_{\mathrm{rel}}} \langle \varphi_{p} \varphi_{j} \parallel \hat{g}_{2}^{\lambda_{\mathrm{rel}}} \parallel \varphi_{i} \varphi_{j} \rangle \right) + \frac{1}{2} \sum_{ij} \langle \varphi_{i} \varphi_{j} \parallel \hat{g}_{12}^{\lambda_{\mathrm{rel}}} \parallel \varphi_{i} \varphi_{j} \rangle$$
(IV.44)

with the $\hat{g}_{12}^{\lambda_{\mathrm{rel}}}$ operator

$$\hat{g}_{12}^{\lambda_{\text{rel}}} = \frac{1}{16m^4} \boldsymbol{\sigma}_1 \hat{\mathbf{p}}_1 \boldsymbol{\sigma}_2 \hat{\mathbf{p}}_2 \frac{1}{r_{12}} \boldsymbol{\sigma}_1 \hat{\mathbf{p}}_1 \boldsymbol{\sigma}_2 \hat{\mathbf{p}}_2.$$
(IV.45)

The second-order $\boldsymbol{\varepsilon}^{(2)}$ matrix is given as (see Appendix IX.3 for details)

$$\varepsilon_{ji}^{(2)} = \left\{ \frac{\partial \langle \Psi_j \mid \hat{\mathbf{f}}_{\mathrm{D}} \mid \Psi_i \rangle}{\partial \lambda_{\mathrm{rel}}} \right\}_{\lambda_{\mathrm{rel}}=0}$$
(IV.46)
$$= -\frac{1}{2} S_{ji}^{\lambda_{\mathrm{rel}}} (\varepsilon_i + \varepsilon_j) + f_{ji}^{(\lambda_{\mathrm{rel}})} + \sum_{k,p} \left(2 \operatorname{Re} U_{pk}^{\lambda_{\mathrm{rel}}} \langle \varphi_j \varphi_p \mid \varphi_i \varphi_k \rangle - U_{pk}^{\lambda_{\mathrm{rel}}} \langle \varphi_j \varphi_k \mid \varphi_p \varphi_i \rangle \right)$$
(IV.47)

with

$$f_{pq}^{(\lambda_{\rm rel})} = h_{pq}^{\lambda_{\rm rel}} + \sum_{k} \langle \varphi_p \varphi_k \mid \mid \hat{g}_1^{\lambda_{\rm rel}} + \hat{g}_2^{\lambda_{\rm rel}} \mid \mid \varphi_q \varphi_k \rangle.$$
(IV.48)

In the derivation of $\varepsilon_{ji}^{(2)}$, the relation

$$U_{qp}^{\lambda_{\rm rel}*} + U_{pq}^{\lambda_{\rm rel}} + S_{pq}^{\lambda_{\rm rel}} = 0, \qquad (\text{IV.49})$$

with the generic indices p, q, is used which is obtained by differentiating the unitary normalization condition

$$\langle \Psi_p \mid \hat{\mathbf{S}}_{\mathrm{D}} \mid \Psi_q \rangle = \delta_{pq}$$
 (IV.50)

with respect to $\lambda_{\rm rel}$.

Using (IV.42), the expansion coefficients $u_{pi}^{\lambda_{\text{rel}}}$ for the perturbed small component can also be eliminated from (IV.44). Doing so, the resulting energy expression is consistent with the usual expressions for second derivatives from non-relativistic derivative theory⁷⁹

$$E^{(4)} = \sum_{ip} \operatorname{Re} \left\{ U_{pi}^{\lambda_{rel}} \left(f_{pi}^{(\lambda_{rel})} - \varepsilon_i S_{pi}^{\lambda_{rel}} \right) \right\} - \frac{1}{2} \sum_{ijkp} S_{kj}^{\lambda_{rel}} \left(2 \operatorname{Re} U_{pi}^{\lambda_{rel}} \langle \varphi_j \varphi_p \mid \varphi_k \varphi_i \rangle - U_{pi}^{\lambda_{rel}*} \langle \varphi_j \varphi_p \mid \varphi_i \varphi_k \rangle - U_{pi}^{\lambda_{rel}} \langle \varphi_j \varphi_i \mid \varphi_p \varphi_k \rangle \right) - \frac{1}{2} \sum_{ij} S_{ij}^{\lambda_{rel}} \left(f_{ji}^{(\lambda_{rel})} - \varepsilon_i S_{ji}^{\lambda_{rel}} \right) + \frac{1}{2} \sum_{ij} \langle \varphi_i \varphi_j \mid | \hat{g}_{12}^{\lambda_{rel}} \mid | \varphi_i \varphi_j \rangle + \sum_{ip} \operatorname{Re} \left\{ A_{pi}^{\lambda_{rel}} \left({}^{Z1} f_{pi}^{(\lambda_{rel})} - \varepsilon_i S_{pi}^{\lambda_{rel}} \right) \right\}$$
(IV.51)

with

$$^{Z1}f_{pq}^{(\lambda_{\rm rel})} = h_{pq}^{\lambda_{\rm rel}} + \sum_{j} \langle \varphi_p \varphi_j \mid \mid \hat{g}_1^{\lambda_{\rm rel}} \mid \mid \varphi_q \varphi_j \rangle.$$
(IV.52)

The first two lines correspond here to the CPHF contribution within the DPT expansion and the third line defines the reorthonormalization terms. Lines four and five are second-order terms with the latter being an additional contribution appearing due to the elimination of the small component.

IV.2.2. Separation of scalar-relativistic and spin-orbit contribution

The relativistic effects accounted for by (IV.51) comprise scalar-relativistic (SR) as well as spin-orbit (SO) corrections, with the latter being the first SO contribution in the DPT expansion. Using the Dirac identity¹⁷

$$\boldsymbol{\sigma} \cdot \mathbf{a} \, \boldsymbol{\sigma} \cdot \mathbf{b} = \mathbf{a} \cdot \mathbf{b} + i \boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b}), \tag{IV.53}$$

SR- (first term) and SO-contributions (second term) can be separated in (IV.51). Since the SR and SO operators are of different types, i.e., of singlet type in the case of the SR operators and of triplet type for the SO operators, no coupling appears between SR and SO terms in the case of closed-shell systems at the DPT4 level. Note that these couplings, however, arise for higher orders of the DPT expansion. Moreover, no coupling arises between the different components of the SO terms.

Writing down the SR-DPT4 energy correction is straightforward. It can be achieved by simply dropping all Pauli spin matrices in the integrals, being left with the momentum operators only. As all integrals are real, the SR part of the DPT4 energy for closed-shell systems reads after spin integration:

$$E_{\rm SR}^{(4)} = \sum_{ip} 2U_{pi}^{\rm SR} \left\{ f_{pi}^{(\rm SR)} - \varepsilon_i S_{pi}^{\rm SR} - \frac{1}{2} \sum_{jk} S_{kj}^{\rm SR} \left(4 \langle \phi_j \phi_p \mid \phi_k \phi_i \rangle - \langle \phi_j \phi_p \mid \phi_i \phi_k \rangle - \langle \phi_j \phi_i \mid \phi_p \phi_k \rangle \right) \right\} - \sum_{ij} S_{ij}^{\rm SR} \left(f_{ji}^{(\rm SR)} - \varepsilon_i S_{ji}^{\rm SR} \right) + \sum_{ij} \left(2 \langle \phi_i \phi_j \mid \hat{g}_{12}^{\rm SR} \mid \phi_i \phi_j \rangle - \langle \phi_i \phi_j \mid \hat{g}_{12}^{\rm SR} \mid \phi_j \phi_i \rangle \right) + \sum_{ip} 2A_{pi}^{\rm SR} \left({}^{Z1}f_{pi}^{(\rm SR)} - \varepsilon_i S_{pi}^{\rm SR} \right)$$
(IV.54)

with the spatial orbitals denoted by ϕ_p . The SR operators and integrals are given as

$$\hat{g}_n^{\lambda_{\rm rel}} \to \hat{g}_n^{\rm SR} = \frac{1}{4m^2} \hat{\mathbf{p}}_n \frac{1}{r_{12}} \hat{\mathbf{p}}_n \tag{IV.55}$$

41

$$\hat{g}_{12}^{\lambda_{\text{rel}}} \to \hat{g}_{12}^{\text{SR}} = \frac{1}{16m^4} \,\hat{\mathbf{p}}_1 \hat{\mathbf{p}}_2 \frac{1}{r_{12}} \hat{\mathbf{p}}_1 \hat{\mathbf{p}}_2$$
(IV.56)

$$h_{pi}^{\lambda_{\rm rel}} = \frac{1}{4m^2} \langle \phi_p \mid \boldsymbol{\sigma} \hat{\mathbf{p}} V \boldsymbol{\sigma} \hat{\mathbf{p}} \mid \phi_i \rangle \to h_{pi}^{\rm SR} = \frac{1}{4m^2} \langle \phi_p \mid \hat{\mathbf{p}} V \hat{\mathbf{p}} \mid \phi_i \rangle \qquad (\text{IV.57})$$

and

$$f_{pq}^{(\mathrm{SR})} = h_{pq}^{\mathrm{SR}} + \sum_{k} \left(2\langle \phi_p \phi_k \mid \hat{g}_1^{\mathrm{SR}} + \hat{g}_2^{\mathrm{SR}} \mid \phi_q \phi_k \rangle - \langle \phi_p \phi_k \mid \hat{g}_1^{\mathrm{SR}} + \hat{g}_2^{\mathrm{SR}} \mid \phi_k \phi_q \rangle \right) \quad (\mathrm{IV.58})$$

$$^{Z1}f_{pq}^{(\mathrm{SR})} = h_{pq}^{\mathrm{SR}} + \sum_{k} \left(2\langle \phi_p \phi_k \mid \hat{g}_1^{\mathrm{SR}} \mid \phi_q \phi_k \rangle - \langle \phi_p \phi_k \mid \hat{g}_1^{\mathrm{SR}} \mid \phi_k \phi_q \rangle \right).$$
(IV.59)

For the SO contributions in (IV.51), all terms containing

$$S_{pi}^{\lambda_{\rm rel}} = S_{pi}^{\rm SR} + S_{pi}^{\rm SO} = \frac{1}{4m^2} \langle \varphi_p \mid \hat{\mathbf{p}}^2 \mid \varphi_i \rangle + \frac{1}{4m^2} \langle \varphi_p \mid i\boldsymbol{\sigma} \underbrace{(\hat{\mathbf{p}} \times \hat{\mathbf{p}})}_{=0} \mid \varphi_i \rangle \qquad (\text{IV.60})$$

vanish. Additionally, contributions involving $U_{pi}^{\lambda_{\rm rel}}$ with index p corresponding to an occupied orbital, can be eliminated due to

$$\operatorname{Re} U_{ji}^{SO} = -\frac{1}{2} S_{ji}^{SO} = 0.$$
 (IV.61)

To determine the remaining coefficients $U_{ai}^{\lambda_{\text{rel}}}$ with indices a, b, c, \ldots referring to virtual orbitals, the CPHF equations need to be solved for the three components of the SO perturbation SOx, SOy, and SOz (see Appendix IX.2 for details).

Due to its cross-product form, the SO part of the relativistically perturbed operators can be written as a sum over its components, i.e.,

$$\hat{g}_{1}^{SO} = \frac{1}{4m^{2}} i \boldsymbol{\sigma}_{1} (\hat{\mathbf{p}}_{1} \frac{1}{r_{12}} \times \hat{\mathbf{p}}_{1})$$
(IV.62)

$$= \frac{1}{4m^2} \left(\boldsymbol{\sigma}_{1x} i(\hat{p}_{1y} \frac{1}{r_{12}} \hat{p}_{1z} - \hat{p}_{1z} \frac{1}{r_{12}} \hat{p}_{1y}) + \boldsymbol{\sigma}_{1y} i(\hat{p}_{1z} \frac{1}{r_{12}} \hat{p}_{1x} - \hat{p}_{1x} \frac{1}{r_{12}} \hat{p}_{1z}) \right. \\ \left. + \boldsymbol{\sigma}_{1z} i(\hat{p}_{1x} \frac{1}{r_{12}} \hat{p}_{1y} - \hat{p}_{1y} \frac{1}{r_{12}} \hat{p}_{1x}) \right)$$
(IV.63)

$$=\boldsymbol{\sigma}_{1x}\hat{g}_1^{\mathrm{SO}x} + \boldsymbol{\sigma}_{1y}\hat{g}_1^{\mathrm{SO}y} + \boldsymbol{\sigma}_{1z}\hat{g}_1^{\mathrm{SO}z} = \sum_{c=x,y,z} \boldsymbol{\sigma}_{1c}\hat{g}_1^{\mathrm{SO}c}.$$
 (IV.64)

Concerning the two-electron integrals containing the operator $\hat{g}_{12}^{\lambda_{\text{rel}}}$, the only non-zero SO contributions are of the type

$$\hat{g}_{12}^{\rm SO} = \frac{1}{16m^4} i\boldsymbol{\sigma}_2(\hat{\mathbf{p}}_2 \times i\boldsymbol{\sigma}_1(\hat{\mathbf{p}}_1 \times \frac{1}{r_{12}}\hat{\mathbf{p}}_1)\hat{\mathbf{p}}_2) \tag{IV.65}$$

due to spin orthogonality (see Appendix IX.4 for details). Furthermore, σ_1 and σ_2 have to be of the same type, i.e., both have to be either σ_x, σ_y , or σ_z to give a non-vanishing contribution.

Using the above expressions, the SO part of the DPT4 energy is finally given as

$$E_{\rm SO}^{(4)} = \sum_{ia} \operatorname{Re}\left(U_{ai}^{\rm SO} f_{ai}^{\rm (SO)}\right) + \frac{1}{2} \sum_{ij} \langle \varphi_i \varphi_j \mid \mid \hat{g}_{12}^{\rm SO} \mid \mid \varphi_i \varphi_j \rangle + \sum_{ip} \operatorname{Re}\left(A_{pi}^{\rm SO} \,^{Z1} f_{pi}^{\rm (SO)}\right). \quad (\text{IV.66})$$

After spin integration for closed-shell systems (see Appendix IX.5 for details), the SO energy correction reads

$$E_{\rm SO}^{(4)} = \sum_{c=x,y,z} \left[\sum_{ia} 2 \operatorname{Re} \left(U_{ai}^{\rm SOc} f_{ai}^{(\rm SOc)} \right) - \sum_{ij} \langle \phi_i \phi_j \mid \hat{g}_{12}^{\rm SOc} \mid \phi_j \phi_i \rangle + \sum_{ip} 2 \operatorname{Re} \left(A_{pi}^{\rm SOc \ Z1} f_{pi}^{(\rm SOc)} \right) \right].$$
(IV.67)

Using the Levi-Cività tensor

$$\epsilon_{\mu\nu\sigma} = \begin{cases} +1, & \text{for cyclic permutations of } x, y, z \\ -1, & \text{for non-cyclic permutations of } x, y, z \\ 0, & \text{for repeatedly occurring indices} \end{cases}$$
(IV.68)

the integrals and operators for a specific SO component c = x, y or z can be expressed via

$$h_{ai}^{\text{SOc}} = \frac{1}{4m^2} \sum_{\mu=x,y,z} \sum_{\nu=x,y,z} \epsilon_{c\mu\nu} \langle \phi_a \mid i\hat{p}_{\mu} V \hat{p}_{\nu} \mid \phi_i \rangle \tag{IV.69}$$

$$\hat{g}_{n}^{\text{SOc}} = \frac{1}{4m^2} \sum_{\mu=x,y,z} \sum_{\nu=x,y,z} \epsilon_{c\mu\nu} i \hat{p}_{n\mu} \frac{1}{r_{12}} \hat{p}_{n\nu}$$
(IV.70)

$$\hat{g}_{12}^{\text{SO}c} = \frac{1}{16m^4} \sum_{\mu=x,y,z} \sum_{\nu=x,y,z} \sum_{\sigma=x,y,z} \sum_{\rho=x,y,z} \epsilon_{c\mu\nu} i^2 \hat{p}_{2\mu} \left[\epsilon_{c\sigma\rho} \hat{p}_{1\sigma} \frac{1}{r_{12}} \hat{p}_{1\rho} \right] \hat{p}_{2\nu} \tag{IV.71}$$

43

$$f_{ai}^{(\text{SOc})} = h_{ai}^{\text{SOc}} + \sum_{j} \left(2 \langle \phi_a \phi_j \mid \hat{g}_1^{\text{SOc}} \mid \phi_i \phi_j \rangle - \langle \phi_a \phi_j \mid \hat{g}_2^{\text{SOc}} \mid \phi_j \phi_i \rangle - \langle \phi_a \phi_j \mid \hat{g}_2^{\text{SOc}} \mid \phi_j \phi_i \rangle \right)$$
(IV.72)

$$^{Z1}f_{pi}^{(\mathrm{SO}c)} = h_{pi}^{\mathrm{SO}c} + \sum_{j} \left(2\langle \phi_p \phi_j \mid \hat{g}_1^{\mathrm{SO}c} \mid \phi_i \phi_j \rangle - \langle \phi_p \phi_j \mid \hat{g}_1^{\mathrm{SO}c} \mid \phi_j \phi_i \rangle \right)$$
(IV.73)

$$A_{pi}^{\text{SOc}} = \frac{1}{2m} \sum_{q} (S^{\lambda_{\text{rel}}})_{pq}^{-1} {}^{Z_1} f_{qi}^{(\text{SOc})}.$$
 (IV.74)

Note that the final expressions for the SR part of the DPT4 energy (IV.54) as well as the SO part (IV.67) are of one-component form and may therefore be implemented within a non-relativistic code given that all additional integrals are available.

IV.2.3. DPT from a non-relativistic Lagrangian

In this section it is shown that it is possible to formulate the DPT4 energy starting from the Schrödinger equation instead of the Dirac equation by expanding the operators and the wave function with respect to $\lambda_{\rm rel}$. In this way, a non-relativistic Lagrangian can be employed to arrive at the desired energy corrections using standard analytic derivative theory.^{77,78} The non-relativistic HF Lagrangian is given as

$$\tilde{E} = \sum_{i} \langle \varphi_i \mid \hat{h} \mid \varphi_i \rangle + \frac{1}{2} \sum_{ij} \langle \varphi_i \varphi_j \mid \mid \hat{g} \mid \mid \varphi_i \varphi_j \rangle - \sum_{ij} \varepsilon_{ji} \Big(\langle \varphi_i \mid \hat{S} \mid \varphi_j \rangle - \delta_{ij} \Big). \quad (IV.75)$$

To make this Lagrangian and the involved operators dependent on the relativistic perturbation, an expansion in terms of λ_{rel} of the operators $\hat{h}, \hat{S}, \hat{g}$ and the orbitals φ_i is necessary.

Starting from the DHF equations formulated using the modified metric (see Appendix IX.1),

$$\langle \Psi_i \mid \hat{\mathbf{f}}_{\mathrm{D}} \mid \Psi_i \rangle = \varepsilon_i \langle \Psi_i \mid \hat{\mathbf{S}}_{\mathrm{D}} \mid \Psi_i \rangle$$
 (IV.76)

$$\langle \Psi_{i} \mid \hat{\mathbf{h}}_{\mathrm{D}} \mid \Psi_{i} \rangle + \sum_{j} \left(\langle \Psi_{i} \Psi_{j} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{i} \Psi_{j} \rangle - \langle \Psi_{i} \Psi_{j} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{j} \Psi_{i} \rangle \right) = \varepsilon_{i} \langle \Psi_{i} \mid \hat{\mathbf{S}}_{\mathrm{D}} \mid \Psi_{i} \rangle$$
(IV.77)

and expressing the small component χ_p via

$$\chi_p = \hat{X}\varphi_p, \tag{IV.78}$$

i.e., by means of the large component φ_p and the coupling operator \hat{X} ,^{45,71} the spinors Ψ_i may be expanded

$$\Psi_{i} = \begin{pmatrix} \varphi_{i} \\ \hat{X}\varphi_{i} \end{pmatrix} = \begin{pmatrix} \varphi_{i}^{(0)} + \lambda_{\mathrm{rel}}\varphi_{i}^{(2)} + \dots \\ \hat{X}(\varphi_{i}^{(0)} + \lambda_{\mathrm{rel}}\varphi_{i}^{(2)} + \dots) \end{pmatrix}$$
(IV.79)

allowing the evaluation of the matrix elements in the DHF equations in the following manner

$$\langle \boldsymbol{\Psi}_{i} \mid \hat{\mathbf{h}}_{\mathrm{D}} \mid \boldsymbol{\Psi}_{i} \rangle = \langle \varphi_{i} \mid V + \hat{X}^{\dagger} \boldsymbol{\sigma} \hat{\mathbf{p}} + \boldsymbol{\sigma} \hat{\mathbf{p}} \hat{X} + \lambda_{\mathrm{rel}} \hat{X}^{\dagger} V \hat{X} - 2m \hat{X}^{\dagger} \hat{X} \mid \varphi_{i} \rangle \quad (\mathrm{IV.80})$$

$$= \langle \varphi_i \mid \hat{h} \mid \varphi_i \rangle \tag{IV.81}$$

$$\langle \boldsymbol{\Psi}_i \mid \hat{\mathbf{S}}_{\mathrm{D}} \mid \boldsymbol{\Psi}_i \rangle = \langle \varphi_i \mid 1 + \lambda_{\mathrm{rel}} \hat{X}^{\dagger} \hat{X} \mid \varphi_i \rangle \tag{IV.82}$$

$$= \langle \varphi_i \mid \hat{S} \mid \varphi_i \rangle \tag{IV.83}$$

$$\langle \boldsymbol{\Psi}_{i} \boldsymbol{\Psi}_{j} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \boldsymbol{\Psi}_{i} \boldsymbol{\Psi}_{j} \rangle = \langle \varphi_{i} \varphi_{j} \mid \frac{1}{r_{12}} + \lambda_{\mathrm{rel}} \hat{X}^{\dagger}(1) \frac{1}{r_{12}} \hat{X}(1)$$

$$+ \lambda_{\mathrm{rel}} \hat{X}^{\dagger}(2) \frac{1}{r_{12}} \hat{X}(2)$$

$$+ \lambda_{\mathrm{rel}}^{2} \hat{X}^{\dagger}(1) \hat{X}^{\dagger}(2) \frac{1}{r_{12}} \hat{X}(1) \hat{X}(2) \mid \varphi_{i} \varphi_{j} \rangle$$

$$(IV.84)$$

$$= \langle \varphi_i \varphi_j \mid \hat{g} \mid \varphi_i \varphi_j \rangle. \tag{IV.85}$$

This procedure results in expressions for the operators \hat{h}, \hat{S} , and \hat{g} that explicitly depend on the relativistic perturbation λ_{rel} . To proceed further, the operator \hat{X} also needs to be expanded in orders of λ_{rel}

$$\hat{X} = \hat{X}^{(0)} + \lambda_{\rm rel} \hat{X}^{(2)} + \lambda_{\rm rel}^2 \hat{X}^{(4)} + \dots$$
(IV.86)

Using (IV.30), $\hat{X}^{(0)}$ can already be determined

$$\hat{X}^{(0)} = \frac{1}{2m} \boldsymbol{\sigma} \hat{\mathbf{p}}.$$
 (IV.87)

With the above relation, it can be shown that the zeroth-order operators are equivalent to the nonrelativistic (nrl) operators that appear in the Schrödinger equation

$$\hat{h}^{(0)} = V + \hat{X}^{(0)\dagger} \boldsymbol{\sigma} \hat{\mathbf{p}} + \boldsymbol{\sigma} \hat{\mathbf{p}} \hat{X}^{(0)} - 2m \hat{X}^{(0)\dagger} \hat{X}^{(0)} = V + \frac{\hat{\mathbf{p}}^2}{2m} = \hat{h}_{\text{nrl}}$$
(IV.88)

$$\hat{S}^{(0)} = 1 = \hat{S}_{\rm nrl}$$
 (IV.89)

$$\hat{g}^{(0)} = \frac{1}{r_{12}} = \hat{g}_{\rm nrl}.$$
 (IV.90)

For the DPT4 energy correction, the corresponding operators in second and fourth order are needed:

$$\hat{h}^{(2)} = \hat{X}^{(0)\dagger} V \hat{X}^{(0)} \tag{IV.91}$$

$$\hat{h}^{(4)} = \hat{X}^{(2)\dagger} V \hat{X}^{(0)} + \hat{X}^{(0)\dagger} V \hat{X}^{(2)} - 2m \hat{X}^{(2)\dagger} \hat{X}^{(2)}$$
(IV.92)

$$\hat{S}^{(2)} = \hat{X}^{(0)\dagger} \hat{X}^{(0)} \tag{IV.93}$$

$$\hat{S}^{(4)} = \hat{X}^{(2)\dagger} \hat{X}^{(0)} + \hat{X}^{(0)\dagger} \hat{X}^{(2)}$$
(IV.94)

$$\hat{g}^{(2)} = (1 + \hat{P}_{1,2}) \left[\hat{X}^{(0)\dagger}(1) \frac{1}{r_{12}} \hat{X}^{(0)}(1) \right]$$
(IV.95)

$$\hat{g}^{(4)} = (1 + \hat{P}_{1,2}) \Big[\hat{X}^{(2)\dagger}(1) \frac{1}{r_{12}} \hat{X}^{(0)}(1) + c.c. \Big] + \hat{X}^{(0)\dagger}(1) \hat{X}^{(0)\dagger}(2) \frac{1}{r_{12}} \hat{X}^{(0)}(1) \hat{X}^{(0)}(2)$$
(IV.96)

with the operator $\hat{P}_{1,2}$ permuting electron 1 and 2 and *c.c.* denoting the complex conjugate of the preceding expression.

The effect of $\hat{X}^{(2)}$ on $\varphi_i^{(0)}$ may be determined using the expansion of the perturbed small component given in (IV.38)

$$\chi_{i}^{(2)} = \sum_{p} u_{pi}^{\lambda_{\rm rel}} \chi_{p}^{(0)}$$
$$\hat{X}^{(0)} \varphi_{i}^{(2)} + \hat{X}^{(2)} \varphi_{i}^{(0)} = \sum_{p} (U_{pi}^{\lambda_{\rm rel}} + A_{pi}^{\lambda_{\rm rel}}) \hat{X}^{(0)} \varphi_{p}^{(0)}$$
$$\sum_{p} U_{pi}^{\lambda_{\rm rel}} \hat{X}^{(0)} \varphi_{p}^{(0)} + \hat{X}^{(2)} \varphi_{i}^{(0)} = \sum_{p} U_{pi}^{\lambda_{\rm rel}} \hat{X}^{(0)} \varphi_{p}^{(0)} + \sum_{p} A_{pi}^{\lambda_{\rm rel}} \hat{X}^{(0)} \varphi_{p}^{(0)}$$
$$\Rightarrow \hat{X}^{(2)} \varphi_{i}^{(0)} = \sum_{p} A_{pi}^{\lambda_{\rm rel}} \hat{X}^{(0)} \varphi_{p}^{(0)}.$$
(IV.97)

On the other hand, using this equation, an expression for the coefficients $A_{pi}^{\lambda_{\text{rel}}}$ can derived by projection onto $\langle \hat{X}^{(0)} \varphi_q |$

$$\langle \varphi_q \mid \hat{X}^{(0)\dagger} \hat{X}^{(2)} \mid \varphi_i \rangle = \sum_p A_{pi}^{\lambda_{\text{rel}}} \underbrace{\langle \varphi_q \mid \hat{X}^{(0)\dagger} \hat{X}^{(0)} \mid \varphi_p \rangle}_{S_{qp}^{\lambda_{\text{rel}}}}, \quad (\text{IV.98})$$

together with multiplication from the left with $\left(S_{rq}^{\lambda_{\rm rel}}\right)^{-1}$ and summation over q

$$A_{pi}^{\lambda_{\rm rel}} = \sum_{q} \left(S_{pq}^{\lambda_{\rm rel}} \right)^{-1} \langle \varphi_q \mid \hat{X}^{(0)\dagger} \hat{X}^{(2)} \mid \varphi_i \rangle.$$
(IV.99)

Using (IV.36), $\hat{X}^{(2)}$ may also be expressed as

$$\hat{X}^{(2)}\varphi_i^{(0)} = \frac{1}{2m} \Big(V - \varepsilon_i^{(0)} + \sum_k \left[\hat{J}_k^{(0)} - \hat{K}_k^{(0)} \right] \Big) \hat{X}^{(0)} \varphi_i^{(0)}$$
(IV.100)

with

$$\langle \varphi_{j}^{(0)} \mid \hat{X}^{(0)\dagger} [\hat{J}_{k}^{(0)} - \hat{K}_{k}^{(0)}] \hat{X}^{(0)} \mid \varphi_{i}^{(0)} \rangle = \\ \langle \varphi_{j}^{(0)} \varphi_{k}^{(0)} \mid \hat{X}^{(0)\dagger} (1) \frac{1}{r_{12}} \hat{X}^{(0)} (1) \mid \varphi_{i}^{(0)} \varphi_{k}^{(0)} \rangle - \langle \varphi_{j}^{(0)} \varphi_{k}^{(0)} \mid \hat{X}^{(0)\dagger} (1) \frac{1}{r_{12}} \hat{X}^{(0)} (1) \mid \varphi_{k}^{(0)} \varphi_{i}^{(0)} \rangle.$$

$$(IV.101)$$

If (IV.100) is inserted into (IV.99), it is seen that both expressions for $A_{pi}^{\lambda_{\text{rel}}}$, i.e., (IV.43) and (IV.99), are equivalent.

To obtain the DPT4 energy correction, the HF Lagrangian has to be differentiated twice with respect to λ_{rel} , thereby again exploiting Wigner's rules in the first differentiation

$$E^{(2)} = \left(\frac{\partial \tilde{E}}{\partial \lambda_{\rm rel}}\right)_{\lambda_{\rm rel}=0}$$
(IV.102)
$$= \left\{ \sum_{i} \langle \varphi_i^{(0)} \mid \frac{\partial \hat{h}}{\partial \lambda_{\rm rel}} \mid \varphi_i^{(0)} \rangle + \frac{1}{2} \sum_{ij} \left(\langle \varphi_i^{(0)} \varphi_j^{(0)} \mid \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid \mid \varphi_i^{(0)} \varphi_j^{(0)} \rangle \right)$$
$$- \sum_{ij} \varepsilon_{ji}^{(0)} \langle \varphi_i^{(0)} \mid \frac{\partial \hat{S}}{\partial \lambda_{\rm rel}} \mid \varphi_j^{(0)} \rangle \right\}_{\lambda_{\rm rel}=0},$$
(IV.103)

$$E^{(4)} = \frac{1}{2} \left(\frac{\partial^2 \tilde{E}}{\partial \lambda_{\rm rel}^2} \right)_{\lambda_{\rm rel} = 0}$$
(IV.104)

47

$$= \frac{1}{2} \Biggl\{ \sum_{i} \left(2 \operatorname{Re} \langle \varphi_{i}^{(2)} \mid \frac{\partial \hat{h}}{\partial \lambda_{\mathrm{rel}}} \mid \varphi_{i}^{(0)} \rangle + \langle \varphi_{i}^{(0)} \mid \frac{\partial^{2} \hat{h}}{\partial \lambda_{\mathrm{rel}}^{2}} \mid \varphi_{i}^{(0)} \rangle \right) \\ + \frac{1}{2} \sum_{ij} \left(4 \operatorname{Re} \langle \varphi_{i}^{(2)} \varphi_{j}^{(0)} \mid \mid \frac{\partial \hat{g}}{\partial \lambda_{\mathrm{rel}}} \mid \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle + \langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \mid \mid \frac{\partial^{2} \hat{g}}{\partial \lambda_{\mathrm{rel}}^{2}} \mid \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \right) \\ - \sum_{i} \varepsilon_{i}^{(0)} \left(2 \operatorname{Re} \langle \varphi_{i}^{(2)} \mid \frac{\partial \hat{S}}{\partial \lambda_{\mathrm{rel}}} \mid \varphi_{i}^{(0)} \rangle + \langle \varphi_{i}^{(0)} \mid \frac{\partial^{2} \hat{S}}{\partial \lambda_{\mathrm{rel}}^{2}} \mid \varphi_{i}^{(0)} \rangle \right) \\ - \sum_{ij} \varepsilon_{ji}^{(2)} \langle \varphi_{i}^{(0)} \mid \frac{\partial \hat{S}}{\partial \lambda_{\mathrm{rel}}} \mid \varphi_{j}^{(0)} \rangle \Biggr\}_{\lambda_{\mathrm{rel}}=0}.$$
(IV.105)

The first and second derivatives of the general operators \hat{O} with respect to $\lambda_{\rm rel}$ are given by

$$\left(\frac{\partial \hat{O}}{\partial \lambda_{\rm rel}}\right)_{\lambda_{\rm rel}=0} = \hat{O}^{(2)} \qquad \text{and} \qquad \left(\frac{\partial^2 \hat{O}}{\partial \lambda_{\rm rel}^2}\right)_{\lambda_{\rm rel}=0} = 2\hat{O}^{(4)}. \tag{IV.106}$$

which allows to evaluate (IV.103) and (IV.105) yielding

$$\begin{split} E^{(2)} &= \sum_{i} \langle \varphi_{i}^{(0)} \mid \hat{X}^{(0)\dagger} V \hat{X}^{(0)} \mid \varphi_{i}^{(0)} \rangle \\ &+ \frac{1}{2} \sum_{ij} \left(\langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \mid | (1 + \hat{P}_{1,2}) \left[\hat{X}^{(0)\dagger} (1) \frac{1}{r_{12}} \hat{X}^{(0)} (1) \right] \mid \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \right) \\ &- \sum_{i} \varepsilon_{i}^{(0)} \langle \varphi_{i}^{(0)} \mid X^{(0)\dagger} \hat{X}^{(0)} \mid \varphi_{i}^{(0)} \rangle \qquad (IV.107) \\ E^{(4)} &= \sum_{i} \left(\operatorname{Re} \langle \varphi_{i}^{(2)} \mid \hat{X}^{(0)\dagger} V \hat{X}^{(0)} \mid \varphi_{i}^{(0)} \rangle + \langle \varphi_{i}^{(0)} \mid \hat{X}^{(2)\dagger} V \hat{X}^{(0)} + c.c. - 2m \hat{X}^{(2)\dagger} \hat{X}^{(2)} \mid \varphi_{i}^{(0)} \rangle \right) \\ &+ \sum_{ij} \operatorname{Re} \langle \varphi_{i}^{(2)} \varphi_{j}^{(0)} \mid | (1 + \hat{P}_{1,2}) \left[\hat{X}^{(0)\dagger} (1) \frac{1}{r_{12}} \hat{X}^{(0)} (1) \right] \mid \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \\ &+ \frac{1}{2} \sum_{ij} \langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \mid | (1 + \hat{P}_{1,2}) \left[\hat{X}^{(2)\dagger} (1) \frac{1}{r_{12}} \hat{X}^{(0)} (1) + c.c. \right] \mid \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \\ &+ \frac{1}{2} \sum_{ij} \langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \mid \hat{X}^{(0)\dagger} (1) \hat{X}^{(0)\dagger} (2) \frac{1}{r_{12}} \hat{X}^{(0)} (1) \hat{X}^{(0)} (2) \mid \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \\ &- \sum_{i} \varepsilon_{i}^{(0)} \left(\operatorname{Re} \langle \varphi_{i}^{(2)} \mid \hat{X}^{(0)\dagger} \hat{X}^{(0)} \mid \varphi_{i}^{(0)} \rangle + \langle \varphi_{i}^{(0)} \mid \hat{X}^{(2)\dagger} \hat{X}^{(0)} + c.c. \mid \varphi_{i}^{(0)} \rangle \right) \\ &- \frac{1}{2} \sum_{ij} \varepsilon_{ji}^{(2)} \langle \varphi_{i}^{(0)} \mid \hat{X}^{(0)\dagger} \hat{X}^{(0)} \mid \varphi_{j}^{(0)} \rangle. \end{split}$$

Using (IV.100), the term $\langle \varphi_i^{(0)} \mid -2m\hat{X}^{(2)\dagger}\hat{X}^{(2)} \mid \varphi_i^{(0)} \rangle$ in (IV.108) may be rewritten as

$$\begin{split} \langle \varphi_i^{(0)} \mid -2m\hat{X}^{(2)\dagger}\hat{X}^{(2)} \mid \varphi_i^{(0)} \rangle &= -\frac{1}{2} \bigg[\langle \varphi_i^{(0)} \mid \hat{X}^{(2)\dagger}V\hat{X}^{(0)} + c.c. \mid \varphi_i^{(0)} \rangle \\ &\quad -\varepsilon_i^{(0)} \langle \varphi_i^{(0)} \mid \hat{X}^{(2)\dagger}\hat{X}^{(0)} + c.c. \mid \varphi_i^{(0)} \rangle \\ &\quad +\sum_j \langle \varphi_i^{(0)}\varphi_j^{(0)} \mid \mid \hat{X}^{(2)\dagger}(1)\frac{1}{r_{12}}\hat{X}^{(0)}(1) + c.c. \mid \varphi_i^{(0)}\varphi_j^{(0)} \rangle \bigg] \\ &\quad (\text{IV.109}) \end{split}$$

which allows to simplify the DPT4 energy expression to

$$\begin{split} E^{(4)} &= \sum_{i} \left(\operatorname{Re} \langle \varphi_{i}^{(2)} \mid \hat{X}^{(0)\dagger} V \hat{X}^{(0)} \mid \varphi_{i}^{(0)} \rangle + \frac{1}{2} \langle \varphi_{i}^{(0)} \mid \hat{X}^{(2)\dagger} V \hat{X}^{(0)} + c.c. \mid \varphi_{i}^{(0)} \rangle \right) \\ &+ \sum_{ij} \operatorname{Re} \langle \varphi_{i}^{(2)} \varphi_{j}^{(0)} \mid | (1 + \hat{P}_{1,2}) \left[\hat{X}^{(0)\dagger} (1) \frac{1}{r_{12}} \hat{X}^{(0)} (1) \right] \mid | \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \\ &+ \frac{1}{2} \sum_{ij} \langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \mid | \hat{X}^{(2)\dagger} (2) \frac{1}{r_{12}} \hat{X}^{(0)} (2) + c.c. \mid | \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \\ &+ \frac{1}{2} \sum_{ij} \langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \mid | \hat{X}^{(0)\dagger} (1) \hat{X}^{(0)\dagger} (2) \frac{1}{r_{12}} \hat{X}^{(0)} (1) \hat{X}^{(0)} (2) \mid | \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \\ &- \sum_{i} \varepsilon_{i}^{(0)} \left(\operatorname{Re} \langle \varphi_{i}^{(2)} \mid \hat{X}^{(0)\dagger} \hat{X}^{(0)} \mid \varphi_{i}^{(0)} \rangle + \frac{1}{2} \langle \varphi_{i}^{(0)} \mid \hat{X}^{(2)\dagger} \hat{X}^{(0)} + c.c. \mid \varphi_{i}^{(0)} \rangle \right) \\ &- \frac{1}{2} \sum_{ij} \varepsilon_{ji}^{(2)} \langle \varphi_{i}^{(0)} \mid \hat{X}^{(0)\dagger} \hat{X}^{(0)} \mid \varphi_{j}^{(0)} \rangle. \end{split}$$
(IV.110)

Since

$$\varepsilon_{ji}^{(2)} = \left\{ \frac{\partial}{\partial \lambda_{\rm rel}} \langle \varphi_j \mid \hat{f} \mid \varphi_i \rangle \right\}_{\lambda_{\rm rel}=0} \tag{IV.111}$$

$$= \left\{ \frac{\partial}{\partial \lambda_{\rm rel}} \left(\langle \varphi_j \mid \hat{h} \mid \varphi_i \rangle + \sum_{ij} \langle \varphi_i \varphi_j \mid \mid \hat{g} \mid \mid \varphi_i \varphi_j \rangle \right) \right\}_{\lambda_{\rm rel}=0}$$
(IV.112)

is equivalent to (IV.47), the use of the \hat{X} operators results in the same final DPT2 and DPT4 corrections as the ones given in (IV.31) and (IV.51), respectively.

It is thus shown that it is possible to derive the DPT4 energy correction within a nonrelativistic framework using standard derivative theory. This approach to DPT can as well be extended to higher orders thus rendering these energy corrections more easily accessible¹⁰⁰ as will also be shown in the following chapter for the DPT6 correction.

IV.2.4. DPT6 corrections from a non-relativistic Lagrangian

At the HF level of theory the DPT6 energy correction is given as a third derivative of the chosen Lagrangian

$$\begin{split} E^{(6)} &= \frac{1}{6} \left(\frac{\partial^{3} \tilde{E}}{\partial \lambda_{\mathrm{rel}}^{3}} \right)_{\lambda_{\mathrm{rel}}=0} \end{split} \tag{IV.113} \\ &= \sum_{i} \left(\operatorname{Re} \langle \varphi_{i}^{(2)} \mid \hat{h}^{(2)} - \varepsilon_{i}^{(0)} \hat{S}^{(2)} \mid \varphi_{i}^{(2)} \rangle + 2 \operatorname{Re} \langle \varphi_{i}^{(2)} \mid \hat{h}^{(4)} - \varepsilon_{i}^{(0)} \hat{S}^{(4)} \mid \varphi_{i}^{(0)} \rangle \\ &+ \langle \varphi_{i}^{(0)} \mid \hat{h}^{(6)} - \varepsilon_{i}^{(0)} \hat{S}^{(6)} \mid \varphi_{i}^{(0)} \rangle \right) \\ &+ \sum_{ij} \left(2 \operatorname{Re} \langle \varphi_{i}^{(2)} \varphi_{j}^{(2)} \mid \| \hat{g}^{(0)} \mid \| \varphi_{i}^{(2)} \varphi_{j}^{(0)} \rangle + \operatorname{Re} \langle \varphi_{i}^{(2)} \varphi_{j}^{(2)} \mid \| \hat{g}^{(2)} \mid \| \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle \\ &+ \langle \varphi_{i}^{(2)} \varphi_{j}^{(0)} \mid \| \hat{g}^{(2)} \mid \| \varphi_{i}^{(2)} \varphi_{j}^{(0)} \rangle + \operatorname{Re} \langle \varphi_{i}^{(2)} \varphi_{j}^{(0)} \mid \| \hat{g}^{(2)} \mid \| \varphi_{i}^{(0)} \varphi_{j}^{(2)} \rangle \\ &+ 2 \operatorname{Re} \langle \varphi_{i}^{(2)} \varphi_{j}^{(0)} \mid \| \hat{g}^{(4)} \mid \| \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle + \frac{1}{2} \langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \mid \| \hat{g}^{(6)} \mid \| \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle) \\ &- \sum_{ij} \left(\varepsilon_{ji}^{(2)} \operatorname{Re} \langle \varphi_{i}^{(2)} \mid \hat{S}^{(0)} \mid \varphi_{j}^{(2)} \rangle + 2 \varepsilon_{ji}^{(2)} \operatorname{Re} \langle \varphi_{i}^{(2)} \mid \hat{S}^{(2)} \mid \varphi_{j}^{(0)} \rangle \\ &+ \varepsilon_{ij}^{(2)} \langle \varphi_{i}^{(0)} \mid \hat{S}^{(4)} \mid \varphi_{j}^{(0)} \rangle). \end{aligned} \tag{IV.114}$$

The (2n + 1) and (2n + 2) rules have here been applied in the last step. According to these rules, the resulting expression contains only the first derivative of the wave function as well as the first derivative of the Lagrange multipliers. In DPT at the HF level this means that no higher derivatives than $\Psi^{(2)}$ and $\varepsilon_{ji}^{(2)}$ are needed for the sixth order. When deriving DPT6 from the non-relativistic Lagrangian as given in (IV.75), the part of the wave function which is given by the small component is incorporated into the operators. Accordingly, when using the (2n + 1) rule in a naive manner, terms containing $\hat{X}^{(2)}\varphi_i^{(2)}$ (due to the operators $\hat{h}^{(4)}, \hat{S}^{(4)}, \hat{g}^{(4)}$) as well as $\hat{X}^{(4)}\varphi_i^{(0)}$ (due to $\hat{h}^{(6)}, \hat{S}^{(6)}, g^{(6)}$) arise which are actually contributions to $\Psi^{(4)}$. In the following it is shown that these terms indeed vanish. The terms containing $\hat{X}^{(2)}\varphi_i^{(2)}$ are given by

$$E^{(6)} = \dots + \sum_{i} \left(\langle \varphi_i^{(2)} \mid \hat{h}^{(4)} \mid \varphi_i^{(0)} \rangle + c.c. \right)$$
$$- \sum_{i} \left(\varepsilon_i^{(0)} \langle \varphi_i^{(2)} \mid \hat{S}^{(4)} \mid \varphi_i^{(0)} \rangle + c.c \right)$$

IV.2. DPT corrections at the Hartree-Fock level

$$+\sum_{ij} \left(\left(\langle \varphi_i^{(2)} \varphi_j^{(0)} \mid \hat{g}^{(4)} \mid \varphi_i^{(0)} \varphi_j^{(0)} \rangle - \langle \varphi_i^{(2)} \varphi_j^{(0)} \mid \hat{g}^{(4)} \mid \varphi_j^{(0)} \varphi_i^{(0)} \rangle \right) + c.c. \right)$$
(IV.115)

with the fourth-order operators given in (IV.92), (IV.94), and (IV.96). The critical terms are now those where $\hat{X}^{(2)}$ is acting on $\varphi_i^{(2)}$, i.e.,

$$E^{(6)} = \dots + \sum_{i} \left(\langle \varphi_{i}^{(2)} \mid \hat{X}^{(2)\dagger} V \hat{X}^{(0)} - 2m \hat{X}^{(2)\dagger} \hat{X}^{(2)} \mid \varphi_{i}^{(0)} \rangle + c.c. \right) - \sum_{i} \left(\varepsilon_{i}^{(0)} \langle \varphi_{i}^{(2)} \mid \hat{X}^{(2)\dagger} \hat{X}^{(0)} \mid \varphi_{i}^{(0)} \rangle + c.c. \right) + \sum_{ij} \left(\left(\langle \varphi_{i}^{(2)} \varphi_{j}^{(0)} \mid \hat{X}^{(2)\dagger} (1) r_{12}^{-1} \hat{X}^{(0)} (1) \mid \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle - \langle \varphi_{i}^{(2)} \varphi_{j}^{(0)} \mid \hat{X}^{(2)\dagger} (1) r_{12}^{-1} \hat{X}^{(0)} (1) \mid \varphi_{j}^{(0)} \varphi_{i}^{(0)} \rangle \right) + c.c. \right).$$
(IV.116)

From (IV.100) it can be seen that it holds

$$\left[-2m\hat{X}^{(2)}(1) + \left(V - \varepsilon_i^{(0)} + \sum_j (\hat{J}_j - \hat{K}_j)\right)\hat{X}^{(0)}(1)\right]\varphi_i^{(0)}(1) = 0.$$
 (IV.117)

Therefore, rewriting (IV.116)

$$E^{(6)} = \dots + \sum_{i} \langle \varphi_{i}^{(2)} \mid \hat{X}^{(2)\dagger} \underbrace{\left[-2m\hat{X}^{(2)} + \left(V - \varepsilon_{i}^{(0)} + \sum_{j} (\hat{J}_{j} - \hat{K}_{j})\right) \hat{X}^{(0)} \right] \mid \varphi_{i}^{(0)} \rangle}_{=0} + c.c.$$

$$\underbrace{\left[-2m\hat{X}^{(2)} + \left(V - \varepsilon_{i}^{(0)} + \sum_{j} (\hat{J}_{j} - \hat{K}_{j})\right) \hat{X}^{(0)} \right] \mid \varphi_{i}^{(0)} \rangle}_{=0} + c.c.$$

$$\underbrace{\left[-2m\hat{X}^{(2)} + \left(V - \varepsilon_{i}^{(0)} + \sum_{j} (\hat{J}_{j} - \hat{K}_{j})\right) \hat{X}^{(0)} \right] \mid \varphi_{i}^{(0)} \rangle}_{=0} + c.c.$$

$$\underbrace{\left[-2m\hat{X}^{(2)} + \left(V - \varepsilon_{i}^{(0)} + \sum_{j} (\hat{J}_{j} - \hat{K}_{j})\right) \hat{X}^{(0)} \right] \mid \varphi_{i}^{(0)} \rangle}_{=0} + c.c.$$

$$\underbrace{\left[-2m\hat{X}^{(2)} + \left(V - \varepsilon_{i}^{(0)} + \sum_{j} (\hat{J}_{j} - \hat{K}_{j})\right) \hat{X}^{(0)} \right] \mid \varphi_{i}^{(0)} \rangle}_{=0} + c.c.$$

$$\underbrace{\left[-2m\hat{X}^{(2)} + \left(V - \varepsilon_{i}^{(0)} + \sum_{j} (\hat{J}_{j} - \hat{K}_{j})\right) \hat{X}^{(0)} \right] \mid \varphi_{i}^{(0)} \rangle}_{=0} + c.c.$$

shows that these terms vanish. Of course, the same holds for the complex conjugate expression.

Concerning the terms in which $\hat{X}^{(4)}$ acts on $\varphi_i^{(0)}$, the contributions are given by

$$E^{(6)} = \dots + \sum_{i} \langle \varphi_{i}^{(0)} | \hat{h}^{(6)} | \varphi_{i}^{(0)} \rangle - \sum_{i} \varepsilon_{i} \langle \varphi_{i}^{(0)} | \hat{S}^{(6)} | \varphi_{i}^{(0)} \rangle + \sum_{ij} \frac{1}{2} \left(\langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} | \hat{g}^{(6)} | \varphi_{i}^{(0)} \varphi_{j}^{(0)} \rangle - \langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} | \hat{g}^{(6)} | \varphi_{j}^{(0)} \varphi_{i}^{(0)} \rangle \right)$$
(IV.119)

with

$$\hat{h}^{(6)} = \left(\hat{X}^{(4)\dagger}V\hat{X}^{(0)} + c.c.\right) + \hat{X}^{(2)\dagger}V\hat{X}^{(2)} - 2m\left(X^{(4)\dagger}\hat{X}^{(2)} + c.c.\right)$$
(IV.120)
$$\hat{c}^{(6)} = \left(\hat{x}^{(4)\dagger}\hat{x}^{(0)}\right) + \hat{c}^{(2)\dagger}\hat{x}^{(2)} + \hat{c}^{(2)} + \hat{c}^{(2)}\hat{x}^{(2)} + c.c.\right)$$
(IV.120)

$$S^{(6)} = \left(X^{(4)} X^{(0)} + c.c.\right) + X^{(2)} X^{(2)}$$
(IV.121)
$$\hat{g}^{(6)} = \left(1 + \hat{P}_{1,2}\right) \left(\hat{X}^{(2)\dagger}(1) \frac{1}{r_{12}} \hat{X}^{(2)}(1) + c.c.\right)$$
$$+ \left(1 + \hat{P}_{1,2}\right) \left(\hat{X}^{(4)\dagger}(1) \frac{1}{r_{12}} \hat{X}^{(0)}(1) + c.c.\right)$$

$$+ \left(1 + \hat{P}_{1,2}\right) \left(\hat{X}^{(2)\dagger}(1)\hat{X}^{(0)\dagger}(2)\frac{1}{r_{12}}\hat{X}^{(0)}(1)\hat{X}^{(0)}(2) + c.c.\right).$$
(IV.122)

Accordingly, the relevant terms are

$$E^{(6)} = \dots + \sum_{i} \left\langle \varphi_{i}^{(0)} \middle| \left(\hat{X}^{(4)\dagger} V \hat{X}^{(0)} + c.c. \right) - 2m \left(X^{(4)\dagger} \hat{X}^{(2)} + c.c. \right) \middle| \varphi_{i}^{(0)} \right\rangle + \sum_{i} \left\langle \varphi_{i}^{(0)} \middle| \left(\hat{X}^{(4)\dagger} \hat{X}^{(0)} + c.c. \right) \middle| \varphi_{i}^{(0)} \right\rangle + \frac{1}{2} \sum_{ij} \left(\left\langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \middle| \left(1 + \hat{P}_{1,2} \right) \left(\hat{X}^{(4)\dagger} (1) \frac{1}{r_{12}} \hat{X}^{(0)} (1) + c.c. \right) \middle| \varphi_{i}^{(0)} \varphi_{j}^{(0)} \right\rangle - \left\langle \varphi_{i}^{(0)} \varphi_{j}^{(0)} \middle| \left(1 + \hat{P}_{1,2} \right) \left(\hat{X}^{(4)\dagger} (1) \frac{1}{r_{12}} \hat{X}^{(0)} (1) + c.c. \right) \middle| \varphi_{j}^{(0)} \varphi_{i}^{(0)} \right\rangle \right)$$
(IV.123)

which can be rearranged to

$$E^{(6)} = \dots + \sum_{i} \langle \varphi_{i}^{(0)} \mid \hat{X}^{(4)\dagger} \underbrace{\left[-2m\hat{X}^{(2)} \left(V - \varepsilon_{i}^{(0)} + \sum_{j} (\hat{J}_{j} - \hat{K}_{j}) \right) \hat{X}^{(0)} \right] \mid \varphi_{i}^{(0)} \rangle}_{=0} + c.c.$$
(IV.124)

again showing that, consistent with the (2n + 1) rule, there appear no contributions due to the fourth-order wave function in the DPT6 energy expression. For a more detailed discussion on DPT6, see also Ref. 100.

IV.3. DPT corrections at correlated levels of theory

In this section the DPT4 energy expression will be derived for correlated methods, i.e., explicitly for the MP2 approach. For convenience, the notation $|p\rangle = |\varphi_p\rangle$ will be used in the following. At the MP2 level, the Lagrangian is given by

$$\tilde{E} = \frac{1}{4} \sum_{ij} \sum_{ab} t_{ij}^{ab} \langle ij || \hat{g} || ab \rangle
+ \frac{1}{4} \sum_{ij} \sum_{ab} \lambda_{ab}^{ij} (\langle ab || \hat{g} || ij \rangle - [\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b] t_{ij}^{ab})
+ \sum_{ai} Z_{ai} (\langle a | \hat{h} | i \rangle + \sum_j \langle aj || \hat{g} || ij \rangle)
+ \sum_{pq} I_{pq} (\langle p | \hat{S} | q \rangle - \delta_{pq})$$
(IV.125)

with the amplitudes t_{ij}^{ab} and the Lagrange multipliers λ_{ab}^{ij} , Z_{ai} , and I_{pq} that are used to account for the amplitude equations, the Brillouin condition, and the orthornormality of the orbitals as side-conditions. From the stationarity conditions $\frac{\partial \tilde{E}}{\partial t_{ij}^{ab}} = 0$ and $\frac{\partial \tilde{E}}{\partial \lambda_{ab}^{ij}} = 0$ (see chapter III.2) the following relations are obtained

$$\lambda_{ab}^{ij} = \frac{\langle ij \mid \mid \hat{g} \mid \mid ab \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \quad t_{ij}^{ab} = \frac{\langle ab \mid \mid \hat{g} \mid \mid ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$
(IV.126)

yielding

$$\lambda_{ab}^{ij} = t_{ij}^{ab*},\tag{IV.127}$$

$$t_{ij}^{ab} = -t_{ji}^{ab} = -t_{ij}^{ba} = t_{ji}^{ba}.$$
 (IV.128)

The one- and two-particle density matrices may be defined as

$$D_{ij} = -\frac{1}{2} \sum_{k} \sum_{ab} \lambda_{ab}^{kj} t_{ki}^{ab}, \quad D_{ab} = \frac{1}{2} \sum_{c} \sum_{ij} \lambda_{ac}^{ij} t_{ij}^{bc}, \quad (IV.129)$$

$$\Gamma_{abij} = \frac{1}{4} \lambda_{ab}^{ij}, \quad \Gamma_{ijab} = \frac{1}{4} t_{ij}^{ab}, \quad (\text{IV.130})$$

leading to a general form of the Lagrangian for correlated methods

$$\tilde{E} = \sum_{pqrs} \Gamma_{pqrs} \langle pq \mid\mid \hat{g} \mid\mid rs \rangle$$

53

$$+\sum_{pq} D_{pq} \Big(\langle p \mid \hat{h} \mid q \rangle + \sum_{j} \langle pj \mid | \hat{g} \mid | qj \rangle \Big) \\ + \sum_{ai} Z_{ai} \Big(\langle a \mid \hat{h} \mid i \rangle + \sum_{j} \langle aj \mid | \hat{g} \mid | ij \rangle \Big) \\ + \sum_{pq} I_{pq} \Big(\langle p \mid \hat{S} \mid q \rangle - \delta_{pq} \Big).$$
(IV.131)

For MP2 it holds that only D_{ij} , D_{ab} , Γ_{abij} , and Γ_{ijab} are nonzero.

The DPT4 energy at the MP2 level is again obtained as the second derivative of the Lagrangian (IV.131) with respect to $\lambda_{\rm rel}$. In the derivation, Wigner's (2n+1) and (2n+2) rules are exploited in the first differentiation step

$$\frac{\partial \tilde{E}}{\partial \lambda_{\rm rel}} = \sum_{pqrs} \Gamma_{pqrs} \langle pq \mid \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid |rs\rangle
+ \sum_{pq} D_{pq} \left(\langle p \mid \frac{\partial \hat{h}}{\partial \lambda_{\rm rel}} \mid q \rangle + \sum_{j} \langle pj \mid \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid |qj\rangle \right)
+ \sum_{ai} Z_{ai} \left(\langle a \mid \frac{\partial \hat{h}}{\partial \lambda_{\rm rel}} \mid i \rangle + \sum_{j} \langle aj \mid \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid |ij\rangle \right)
+ \sum_{pq} I_{pq} \langle p \mid \frac{\partial \hat{S}}{\partial \lambda_{\rm rel}} \mid q \rangle$$
(IV.132)

At the point $\lambda_{rel} = 0$, this leads to the DPT2 energy which at the MP2 level is given as

$$\left(\frac{\partial \tilde{E}}{\partial \lambda_{\rm rel}}\right)_{\lambda_{\rm rel}=0} = \sum_{pqrs} \Gamma_{pqrs} \langle pq \mid \mid \hat{g}_{1}^{\lambda_{\rm rel}} + \hat{g}_{2}^{\lambda_{\rm rel}} \mid \mid rs \rangle \\
+ \sum_{pq} D_{pq} f_{pq}^{(\lambda_{\rm rel})} \\
+ \sum_{ai} Z_{ai} f_{ai}^{(\lambda_{\rm rel})} \\
+ \sum_{pq} I_{pq} S_{pq}^{\lambda_{\rm rel}} \qquad (\text{IV.133})$$

with $f_{pq}^{(\lambda_{\text{rel}})}$ and $S_{pq}^{\lambda_{\text{rel}}}$ as given in (IV.32) and (IV.48). For the second derivative of the energy functional \tilde{E} , all terms in (IV.132) need to be differentiated yielding

$$E^{(4)} = \frac{1}{2} \left(\frac{\partial^2 \tilde{E}}{\partial \lambda_{\rm rel}^2} \right)_{\lambda_{\rm rel}=0}$$

$$= \frac{1}{2} \left(\sum_{pqrs} \left\{ \frac{\partial \Gamma_{pqrs}}{\partial \lambda_{\rm rel}} \langle pq \mid\mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid\mid rs \rangle + \Gamma_{pqrs} \left[\frac{\partial \langle pq \mid\mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid\mid rs \rangle}{\partial \lambda_{\rm rel}} \right] \right\}$$

$$+ \sum_{pq} \left\{ \frac{\partial D_{pq}}{\partial \lambda_{\rm rel}} f_{pq}^{(\lambda_{\rm rel})} + D_{pq} \frac{\partial f_{pq}^{(\lambda_{\rm rel})}}{\partial \lambda_{\rm rel}} \right\}$$

$$+ \sum_{ai} \left\{ \frac{\partial Z_{ai}}{\partial \lambda_{\rm rel}} f_{ai}^{(\lambda_{\rm rel})} + Z_{ai} \frac{\partial f_{ai}^{(\lambda_{\rm rel})}}{\partial \lambda_{\rm rel}} \right\}$$

$$+ \sum_{pq} \left\{ \frac{\partial I_{pq}}{\partial \lambda_{\rm rel}} S_{pq}^{\lambda_{\rm rel}} + I_{pq} \frac{\partial S_{pq}^{\lambda_{\rm rel}}}{\partial \lambda_{\rm rel}} \right\} \right)_{\lambda_{\rm rel}=0}.$$
(IV.134)

In the following, explicit expressions for the terms arising in the above equation are evaluated, thereby assuming that they are given for $\lambda_{rel} = 0$. The perturbed amplitudes are given by:

$$\frac{1}{4} \frac{\partial t_{ij}^{ab}}{\partial \lambda_{\rm rel}} = \frac{1}{4} \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \left[\frac{\partial \langle ab \mid \mid \hat{g} \mid \mid ij \rangle}{\partial \lambda_{\rm rel}} - \sum_m \left(\frac{\partial f_{mi}}{\partial \lambda_{\rm rel}} t_{mj}^{ab} + \frac{\partial f_{mj}}{\partial \lambda_{\rm rel}} t_{im}^{ab} \right) + \sum_e \left(\frac{\partial f_{ae}}{\partial \lambda_{\rm rel}} t_{ij}^{eb} + \frac{\partial f_{be}}{\partial \lambda_{\rm rel}} t_{ij}^{ae} \right) \right]$$
(IV.135)

with

$$\frac{\partial \langle pq \mid \hat{g} \mid rs \rangle}{\partial \lambda_{\rm rel}} = \sum_{t} U_{tp}^{\lambda_{\rm rel}*} \langle tq \mid rs \rangle + \sum_{t} U_{tq}^{\lambda_{\rm rel}*} \langle pt \mid rs \rangle
+ \sum_{t} U_{tr}^{\lambda_{\rm rel}} \langle pq \mid ts \rangle + \sum_{t} U_{ts}^{\lambda_{\rm rel}} \langle pq \mid rt \rangle
+ \langle pq \mid \hat{g}_{1}^{\lambda_{\rm rel}} + \hat{g}_{2}^{\lambda_{\rm rel}} \mid rs \rangle, \qquad (\text{IV.136})$$

$$\frac{\partial f_{pq}}{\partial \lambda_{\text{rel}}} = \frac{\partial}{\partial \lambda_{\text{rel}}} \left[\langle p \mid \hat{h} \mid q \rangle + \sum_{k} \langle pk \mid \mid \hat{g} \mid \mid qk \rangle \right]$$

$$=\sum_{t} U_{tp}^{\lambda_{rel}*} f_{tq} + \sum_{t} U_{tq}^{\lambda_{rel}} f_{pt} + h_{pq}^{\lambda_{rel}} + \sum_{k} \langle pk \mid | \hat{g}_{1} + \hat{g}_{2} \mid | qk \rangle$$
$$+ \sum_{tk} \left(U_{tk}^{\lambda_{rel}*} \langle pt \mid | qk \rangle + U_{tk}^{\lambda_{rel}} \langle pk \mid | qt \rangle \right)$$
$$= U_{qp}^{\lambda_{rel}*} \varepsilon_{q} + U_{pq}^{\lambda_{rel}} \varepsilon_{p} + f_{pq}^{(\lambda_{rel})} + \sum_{tk} \left(U_{tk}^{\lambda_{rel}*} \langle pt \mid | qk \rangle + U_{tk}^{\lambda_{rel}} \langle pk \mid | qt \rangle \right), \quad (IV.137)$$

and

$$\frac{\partial \Gamma_{ijab}}{\partial \lambda_{\rm rel}} = \frac{\partial \Gamma^*_{abij}}{\partial \lambda_{\rm rel}} = \frac{1}{4} \frac{\partial t^{ab}_{ij}}{\partial \lambda_{\rm rel}} = \frac{1}{4} \frac{\partial \left(\lambda^{ij}_{ab}\right)^*}{\partial \lambda_{\rm rel}}.$$
 (IV.138)

For the perturbed one-particle density matrix it holds

$$\frac{\partial D_{ij}}{\partial \lambda_{\rm rel}} = -\frac{1}{2} \sum_{k} \sum_{ab} \frac{\partial \lambda_{ab}^{kj}}{\partial \lambda_{\rm rel}} t_{ki}^{ab} + \lambda_{ab}^{kj} \frac{\partial t_{ki}^{ab}}{\partial \lambda_{\rm rel}}, \qquad (\text{IV.139})$$

$$\frac{\partial D_{ab}}{\partial \lambda_{\rm rel}} = \frac{1}{2} \sum_{c} \sum_{ij} \frac{\partial \lambda_{ac}^{ij}}{\partial \lambda_{\rm rel}} t_{ij}^{bc} + \lambda_{ac}^{ij} \frac{\partial t_{ij}^{bc}}{\partial \lambda_{\rm rel}}.$$
 (IV.140)

Moreover, explicit expressions for the remaining integrals are needed

$$\begin{split} \frac{\partial \langle pq \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid rs \rangle}{\partial \lambda_{\rm rel}} = & \langle p^{(2)}q \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid rs \rangle + \langle pq^{(2)} \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid rs \rangle \\ & + \langle pq \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid r^{(2)}s \rangle + \langle pq \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid rs^{(2)} \rangle + \langle pq \mid \frac{\partial^2 \hat{g}}{\partial \lambda_{\rm rel}^2} \mid rs \rangle, \\ \langle p^{(2)}q \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid rs \rangle = \langle p^{(2)}q \mid \hat{g}^{(2)} \mid rs \rangle = \sum_{p} U_{tp}^{\lambda_{\rm rel}*} \langle tq \mid \hat{g}_{1}^{\lambda_{\rm rel}} + \hat{g}_{2}^{\lambda_{\rm rel}} \mid rs \rangle, \\ \langle p^{(2)}q \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}^2} \mid rs \rangle = \langle pq \mid 2\hat{g}^{(4)} \mid rs \rangle = \sum_{p} U_{tp}^{\lambda_{\rm rel}*} \langle tq \mid \hat{g}_{1}^{\lambda_{\rm rel}} + \hat{g}_{2}^{\lambda_{\rm rel}} \mid rs \rangle, \\ \langle pq \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}^2} \mid rs \rangle = \langle pq \mid 2\hat{g}^{(4)} \mid rs \rangle \\ = 2 \Big\{ \sum_{t} A_{tp}^{\lambda_{\rm rel}*} \langle tq \mid \hat{g}_{1}^{\lambda_{\rm rel}} \mid rs \rangle + \sum_{t} A_{tq}^{\lambda_{\rm rel}*} \langle pt \mid \hat{g}_{2}^{\lambda_{\rm rel}} \mid rs \rangle \\ + \sum_{t} A_{tr}^{\lambda_{\rm rel}} \langle pq \mid \hat{g}_{1}^{\lambda_{\rm rel}} \mid ts \rangle \\ + \sum_{t} A_{ts}^{\lambda_{\rm rel}} \langle pq \mid \hat{g}_{2}^{\lambda_{\rm rel}} \mid rt \rangle + \langle pq \mid \hat{g}_{12}^{\lambda_{\rm rel}} \mid rs \rangle \Big\}, \quad (IV.141) \end{split}$$

as well as the definitions of the derivatives

$$\frac{\partial f_{pq}^{(\lambda_{\rm rel})}}{\partial \lambda_{\rm rel}} = \frac{\partial}{\partial \lambda_{\rm rel}} \Big(\langle p \mid \frac{\partial \hat{h}}{\partial \lambda_{\rm rel}} \mid q \rangle + \sum_{k} \langle pk \mid \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm rel}} \mid \mid qk \rangle \Big)$$

$$\begin{split} &= \langle p^{(2)} \mid \hat{h}^{(2)} \mid q \rangle + \langle p \mid \hat{h}^{(2)} \mid q^{(2)} \rangle + \langle p \mid 2\hat{h}^{(4)} \mid q \rangle \\ &+ \sum_{k} \left(\langle p^{(2)}k \mid | \hat{g}^{(2)} \mid | qk \rangle + \langle pq \mid | \hat{g}^{(2)} \mid | q^{(2)}k \rangle + \langle pk^{(2)} \mid | \hat{g}^{(2)} \mid | qk \rangle \right) \\ &+ \langle pk \mid | \hat{g}^{(2)} \mid | qk^{(2)} \rangle + \langle pk \mid | 2\hat{g}^{(4)} \mid | qk \rangle \right) \\ &= \sum_{t} \left[\left(U_{tp}^{\lambda_{rel}*} + 2A_{tp}^{\lambda_{rel}*} \right) h_{tq}^{\lambda_{rel}} + \left(U_{tq}^{\lambda_{rel}} + 2A_{tq}^{\lambda_{rel}} \right) h_{pt}^{\lambda_{rel}} \right] - 4m \sum_{ts} A_{tp}^{\lambda_{rel}*} S_{ts}^{\lambda_{rel}} A_{sq}^{\lambda_{rel}} \\ &+ \sum_{tk} \left(U_{tp}^{\lambda_{rel}*} \langle tk \mid | \hat{g}_{1}^{\lambda_{rel}} + \hat{g}_{2}^{\lambda_{rel}} \mid | qk \rangle + 2A_{tq}^{\lambda_{rel}*} \langle tk \mid | \hat{g}_{1}^{\lambda_{rel}} \mid | qk \rangle \right) \\ &+ \sum_{tk} \left(U_{tq}^{\lambda_{rel}} \langle tk \mid | \hat{g}_{1}^{\lambda_{rel}} + \hat{g}_{2}^{\lambda_{rel}} \mid | pk \rangle^{*} + 2A_{tq}^{\lambda_{rel}} \langle tk \mid | \hat{g}_{1}^{\lambda_{rel}} \mid | pk \rangle^{*} \right) \\ &+ \sum_{tk} \left(U_{tk}^{\lambda_{rel}} \langle pt \mid | \hat{g}_{1}^{\lambda_{rel}} + \hat{g}_{2}^{\lambda_{rel}} \mid | pk \rangle^{*} + 2A_{tk}^{\lambda_{rel}} \langle pt \mid | \hat{g}_{2}^{\lambda_{rel}} \mid | pk \rangle^{*} \right) \\ &+ \sum_{tk} \left(U_{tk}^{\lambda_{rel}} \langle qt \mid | \hat{g}_{1}^{\lambda_{rel}} + \hat{g}_{2}^{\lambda_{rel}} \mid | pk \rangle^{*} + 2A_{tk}^{\lambda_{rel}} \langle qt \mid | \hat{g}_{2}^{\lambda_{rel}} \mid | pk \rangle^{*} \right) \\ &+ 2\sum_{k} \langle pk \mid | \hat{g}_{12}^{\lambda_{rel}} \mid | qk \rangle, \end{split}$$
(IV.143)

and

$$\frac{\partial S_{pq}^{\lambda_{\text{rel}}}}{\partial \lambda_{\text{rel}}} = \frac{\partial}{\partial \lambda_{\text{rel}}} \langle p \mid \frac{\partial \hat{S}}{\partial \lambda_{\text{rel}}} \mid q \rangle = \langle p^{(2)} \mid \hat{S}^{(2)} \mid q \rangle + \langle p \mid \hat{S}^{(2)} \mid q^{(2)} \rangle + \langle p \mid 2\hat{S}^{(4)} \mid q \rangle$$

$$= \sum_{t} \left\{ (U_{tp}^{\lambda_{\text{rel}}*} + 2A_{tp}^{\lambda_{\text{rel}}*}) S_{tq}^{\lambda_{\text{rel}}} + (U_{tq}^{\lambda_{\text{rel}}} + 2A_{tq}^{\lambda_{\text{rel}}}) S_{pt}^{\lambda_{\text{rel}}} \right\}. \quad (\text{IV.144})$$

For the evaluation of Z_{ai} and I_{pq} instead of taking the derivative of the Lagrangian with respect to the MO coefficients $\partial \tilde{E}/\partial c_{\mu q}$ as discussed in chapter III.2, (IV.131) is rewritten using the orbital rotation

$$c'_{\mu p} = \sum_{q} c_{\mu q} T_{qp} \tag{IV.145}$$

with the stationarity condition for the Lagrangian

$$\left(\frac{\partial \tilde{E}}{\partial T_{qp}}\right)_{T=1} = 0 \tag{IV.146}$$

yielding

$$\tilde{E} = \sum_{pqrs} \Gamma_{pqrs} \sum_{tuvw} T_{tp}^* T_{uq}^* T_{vr} T_{ws} \langle tu \mid\mid \hat{g} \mid\mid vw \rangle$$

57

$$+\sum_{pq} D_{pq} \sum_{tv} T_{tp}^{*} T_{vq} \left[h_{tv} + \sum_{uw} \sum_{l} T_{ul}^{*} T_{wl} \langle tu \mid| \hat{g} \mid| vw \rangle \right] \\ + \sum_{bj} Z_{bj} \sum_{tv} T_{tb}^{*} T_{vj} \left[h_{tv} + \sum_{uw} \sum_{l} T_{ul}^{*} T_{wl} \langle tu \mid| \hat{g} \mid| vw \rangle \right] \\ + \sum_{pq} I_{pq} \sum_{tv} (T_{tp}^{*} T_{vq} S_{tv} - \delta_{tv}).$$
(IV.147)

Taking the derivative of \tilde{E} with respect to T_{ai} at T = 1 gives

$$\begin{pmatrix} \frac{\partial \tilde{E}}{\partial T_{ai}} \end{pmatrix}_{T=1} = 0$$

$$= \sum_{qrs} \Gamma_{iqrs}^{*} \langle aq \mid | \hat{g} \mid | rs \rangle^{*} + \sum_{prs} \Gamma_{pirs}^{*} \langle pa \mid | \hat{g} \mid | rs \rangle^{*}$$

$$+ \sum_{pqs} \Gamma_{pqis} \langle pq \mid | \hat{g} \mid | as \rangle + \sum_{pqr} \Gamma_{pqri} \langle pq \mid | \hat{g} \mid | ra \rangle$$

$$+ \sum_{q} D_{iq}^{*} f_{aq}^{*} + \sum_{p} D_{pi} f_{pa}$$

$$+ \sum_{pq} D_{pq}^{*} \langle pa \mid | \hat{g} \mid | qi \rangle^{*} + \sum_{pq} D_{pq} \langle pi \mid | \hat{g} \mid | qa \rangle$$

$$+ \sum_{b} Z_{bi} f_{ba} + \sum_{bj} Z_{bj}^{*} \langle ba \mid | \hat{g} \mid | ji \rangle^{*} + \sum_{bj} Z_{bj} \langle bi \mid | \hat{g} \mid | ja \rangle$$

$$+ \sum_{q} I_{iq}^{*} S_{aq}^{*} + \sum_{p} I_{pi} S_{pa}$$
(IV.148)

which for MP2 yields

$$I_{ia}^{*} + I_{ai} = -2 \sum_{jbc} (\Gamma_{ijbc}^{*} \langle aj \mid \mid \hat{g} \mid \mid bc \rangle^{*} + \Gamma_{bcij} \langle bc \mid \mid \hat{g} \mid \mid aj \rangle)$$

$$- \sum_{pq} (D_{pq}^{*} \langle pa \mid \mid \hat{g} \mid \mid qi \rangle^{*} + D_{pq} \langle pi \mid \mid \hat{g} \mid \mid qa \rangle)$$

$$- \sum_{b} Z_{bi} f_{ba} - \sum_{bj} Z_{bj}^{*} \langle ba \mid \mid \hat{g} \mid \mid ji \rangle^{*} - \sum_{bj} Z_{bj} \langle bi \mid \mid \hat{g} \mid \mid ja \rangle.$$
(IV.149)

The derivative of \tilde{E} with respect to T_{ia} is given by

$$\left(\frac{\partial \tilde{E}}{\partial T_{ia}}\right)_{T=1} = 0$$

 $IV.3.\ DPT$ corrections at correlated levels of theory

$$= \sum_{qrs} \Gamma_{aqrs}^* \langle iq \mid | \hat{g} \mid | rs \rangle^* + \sum_{prs} \Gamma_{pars}^* \langle pi \mid | \hat{g} \mid | rs \rangle^* + \sum_{pqs} \Gamma_{pqas} \langle pq \mid | \hat{g} \mid | is \rangle + \sum_{pqr} \Gamma_{pqra} \langle pq \mid | \hat{g} \mid | ri \rangle + \sum_{q} D_{aq}^* f_{iq}^* + \sum_{p} D_{pa} f_{pi} + \sum_{q} I_{aq}^* f_{ij}^* + \sum_{p} I_{pa} S_{pi}$$
(IV.150)

which leads to

$$I_{ai}^{*} + I_{ia} = -2\sum_{bkj} (\Gamma_{abkj}^{*} \langle ib \mid \mid \hat{g} \mid \mid kj \rangle^{*} + \Gamma_{kjab} \langle kj \mid \mid \hat{g} \mid \mid ib \rangle)$$
$$-\sum_{j} Z_{aj}^{*} f_{ij}^{*}.$$
(IV.151)

In addition, the derivatives with respect to T_{ab} and T_{ij} lead to expressions for $I_{ab} + I_{ba}^*$ and $I_{ij} + I_{ji}^*$

$$\begin{pmatrix} \frac{\partial \tilde{E}}{\partial T_{ab}} \end{pmatrix}_{T=1} = 0$$

$$= \sum_{qrs} \Gamma^*_{bqrs} \langle aq \mid |\hat{g}| \mid rs \rangle^* + \sum_{prs} \Gamma^*_{pbrs} \langle pa \mid |\hat{g}| \mid rs \rangle^*$$

$$+ \sum_{pqs} \Gamma_{pqbs} \langle pq \mid |\hat{g}| \mid as \rangle + \sum_{pqr} \Gamma_{pqrb} \langle pq \mid |\hat{g}| \mid ra \rangle$$

$$+ \sum_{q} D^*_{bq} f^*_{aq} + \sum_{p} D_{pb} f_{pa}$$

$$+ \sum_{q} I^*_{bq} S^*_{aq} + \sum_{p} I_{pb} S_{pa}$$
(IV.152)

$$I_{ba}^{*} + I_{ab} = -2\sum_{cij} (\Gamma_{bcij}^{*} \langle ac \mid \mid \hat{g} \mid \mid ij \rangle^{*} + \Gamma_{ijbc} \langle ij \mid \mid \hat{g} \mid \mid ac \rangle)$$
$$-\sum_{c} (D_{bc}^{*} f_{ac}^{*} + D_{cb} f_{ca})$$
(IV.153)

59

$$\begin{pmatrix} \frac{\partial \tilde{E}}{\partial T_{ij}} \end{pmatrix}_{T=1} = 0$$

$$= \sum_{qrs} \Gamma_{jqrs}^{*} \langle iq \parallel \hat{g} \parallel rs \rangle^{*} + \sum_{prs} \Gamma_{pjrs}^{*} \langle pi \parallel \hat{g} \parallel rs \rangle^{*} \\
+ \sum_{pqs} \Gamma_{pqjs} \langle pq \parallel \hat{g} \parallel is \rangle + \sum_{pqr} \Gamma_{pqrj} \langle pq \parallel \hat{g} \parallel ri \rangle \\
+ \sum_{q} D_{jq}^{*} f_{iq}^{*} + \sum_{p} D_{pj} f_{pi} \\
+ \sum_{pq} D_{pq}^{*} \langle pi \parallel \hat{g} \parallel qj \rangle^{*} + \sum_{pq} D_{pq} \langle pj \parallel \hat{g} \parallel qi \rangle \\
+ \sum_{b} Z_{bj} f_{bi} \\
+ \sum_{bk} Z_{bk}^{*} \langle bi \parallel \hat{g} \parallel kj \rangle^{*} + \sum_{bk} Z_{bk} \langle bj \parallel \hat{g} \parallel ki \rangle \\
+ \sum_{q} I_{jq}^{*} S_{iq}^{*} + \sum_{p} I_{pj} S_{pi} \qquad (IV.154)$$

$$I_{ji}^{*} + I_{ij} = -2 \sum_{kab} (\Gamma_{jkab}^{*} \langle ik || \hat{g} || ab \rangle^{*} + \Gamma_{abjk} \langle ab || \hat{g} || ik \rangle) - \sum_{k} (D_{jk}^{*} f_{ik}^{*} + D_{kj} f_{ki}) - \sum_{pq} (D_{pq}^{*} \langle pi || \hat{g} || qj \rangle^{*} + D_{pq} \langle pj || \hat{g} || qi \rangle) - \sum_{bk} (Z_{bk}^{*} \langle bi || \hat{g} || kj \rangle^{*} + Z_{bk} \langle bj || \hat{g} || ki \rangle).$$
(IV.155)

Note that the Lagrange multipliers ${\cal I}_{pq}$ may then be evaluated in a symmetrized form, i.e.,

$$I_{pq} \to \frac{1}{2}(I_{pq} + I_{qp}^*).$$
 (IV.156)

Subtracting the complex conjugate of (IV.151) from (IV.149) yields the Z-vector equations

$$\sum_{bj} \left[Z_{bj}^* \langle ba \mid| \hat{g} \mid| ji \rangle^* + Z_{bj} (\langle bi \mid| \hat{g} \mid| ja \rangle + f_{ba} \delta_{ij} - f_{ij} \delta_{ab}) \right]$$
$$= -4 \sum_{jbc} \Gamma_{bcij} \langle bc \mid| \hat{g} \mid| aj \rangle$$
$$+ 4 \sum_{bkj} \Gamma_{abkj} \langle ib \mid| \hat{g} \mid| kj \rangle$$

60

IV.3. DPT corrections at correlated levels of theory

$$-\sum_{pq} (D_{pq}^* \langle pa \mid\mid \hat{g} \mid\mid qi \rangle^* + D_{pq} \langle pi \mid\mid \hat{g} \mid\mid qa \rangle).$$
(IV.157)

In the DPT4 energy equation, the derivative of Z_{ai} is needed as well. Accordingly, the obtained Z-vector equations are differentiated once more with respect to λ_{rel}

$$\begin{split} \sum_{bj} \left[\frac{\partial Z_{bj}^{*}}{\partial \lambda_{\text{rel}}} \langle ba \mid\mid \hat{g} \mid\mid ji \rangle^{*} + \frac{\partial Z_{bj}}{\partial \lambda_{\text{rel}}} (\langle bi \mid\mid \hat{g} \mid\mid ja \rangle + (\varepsilon_{a} - \varepsilon_{i})\delta_{ij}\delta_{ab}) \right] \\ &= -\sum_{bj} \left[Z_{bj}^{*} \frac{\partial \langle ba \mid\mid \hat{g} \mid\mid ji \rangle^{*}}{\partial \lambda_{\text{rel}}} + Z_{bj} \left(\frac{\partial \langle bi \mid\mid \hat{g} \mid\mid ja \rangle}{\partial \lambda_{\text{rel}}} + \frac{\partial f_{ba}}{\partial \lambda_{\text{rel}}} \delta_{ij} - \frac{\partial f_{ij}}{\partial \lambda_{\text{rel}}} \delta_{ab} \right) \right] \\ &- 4\sum_{jbc} \left[\frac{\partial \Gamma_{bcij}}{\partial \lambda_{\text{rel}}} \langle bc \mid\mid \hat{g} \mid\mid aj \rangle + \Gamma_{bcij} \frac{\partial \langle bc \mid\mid \hat{g} \mid\mid aj \rangle}{\partial \lambda_{\text{rel}}} \right] \\ &+ 4\sum_{bkj} \left[\frac{\partial \Gamma_{abkj}}{\partial \lambda_{\text{rel}}} \langle ib \mid\mid \hat{g} \mid\mid kj \rangle + \Gamma_{abkj} \frac{\partial \langle ib \mid\mid \hat{g} \mid\mid kj \rangle}{\partial \lambda_{\text{rel}}} \right] \\ &- \sum_{pq} \left[\frac{\partial D_{pq}^{*}}{\partial \lambda_{\text{rel}}} \langle pa \mid\mid \hat{g} \mid\mid qi \rangle^{*} + \frac{\partial D_{pq}}{\partial \lambda_{\text{rel}}} \langle pi \mid\mid \hat{g} \mid\mid qa \rangle \\ &+ D_{pq}^{*} \frac{\partial \langle pa \mid\mid \hat{g} \mid\mid qi \rangle^{*}}{\partial \lambda_{\text{rel}}} + D_{pq} \frac{\partial \langle pi \mid\mid \hat{g} \mid\mid qa \rangle}{\partial \lambda_{\text{rel}}} \right]. \end{split}$$
(IV.158)

Furthermore, the derivatives of I_{pq} with respect to λ_{rel} are needed and may be obtained by differentiating (IV.151), (IV.153), and (IV.155) respectively, leading to

$$\frac{\partial (I_{ai}^{*} + I_{ia})}{\partial \lambda_{\rm rel}} = -2 \sum_{bkj} \left(\frac{\partial \Gamma_{abkj}^{*}}{\partial \lambda_{\rm rel}} \langle ib \mid |\hat{g} \mid |kj\rangle^{*} + \Gamma_{abkj}^{*} \frac{\partial \langle ib \mid |\hat{g} \mid |kj\rangle^{*}}{\partial \lambda_{\rm rel}} \right. \\
\left. + \frac{\partial \Gamma_{kjab}}{\partial \lambda_{\rm rel}} \langle kj \mid |\hat{g} \mid |ib\rangle + \Gamma_{kjab} \frac{\partial \langle kj \mid |\hat{g} \mid |ib\rangle}{\lambda_{\rm rel}} \right) \right) \\
\left. - \sum_{j} \left(\frac{\partial Z_{aj}^{*}}{\partial \lambda_{\rm rel}} f_{ij}^{*} + Z_{aj}^{*} \frac{\partial f_{ij}^{*}}{\partial \lambda_{\rm rel}} \right), \qquad (IV.159) \\
\frac{\partial (I_{ba}^{*} + I_{ab})}{\partial \lambda_{\rm rel}} = -2 \sum_{cij} \left(\frac{\partial \Gamma_{bcij}^{*}}{\partial \lambda_{\rm rel}} \langle ac \mid |\hat{g} \mid |ij\rangle^{*} + \Gamma_{bcij}^{*} \frac{\partial \langle ac \mid |\hat{g} \mid |ij\rangle^{*}}{\partial \lambda_{\rm rel}} \right. \\
\left. + \frac{\partial \Gamma_{ijbc}}{\partial \lambda_{\rm rel}} \langle ij \mid |\hat{g} \mid |ac\rangle + \Gamma_{ijbc} \frac{\partial \langle ij \mid |\hat{g} \mid |ac\rangle}{\partial \lambda_{\rm rel}} \right)$$

$$-\sum_{c} \left(\frac{\partial D_{bc}^{*}}{\partial \lambda_{rel}} f_{ac}^{*} + D_{bc}^{*} \frac{\partial f_{ac}^{*}}{\partial \lambda_{rel}} + \frac{\partial D_{cb}}{\partial \lambda_{rel}} f_{ca} + D_{cb} \frac{\partial f_{ca}}{\partial \lambda_{rel}} \right), \quad (IV.160)$$

$$\frac{\partial (I_{ji}^{*} + I_{ij})}{\partial \lambda_{rel}} = -2\sum_{kab} \left(\frac{\partial \Gamma_{jkab}^{*}}{\partial \lambda_{rel}} \langle ik \parallel \hat{g} \parallel ab \rangle^{*} + \Gamma_{jkab}^{*} \frac{\partial \langle ik \parallel \hat{g} \parallel ab \rangle^{*}}{\partial \lambda_{rel}} + \frac{\partial \Gamma_{abjk}}{\partial \lambda_{rel}} \langle ab \parallel \hat{g} \parallel ik \rangle + \Gamma_{abjk} \frac{\partial \langle ab \parallel \hat{g} \parallel ik \rangle}{\partial \lambda_{rel}} \right)$$

$$-\sum_{k} \left(\frac{\partial D_{jk}^{*}}{\partial \lambda_{rel}} f_{ik}^{*} + D_{jk}^{*} \frac{\partial f_{ik}^{*}}{\partial \lambda_{rel}} + \frac{\partial D_{kj}}{\partial \lambda_{rel}} f_{ki} + D_{kj} \frac{\partial f_{ki}}{\partial \lambda_{rel}} \right)$$

$$-\sum_{pq} \left(\frac{\partial D_{pq}^{*}}{\partial \lambda_{rel}} \langle pi \parallel \hat{g} \parallel qj \rangle^{*} + D_{pq}^{*} \frac{\partial \langle pi \parallel \hat{g} \parallel qj \rangle^{*}}{\partial \lambda_{rel}} \right)$$

$$-\sum_{bk} \left(\frac{\partial Z_{bk}^{*}}{\partial \lambda_{rel}} \langle bi \parallel \hat{g} \parallel kj \rangle^{*} + Z_{bk} \frac{\partial \langle bi \parallel \hat{g} \parallel kj \rangle^{*}}{\partial \lambda_{rel}} \right)$$

$$(IV.161)$$

IV.3.1. Separation of scalar-relativistic and spin-orbit contribution

As in the HF case, the separation of the SR and SO contributions is achieved using the Dirac identity (IV.53). Writing down the SR-DPT4 energy for MP2 is therefore straightforward, i.e., all Pauli spin matrices are dropped and as all quantities are real, no special care needs to be taken for the complex-conjugate expressions. The spin adaptation for closed-shell systems is achieved as in the non-relativistic case which means that all quantities involving two-electron integrals are expressed in terms of the ' $\alpha\beta\alpha\beta$ ' spin case, i.e., it is exploited that

$$\langle pq \mid \mid \hat{g} \mid \mid rs \rangle = \langle \overline{pq} \mid \mid \hat{g} \mid \mid \overline{rs} \rangle$$

$$= \langle pq \mid \hat{g} \mid rs \rangle - \langle pq \mid \hat{g} \mid sr \rangle$$

$$= \langle \overline{pq} \mid \hat{g} \mid \overline{rs} \rangle - \langle \overline{pq} \mid \hat{g} \mid \overline{sr} \rangle$$

$$= \langle p\overline{q} \mid \hat{g} \mid r\overline{s} \rangle - \langle p\overline{q} \mid \hat{g} \mid s\overline{r} \rangle$$

$$\langle p\overline{q} \mid \mid \hat{g} \mid \mid r\overline{s} \rangle = \langle \overline{pq} \mid \mid \hat{g} \mid \mid \overline{rs} \rangle$$

$$= \langle p\overline{q} \mid \hat{g} \mid r\overline{s} \rangle$$

$$\langle p\overline{q} \mid| \hat{g} \mid| \overline{r}s \rangle = \langle \overline{p}q \mid| \hat{g} \mid| r\overline{s} \rangle$$
$$= - \langle p\overline{q} \mid \hat{g} \mid s\overline{r} \rangle$$

with

$$|p\rangle = |\phi_p \alpha\rangle, \quad |\overline{p}\rangle = |\phi_p \beta\rangle.$$
 (IV.162)

The spin-adapted SR-DPT4 energy at the MP2 level is then given by

$$E_{\rm SR}^{(4)} = \frac{1}{2} \left[\sum_{ij} \sum_{ab} \frac{1}{2} \frac{\partial t_{ij}^{a\bar{b}}}{\partial \lambda_{\rm SR}} \left(8\langle ij \mid \hat{g}_1^{\rm SR} + \hat{g}_2^{\rm SR} \mid ab \rangle - 4\langle ij \mid \hat{g}_1^{\rm SR} + \hat{g}_2^{\rm SR} \mid ba \rangle \right) + \sum_{ij} \sum_{ab} \frac{1}{2} t_{i\bar{j}}^{a\bar{b}} \left(8 \frac{\partial \langle ij \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm SR}} \mid ab \rangle}{\partial \lambda_{\rm SR}} - 4 \frac{\partial \langle ij \mid \frac{\partial \hat{g}}{\partial \lambda_{\rm SR}} \mid ba \rangle}{\partial \lambda_{\rm SR}} \right) + 2 \sum_{ij} \left[\frac{\partial D_{ij}}{\partial \lambda_{\rm SR}} f_{ij}^{(\rm SR)} + D_{ij} \frac{\partial f_{ij}^{(\rm SR)}}{\partial \lambda_{\rm SR}} \right] + 2 \sum_{ab} \left[\frac{\partial D_{ab}}{\partial \lambda_{\rm SR}} f_{ab}^{(\rm SR)} + D_{ab} \frac{\partial f_{ab}^{(\rm SR)}}{\partial \lambda_{\rm SR}} \right] + 2 \sum_{ai} \left[\frac{\partial Z_{ai}}{\partial \lambda_{\rm SR}} f_{ai}^{(\rm SR)} + Z_{ai} \frac{\partial f_{ai}^{(\rm SR)}}{\partial \lambda_{\rm SR}} \right] + 2 \sum_{pq} \left[\frac{\partial I_{pq}}{\partial \lambda_{\rm SR}} S_{pq}^{\rm SR} + I_{pq} \frac{\partial S_{pq}^{\rm SR}}{\partial \lambda_{\rm SR}} \right] \right]$$
(IV.163)

with the definitions of the SR perturbed and unperturbed density matrices, Lagrange multipliers, and integrals given in Appendix IX.6.

In order to get the same basic equations after spin integration for the three SO components, i.e., SOx, SOy, and SOz, as well as to reduce all terms to a single spin case, it is useful to define the following skeleton quantities

$$\frac{\partial \tilde{t}_{ij}^{ab}}{\partial \lambda_{\text{SO}c}} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \Biggl[\sum_p U_{pa}^{\text{SO}c*} \langle pb \mid ij \rangle + \sum_p U_{pi}^{\text{SO}c} \langle ab \mid pj \rangle \\ + \langle ab \mid g_1^{\text{SO}c} \mid ij \rangle - \sum_m \frac{\partial f_{mi}}{\partial \lambda_{\text{SO}c}} t_{m\bar{j}}^{a\bar{b}} + \sum_e \frac{\partial f_{ae}}{\partial \lambda_{\text{SO}c}} t_{i\bar{j}}^{e\bar{b}} \Biggr], \quad (\text{IV.164})$$

$$\frac{\partial G_{rs}^{pq}}{\partial \lambda_{\text{SO}c}} = \sum_{t} U_{tp}^{\text{SO}c*} \langle tq \mid rs \rangle + \sum_{t} U_{tr}^{\text{SO}c} \langle pq \mid ts \rangle + \langle pq \mid \hat{g}_{1}^{\text{SO}c} \mid rs \rangle.$$
(IV.165)

This procedure may be exemplary shown for the different spin cases of the perturbed amplitudes of the SOx component. From (IV.135) it follows

$$\frac{\partial t_{i\bar{j}}^{\bar{a}\bar{b}}}{\partial\lambda_{SOx}} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \left[\sum_p U_{p\bar{a}}^{SOx*} \langle pb \mid ij \rangle + \sum_p U_{p\bar{b}}^{SOx*} (-\langle qp \mid ji \rangle) + \sum_p U_{p\bar{b}}^{SOx} (\langle ab \mid pj \rangle - \langle ab \mid jp \rangle) + \langle \bar{a}\bar{b} \mid \hat{g}_1^{SOx} \mid i\bar{j} \rangle - \langle \bar{a}\bar{b} \mid \hat{g}_2^{SOx} \mid \bar{j}i \rangle - \sum_m \frac{\partial f_{\bar{m}i}}{\partial\lambda_{SOx}} t_{\bar{m}\bar{j}}^{\bar{a}\bar{b}} + \sum_e \frac{\partial f_{\bar{a}e}}{\partial\lambda_{SOx}} t_{i\bar{j}}^{\bar{b}\bar{b}} + \sum_e \frac{\partial f_{\bar{b}e}}{\partial\lambda_{SOx}} t_{i\bar{j}}^{\bar{a}e} \right] = \frac{\partial t_{ij}^{ab}}{\partial\lambda_{SOx}} = \frac{\partial \tilde{t}_{ij}^{ab}}{\partial\lambda_{SOx}} - \frac{\partial \tilde{t}_{ij}^{ba}}{\partial\lambda_{SOx}}, \quad (IV.166)$$

$$\frac{\partial t_{\bar{i}\bar{j}}^{\bar{a}\bar{b}}}{\partial\lambda_{\rm SOx}} = \frac{\partial t_{i\bar{j}}^{a\bar{b}}}{\partial\lambda_{\rm SOx}} = \frac{\partial t_{j\bar{i}}^{\bar{a}\bar{b}}}{\partial\lambda_{\rm SOx}} = \frac{\partial \tilde{t}_{ji}^{ba}}{\partial\lambda_{\rm SOx}} - \frac{\partial \tilde{t}_{ji}^{ab}}{\partial\lambda_{\rm SOx}}, \qquad (\text{IV.167})$$

$$\frac{\partial t_{ij}^{a\bar{b}}}{\partial \lambda_{aa}} = \frac{\partial t_{ij}^{\bar{a}b}}{\partial \lambda_{aa}} = \frac{\partial \tilde{t}_{ij}^{ab}}{\partial \lambda_{aa}} - \frac{\partial \tilde{t}_{ji}^{ab}}{\partial \lambda_{aa}}, \qquad (IV.168)$$

$$\frac{\partial t_{\rm SOx}^{\bar{a}\bar{b}}}{\partial \lambda_{\rm SOx}} = \frac{\partial t_{ij}^{\bar{a}\bar{b}}}{\partial \lambda_{\rm SOx}} = \frac{\partial t_{\bar{i}\bar{j}}^{\bar{b}\bar{a}}}{\partial \lambda_{\rm SOx}} = \frac{\partial t_{ji}^{\bar{b}\bar{a}}}{\partial \lambda_{\rm SOx}} = \frac{\partial t_{ji}^{\bar{b}\bar{a}}}{\partial \lambda_{\rm SOx}} - \frac{\partial \tilde{t}_{ij}^{\bar{b}a}}{\partial \lambda_{\rm SOx}}.$$
 (IV.169)

After spin adaptation, the DPT4-SO energy at the MP2 level for a specific SO component c=x,y,z reads

$$\begin{split} E_{\mathrm{SOc}}^{(4)} = &\frac{1}{2} \sum_{ij} \sum_{ab} \frac{\partial \tilde{t}_{ij}^{ab}}{\partial \lambda_{\mathrm{SOc}}} \left(8\langle ij \mid \hat{g}_{1}^{\mathrm{SOc}} \mid ab \rangle - 4\langle ij \mid \hat{g}_{1}^{\mathrm{SOc}} \mid ba \rangle - 4\langle ij \mid \hat{g}_{2}^{\mathrm{SOc}} \mid ba \rangle \right) \\ &+ \frac{1}{2} \sum_{ij} \sum_{ab} t_{i\bar{j}}^{a\bar{b}} \left(\sum_{c} U_{ci}^{\mathrm{SOc}*} (8\langle cj \mid \hat{g}_{1}^{\mathrm{SOc}} \mid ab \rangle - 4\langle cj \mid \hat{g}_{1}^{\mathrm{SOc}} \mid ba \rangle - 4\langle cj \mid \hat{g}_{2}^{\mathrm{SOc}} \mid ba \rangle \right) \\ &+ \sum_{k} U_{ak}^{\mathrm{SOc}} (8\langle kb \mid \hat{g}_{1}^{\mathrm{SOc}} \mid ij \rangle^{*} - 4\langle kb \mid \hat{g}_{1}^{\mathrm{SOc}} \mid ji \rangle^{*} - 4\langle kb \mid \hat{g}_{2}^{\mathrm{SOc}} \mid ji \rangle^{*} \right) \\ &+ 2 \sum_{p} A_{pi}^{\mathrm{SOc}*} (8\langle pj \mid \hat{g}_{1}^{\mathrm{SOc}} \mid ab \rangle - 4\langle pj \mid \hat{g}_{1}^{\mathrm{SOc}} \mid ba \rangle) \end{split}$$

$$+ 2\sum_{p} A_{pa}^{\text{SOc}} (8\langle pb \mid \hat{g}_{1}^{\text{SOc}} \mid ij \rangle^{*} - 4\langle pb \mid \hat{g}_{1}^{\text{SOc}} \mid ji \rangle^{*}) - 4\langle ij \mid \hat{g}_{12}^{\text{SOc}} \mid ba \rangle \right)$$

$$+ \sum_{ij} \left(\frac{\partial D_{ij}}{\partial \lambda_{\text{SOc}}} f_{ij}^{(\text{SO})c} + D_{ij} \frac{\partial f_{ij}^{(\text{SO})c}}{\partial \lambda_{\text{SOc}}} \right)$$

$$+ \sum_{ab} \left(\frac{\partial D_{ab}}{\partial \lambda_{\text{SOc}}} f_{ab}^{(\text{SO})c} + D_{ab} \frac{\partial f_{ab}^{(\text{SO})c}}{\partial \lambda_{\text{SOc}}} \right)$$

$$+ \sum_{ai} \left(\frac{\partial Z_{ai}}{\partial \lambda_{\text{SOc}}} f_{ai}^{(\text{SO})c} + Z_{ai} \frac{\partial f_{ai}^{(\text{SO})c}}{\partial \lambda_{\text{SOc}}} \right)$$
(IV.170)

with

$$\frac{\partial D_{ij}}{\partial \lambda_{SOc}} = -\frac{1}{2} \sum_{k} \sum_{ab} \left[\left(-4 \frac{\partial \tilde{t}_{jk}^{ba}}{\partial \lambda_{SOc}} + 2 \frac{\partial \tilde{t}_{jk}^{ab}}{\partial \lambda_{SOc}} + 2 \frac{\partial \tilde{t}_{kj}^{ba}}{\partial \lambda_{SOc}} \right) t_{k\bar{i}}^{a\bar{b}} + t_{k\bar{j}}^{a\bar{b}} \left(4 \frac{\partial \tilde{t}_{ik}^{ba}}{\partial \lambda_{SOc}} - 2 \frac{\partial \tilde{t}_{ik}^{ab}}{\partial \lambda_{SOc}} - 2 \frac{\partial \tilde{t}_{ki}^{ba}}{\partial \lambda_{SOc}} \right) \right], \quad (IV.171)$$

$$\frac{\partial D_{ab}}{\partial \lambda_{SOc}} = \frac{1}{2} \sum_{a} \sum_{ij} \left[\left(-4 \frac{\partial \tilde{t}_{ij}^{ac}}{\partial \lambda_{SOc}} + 2 \frac{\partial \tilde{t}_{ji}^{ac}}{\partial \lambda_{SOc}} + 2 \frac{\partial \tilde{t}_{ij}^{ca}}{\partial \lambda_{SOc}} \right) t_{i\bar{j}}^{b\bar{c}} + t_{i\bar{j}}^{a\bar{c}} \left(4 \frac{\partial \tilde{t}_{ij}^{bc}}{\partial \lambda_{SOc}} - 2 \frac{\partial \tilde{t}_{ji}^{bc}}{\partial \lambda_{SOc}} - 2 \frac{\partial \tilde{t}_{ij}^{cb}}{\partial \lambda_{SOc}} \right) \right], \quad (IV.172)$$

$$\frac{\partial f_{pq}}{\partial \lambda_{\text{SO}c}} = f_{pq}^{\text{SO}c} = f_{pq}^{(\text{SO})c} + \sum_{k} \sum_{a} U_{ak}^{\text{SO}c} \left(\langle pa \mid kq \rangle - \langle pk \mid aq \rangle \right), \qquad (\text{IV.173})$$

$$\begin{split} \frac{\partial f_{pq}^{(\mathrm{SO})c}}{\partial \lambda_{(\mathrm{SO})c}} &= \sum_{r} \left(U_{rp}^{\mathrm{SO}c*} f_{rq}^{(\mathrm{SO})c} + U_{rq}^{\mathrm{SO}c} f_{rp}^{(\mathrm{SO})c*} \right) \\ &+ \sum_{r} 2A_{rp}^{\mathrm{SO}c*} \left[h_{rq}^{\mathrm{SO}c} + \sum_{j} (\langle rj \mid \hat{g}_{1}^{\mathrm{SO}c} \mid qj \rangle - \langle rj \mid \hat{g}_{1}^{\mathrm{SO}c} \mid jq \rangle) \right] \\ &+ \sum_{r} 2A_{rq}^{\mathrm{SO}c} \left[h_{rp}^{\mathrm{SO}c} + \sum_{j} (\langle rj \mid \hat{g}_{1}^{\mathrm{SO}c} \mid pj \rangle - \langle rj \mid \hat{g}_{1}^{\mathrm{SO}c} \mid jp \rangle) \right]^{*} \\ &- 4m \sum_{rs} A_{rp}^{\mathrm{SO}c*} S_{rs}^{\lambda_{rel}} A_{sq}^{\mathrm{SO}c} \\ &+ \sum_{j} U_{rj}^{\mathrm{SO}c*} (2\langle pr \mid \hat{g}_{2}^{\mathrm{SO}c} \mid qj \rangle - \langle pr \mid \hat{g}_{2}^{\mathrm{SO}c} \mid jq \rangle - \langle pr \mid \hat{g}_{1}^{\mathrm{SO}c} \mid jq \rangle) \\ &+ \sum_{j} U_{rj}^{\mathrm{SO}c} (2\langle qr \mid \hat{g}_{2}^{\mathrm{SO}c} \mid pj \rangle - \langle qr \mid \hat{g}_{2}^{\mathrm{SO}c} \mid jp \rangle - \langle qr \mid \hat{g}_{1}^{\mathrm{SO}c} \mid jp \rangle)^{*} \end{split}$$

$$+\sum_{j} 2A_{rj}^{\text{SO}c*}(2\langle pr \mid \hat{g}_{2}^{\text{SO}c} \mid qj \rangle - \langle pr \mid \hat{g}_{2}^{\text{SO}c} \mid jq \rangle) +\sum_{j} 2A_{rj}^{\text{SO}c}(2\langle qr \mid \hat{g}_{2}^{\text{SO}c} \mid pj \rangle - \langle qr \mid \hat{g}_{2}^{\text{SO}c} \mid jp \rangle)^{*} -\sum_{j} \langle pj \mid \hat{g}_{12}^{\text{SO}c} \mid jq \rangle,$$
(IV.174)

and the perturbed Z-vector equations for the SO perturbation

$$\begin{split} \sum_{bj} \frac{\partial Z_{\text{SOc}}^{\text{SOc}}}{\partial \lambda_{\text{SOc}}} \left[\langle ba \mid ij \rangle - \langle bi \mid aj \rangle + \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) \right] \\ &= -\sum_{bj} Z_{bj} \left[4 \frac{\partial \tilde{G}_{aj}^{ib}}{\partial \lambda_{\text{SOc}}} - \frac{\partial \tilde{G}_{aj}^{ib}}{\partial \lambda_{\text{SOc}}} + \frac{\partial \tilde{G}_{ja}^{ab}}{\partial \lambda_{\text{SOc}}} + \frac{\partial \tilde{G}_{ij}^{ba}}{\partial \lambda_{\text{SOc}}} + \frac{\partial f_{ba}}{\partial \lambda_{\text{SOc}}} \delta_{ij} - \frac{\partial f_{ij}}{\partial \lambda_{\text{SOc}}} \delta_{ab} \right] \\ &- \sum_{kj} \sum_{b} \left[4 \frac{\partial \tilde{t}_{kj}^{kb}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{t}_{kj}^{ib}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{t}_{jk}^{ab}}{\partial \lambda_{\text{SOc}}} \right] \langle kj \mid ib \rangle \\ &- \sum_{kj} \sum_{b} t_{kj}^{ab} \left[4 \frac{\partial \tilde{G}_{ib}^{kj}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{G}_{jk}^{ib}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{G}_{bi}^{kj}}{\partial \lambda_{\text{SOc}}} \right] \\ &+ \sum_{bc} \sum_{j} t_{ij}^{ab} \left[4 \frac{\partial \tilde{G}_{ib}^{c}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{G}_{bi}^{jc}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{G}_{bi}^{kj}}{\partial \lambda_{\text{SOc}}} \right] \langle aj \mid cb \rangle \\ &+ \sum_{bc} \sum_{j} t_{ij}^{cb} \left[4 \frac{\partial \tilde{G}_{ab}^{c}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{G}_{bc}^{aj}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{G}_{cb}^{ja}}{\partial \lambda_{\text{SOc}}} \right] \\ &- \sum_{km} \left\{ \frac{\partial D_{mk}}{\partial \lambda_{\text{SOc}}} (\langle ma \mid ik \rangle - \langle mi \mid ak \rangle) + D_{mk} \left[4 \frac{\partial \tilde{G}_{ak}^{ci}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{G}_{ka}^{ci}}{\partial \lambda_{\text{SOc}}} \right] \right\} \\ &- \sum_{bc} \left\{ \frac{\partial D_{bc}}{\partial \lambda_{\text{SOc}}} (\langle ba \mid ic \rangle - \langle bi \mid ac \rangle) + D_{ab} \left[4 \frac{\partial \tilde{G}_{ac}^{ci}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{G}_{ac}^{ib}}{\partial \lambda_{\text{SOc}}} - 2 \frac{\partial \tilde{G}_{ac}^{ib}}}{\partial \lambda_{\text{SOc}}} \right] \right\} . \end{split}$$
(IV.175)

Note that no SO contributions appear for the last two terms in (IV.134), i.e., those that involve the perturbed and unperturbed Lagrange multipliers I_{pq} and $\partial I_{pq}/\partial \lambda_{rel}$.

IV.4. DPT4 for electrical properties

First-order properties may be expressed as first derivatives of the energy with respect to an adequately chosen perturbation parameter.¹⁰¹ In this way, the electrical-field gradient (efg) at a specific nucleus is obtained by differentiating the energy with respect to the corresponding nuclear quadrupole moment while the dipole moment is computed as first derivative of the energy with respect to the components of an external electrical field $\boldsymbol{\epsilon}$. For the quadrupole moment the differentiation has to be carried out with respect to the gradient of the electric field $\mathbf{E} = \nabla \boldsymbol{\epsilon}$. As the DPT4 energy is already given as a second derivative of the energy, the corresponding corrections to first-order electrical properties are defined by means of third derivatives. However, since in this work the corrections are calculated using finite-difference techniques, the main issue in the following is how the DPT energy expression is affected by switching on an external perturbation. Due to such a perturbation, the potential V is augmented by the following additional contributions:

$$V \to V - \hat{\mu} \epsilon$$
 (dipole moment) (IV.176)

$$V \to V - \hat{Q} \mathbf{E}$$
 (quadrupole moment) (IV.177)

$$V \to V + \hat{\mathbf{q}} \, \boldsymbol{Q}$$
 (efg) (IV.178)

with the dipole operator $\hat{\mu}$, the quadrupole operator \hat{Q} , the nuclear quadrupole moment tensor Q, and the operator \hat{q} for the efg at this nucleus.

Considering the DPT energy expressions given in Eqs. (IV.31) and (IV.51), this leads, beside a change in the unperturbed non-relativistic orbitals and orbital energies, to the following corrections: for the dipole moment, the potential in the perturbed operator $\hat{h}^{\lambda_{\text{rel}}}$ has to be augmented by the term $-\hat{\mu}\epsilon$ leading to

$$h_{pq}^{\lambda_{\rm rel}} = \frac{1}{4m^2} \langle \varphi_p \mid \boldsymbol{\sigma} \hat{\mathbf{p}} V \boldsymbol{\sigma} \hat{\mathbf{p}} \mid \varphi_q \rangle \to \frac{1}{4m^2} \langle \varphi_p \mid \boldsymbol{\sigma} \hat{\mathbf{p}} (V - \hat{\boldsymbol{\mu}} \boldsymbol{\epsilon}) \boldsymbol{\sigma} \hat{\mathbf{p}} \mid \varphi_q \rangle, \qquad (\text{IV.179})$$

for the quadrupole moment by the term $-\hat{\mathbf{Q}}\mathbf{E}$,

$$h_{pq}^{\lambda_{\rm rel}} = \frac{1}{4m^2} \langle \varphi_p \mid \boldsymbol{\sigma} \hat{\mathbf{p}} V \boldsymbol{\sigma} \hat{\mathbf{p}} \mid \varphi_q \rangle \to \frac{1}{4m^2} \langle \varphi_p \mid \boldsymbol{\sigma} \hat{\mathbf{p}} (V - \hat{\mathbf{Q}} \mathbf{E}) \boldsymbol{\sigma} \hat{\mathbf{p}} \mid \varphi_q \rangle, \qquad (\text{IV.180})$$

while for the efg the term $+\hat{\mathbf{q}}\mathbf{Q}$ has to be inserted

$$h_{pq}^{\lambda_{\text{rel}}} = \frac{1}{4m^2} \langle \varphi_p \mid \boldsymbol{\sigma} \hat{\mathbf{p}} V \boldsymbol{\sigma} \hat{\mathbf{p}} \mid \varphi_q \rangle \to \frac{1}{4m^2} \langle \varphi_p \mid \boldsymbol{\sigma} \hat{\mathbf{p}} (V + \hat{\mathbf{q}} \boldsymbol{Q}) \boldsymbol{\sigma} \hat{\mathbf{p}} \mid \varphi_q \rangle.$$
(IV.181)

A further change is required in the CPHF equations, since for the determination of $U_{pi}^{\lambda_{\text{rel}}}$ and $u_{pi}^{\lambda_{\text{rel}}}$ the modified integrals $h_{pq}^{\lambda_{\text{rel}}}$ have to be used as well.

Using the Dirac identity as given in (IV.53), the $h_{pq}^{\lambda_{\text{rel}}}$ integrals in (IV.179) can be split up

into SR and SO contributions

$$h_{pq}^{\lambda_{\text{rel}}} = h_{pq}^{\text{SR}} + h_{pq}^{\text{SO}} \to \tag{IV.182}$$

$$\frac{1}{4m^2} \left\{ \langle \varphi_p \mid \hat{\mathbf{p}} V \hat{\mathbf{p}} \mid \varphi_q \rangle + \langle \varphi_p \mid \hat{\mathbf{p}} (-\hat{\boldsymbol{\mu}} \boldsymbol{\epsilon}) \hat{\mathbf{p}} \mid \varphi_q \rangle \right\}$$
SR

$$+\frac{1}{4m^2} \{ \langle \varphi_p \mid i\boldsymbol{\sigma} \left[\hat{\mathbf{p}} V \times \hat{\mathbf{p}} \right] \mid \varphi_q \rangle + \langle \varphi_p \mid i\boldsymbol{\sigma} \left[\hat{\mathbf{p}} (-\hat{\boldsymbol{\mu}} \boldsymbol{\epsilon}) \times \hat{\mathbf{p}} \right] \mid \varphi_q \rangle \}.$$
 SO

For the quadrupole and efg integrals, see (IV.180) and (IV.181), a separation into SR and SO parts is possible in an analogous manner.

At the DPT2 level, only the SR integrals are needed¹⁰² while at the DPT4 level both SR and SO integrals contribute.

IV.5. Further ideas for relativistic corrections

As the increased cost of a four-component relativistic calculation versus its non-relativistic counterpart is mainly due to the symmetry breaking of the SO operators, and, as usually the SO contributions are significantly smaller than the SR terms (at least for closed-shell molecules up to the fifth row of the periodic table), a further possible route to treat relativistic effects is to calculate the SR contribution in a rigorous manner and treat only the SO terms perturbatively.⁴¹

To discuss this general idea the starting point is given by the Dirac equation (neglecting all two-electron contributions) given in a projected form as

$$\begin{pmatrix} \overline{\varphi}_p \\ \overline{\chi}_p \end{pmatrix}^{\dagger} \begin{pmatrix} V & c\boldsymbol{\sigma}\hat{\mathbf{p}} \\ c\boldsymbol{\sigma}\hat{\mathbf{p}} & V - 2mc^2 \end{pmatrix} \begin{pmatrix} \overline{\varphi}_q \\ \overline{\chi}_q \end{pmatrix} = \varepsilon_q \begin{pmatrix} \overline{\varphi}_p \\ \overline{\chi}_p \end{pmatrix}^{\dagger} \begin{pmatrix} \overline{\varphi}_q \\ \overline{\chi}_q \end{pmatrix}.$$
(IV.183)

The 'kinetic-balance condition'⁸² is then used to rewrite the small component

$$\overline{\chi}_p = \frac{1}{2mc} \boldsymbol{\sigma} \hat{\mathbf{p}} \phi_p \tag{IV.184}$$

with the so-called 'pseudo-large' component ϕ_p which possesses (for electronic solutions) the same symmetry and the same order of magnitude as the large component. It should be noted that in the non-relativistic limit, the pseudo-large component is equal to the true large component as can be seen from (IV.30) when (IV.1) is inserted. While in DPT the exact relation between large and small component is recovered via a perturbative expansion and calculated at the operator level, i.e., as given in (IV.78), this relation, i.e., everything higher than the zeroth order, is here folded into the structure of the pseudolarge component ϕ_p while the large component remains unchanged, i.e.,

$$\overline{\varphi}_p = \varphi_p. \tag{IV.185}$$

Inserting (IV.184) into (IV.183) yields

$$\begin{pmatrix} \varphi_p \\ \phi_p \end{pmatrix}^{\dagger} \underbrace{\begin{pmatrix} V & \hat{T} \\ \hat{T} & \frac{\sigma \hat{\mathbf{p}} V \sigma \hat{\mathbf{p}}}{4m^2 c^2} - \hat{T} \end{pmatrix}}_{\hat{\mathbf{h}}_{\mathrm{DP}}} \begin{pmatrix} \varphi_q \\ \phi_q \end{pmatrix} = \varepsilon_q \begin{pmatrix} \varphi_p \\ \phi_p \end{pmatrix}^{\dagger} \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{2mc^2} \hat{T} \end{pmatrix}}_{\hat{\mathbf{S}}_{\mathrm{DP}}} \begin{pmatrix} \varphi_q \\ \phi_q \end{pmatrix}$$
(IV.186)

with

$$\hat{T} = \frac{\hat{\mathbf{p}}^2}{2m}.\tag{IV.187}$$

The procedure sketched here again leads to a change of the metric and a new Hamiltonian $\hat{\mathbf{h}}_{\text{DP}}$. Using the Dirac identity as given in (IV.53), the SO contributions in $\hat{\mathbf{h}}_{\text{DP}}$ can be split off yielding¹⁰³

$$\hat{\mathbf{h}}_{\mathrm{DP}} = \hat{\mathbf{h}}_{\mathrm{DP}}^{\mathrm{SR}} + \hat{\mathbf{h}}_{\mathrm{DP}}^{\mathrm{SO}} \tag{IV.188}$$

$$= \begin{pmatrix} V & \hat{T} \\ \hat{T} & \frac{\hat{\mathbf{p}}V\hat{\mathbf{p}}}{4m^2c^2} - \hat{T} \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & \frac{i\boldsymbol{\sigma}(\hat{\mathbf{p}}V \times \hat{\mathbf{p}})}{4m^2c^2} \end{pmatrix}$$
(IV.189)

If this separation is employed, and the SR, or so-called spin-free (SF) part is treated in a full, i.e., non-perturbative manner, this leads to the spin-free Dirac Coulomb (SFDC) versions of a given method which also provide the proper SR limit of the corresponding DPT expansions. When calculating the SO part perturbatively, the resulting equations are very similar to those used in the present SO-DPT4 treatment. Accordingly, it is expected that only a few modifications are needed to provide such a perturbative scheme as an addition to a SFDC calculation. In a first step, one can simply augment the SFDC energy by the SO-DPT4 correction. This should already account for a major fraction of the SO effects that are missing in the SFDC results. In a second step, the SO contributions may be evaluated using the SFDC orbitals which should improve the results further, as there are indications that the coupling between SR and SO effects becomes important for elements in the higher rows of the periodic table (see chapter VII).

The advantage of such a two-step procedure is especially evident for CC treatments as

here the additional cost for a perturbative SO treatment is much less than that for a full four-component calculation in comparison to a SFDC computation.

The SFDC approach has been recently implemented by Lan Cheng⁴¹ into the CFOUR program package⁸⁰ so that the here suggested cost-effective treatment of SO corrections can be explored in the near future. Work along these lines is currently pursued.

V. Calculation of Relativistic Integrals

In quantum-chemical calculations it is always necessary to evaluate integrals over the basis functions which define the chosen basis set. Usually, these basis functions are given as a linear combination of primitive Gaussians and are referred to as contracted Gaussians. In practice, the corresponding integrals are evaluated over Cartesian Gaussian functions and the contraction is done afterwards. To evaluate these integrals it is possible to use, for example, the schemes of Obara and Saika,^{104,105} Rys,¹⁰⁶ or McMurchie and Davidson.¹⁰⁷ In this work, the scheme of McMurchie and Davidson is chosen. Therefore, following Ref. 107, an overview over the calculation of standard integrals via this scheme is given while the relativistic integrals that have been implemented as part of this work are discussed afterwards.

V.1. Cartesian Gaussians

A (unnormalized) Cartesian Gaussian with its center at **A** and exponential coefficient α_A which determines the width of the function is given by

$$g_{\mathbf{A}}^{nlm}(\mathbf{r}) = x_A^n y_A^l z_A^m \mathrm{e}^{-\alpha_A \mathbf{r}_{\mathbf{A}}^2} \tag{V.1}$$

with

$$\mathbf{r}_{\mathbf{A}} = \mathbf{r} - \mathbf{A} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} - \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} = \begin{pmatrix} x_A \\ y_A \\ z_A \end{pmatrix}.$$
 (V.2)

These functions are distinguished by the values of L = n + l + m = 0, 1, 2, ... as:

$$\begin{array}{ccc} L & \text{type} \\ 0 & \text{s-function} \\ 1 & \text{p-function} \\ 2 & \text{d-function} \\ \vdots & \vdots \end{array}$$

Since Cartesian Gaussians can be factorized as

$$g_{\mathbf{A}}^{nlm}(\mathbf{r}) = x_A^n e^{-\alpha_A x_A^2} y_A^l e^{-\alpha_A y_A^2} z_A^m e^{-\alpha_A z_A^2}, \qquad (V.3)$$

it is sufficient to discuss in the following only the one-dimensional case for the sake of simplicity. Gaussian functions have the advantage that it is rather easy to calculate products, take derivatives, and to integrate, as is shown in the following. The product of two Cartesian Gaussians, which will be referred to as charge distribution Ω_{BA} , is given again by a Gaussian centered at the new center P_x

$$\Omega_{BA} = g_B^{n_B} g_A^{n_A} = x_B^{n_B} e^{-\alpha_B x_B^2} x_A^{n_A} e^{-\alpha_A x_A^2} = E_{AB} x_B^{n_B} x_A^{n_A} e^{-\alpha_P x_P^2}$$
(V.4)

with

$$\alpha_P = \alpha_A + \alpha_B, \quad x_P = x - P_x, \quad P_x = \frac{\alpha_A A_x + \alpha_B B_x}{\alpha_P},$$
 (V.5)

and

$$E_{AB} = \exp\left(\frac{-\alpha_A \alpha_B}{\alpha_P}\right) (\overline{\mathbf{AB}}_x)^2, \quad \overline{\mathbf{AB}}_x = A_x - B_x$$
(V.6)

determining the extent of the overlap.

When taking the derivative with respect to A_x , two new Cartesian Gaussians are obtained; one with increased quantum number L and one with decreased L:

$$\frac{\mathrm{d}}{\mathrm{d}A_x} x_A^n \mathrm{e}^{-\alpha_A x_A^2} = 2\alpha_A x_A^{n+1} \mathrm{e}^{-\alpha_A x_A^2} - n x_A^{n-1} \mathrm{e}^{-\alpha_A x_A^2} \tag{V.7}$$

$$= 2\alpha_A g_A^{n+1} - n g_A^{n-1} . (V.8)$$

Due to the definition of x_A , (V.2), differentiation with respect to x instead of A_x leads to a sign change.

Integrating a simple Gaussian leads to

$$\int_{-\infty}^{+\infty} e^{-\alpha_A x_A^2} dx = \sqrt{\frac{\pi}{\alpha_A}} .$$
 (V.9)
V.2. The McMurchie-Davidson scheme

V.2.1. Expansion with respect to Hermite Gaussians

To rewrite the prefactors in the charge distribution (V.4) with respect to the new center P_x , the following relation of a Hermite Gaussian to the derivatives of a Gaussian

$$\left(\frac{\partial}{\partial P_x}\right)^N e^{-\alpha_P x_P^2} = \Lambda_N(x_P; \alpha_P) e^{-\alpha_P x_P^2}$$
(V.10)

is used together with an expansion of the polynomials $x_A^{n_A} x_B^{n_B}$ in terms of the functions Λ_N and coefficients $d_N^{n_A n_B}$

$$x_A^{n_A} e^{-\alpha_A x_A^2} x_B^{n_B} e^{-\alpha_B x_B^2} = E_{AB} \sum_{N=0}^{n_A + n_B} d_N^{n_A n_B} \Lambda_N(x_P; \alpha_P) e^{-\alpha_P x_P^2}.$$
 (V.11)

As the functions Λ_N up to order *n* constitute a complete basis for the representation of another polynomial of the same order, the sum in the above expression runs only up to $n_A + n_B$.

V.2.2. Recursion relations for the coefficients

Via the relation

$$\Lambda_N(x_P; \alpha_P) = \alpha_P^{N/2} H_N(\alpha_P^{1/2} x_P), \qquad (V.12)$$

the functions Λ_N are connected to the Hermite polynomials H_N for which the following recursion relations

$$tH_N(t) = NH_{N-1}(t) + \frac{1}{2}H_{N+1}(t)$$
 (V.13)

hold. Therefore, the recursion relations for Λ_N are given as

$$x_A \Lambda_N = N \Lambda_{N-1} + (P_x - A_x) \Lambda_N + \frac{1}{2\alpha_P} \Lambda_{N+1}.$$
 (V.14)

Inserting this into (V.11) and equating coefficients yields the recursive conditional equations for the coefficients $d_N^{n_A n_B}$

$$d_N^{(n_A+1)n_B} = \overline{\mathbf{PA}}_x \ d_N^{n_A n_B} + \frac{1}{2\alpha_P} d_{N-1}^{n_A n_B} + (N+1) d_{N+1}^{n_A n_B}$$
(V.15)

$$d_N^{n_A(n_B+1)} = \overline{\mathbf{PB}}_x \ d_N^{n_A n_B} + \frac{1}{2\alpha_P} d_{N-1}^{n_A n_B} + (N+1) d_{N+1}^{n_A n_B}$$
(V.16)

with the starting point for the recursion relation being $d_0^{00} = 1$ and

$$d_N^{n_A n_B} = 0 \quad \forall \quad N > n_A + n_B. \tag{V.17}$$

V.2.3. One-electron integrals with factorizable operators

In order to calculate one-electron integrals with factorizable operators it is exploited that

- a factorization of three dimensional integrals into a product of one-dimensional integrals is possible,
- the Hermite Gaussians are orthogonal with respect to $\exp\left(-\alpha_P x_P^2\right)$ so that

$$\int \mathrm{d}x \Lambda_N(x_P; \alpha_P) \Lambda_M(x_P; \alpha_P) \mathrm{e}^{\alpha_P x_P^2} = \delta_{NM} \sqrt{\frac{\pi}{\alpha_P}}, \qquad (V.18)$$

• as $\Lambda_0 = 1$, it follows

$$\int \mathrm{d}x \Lambda_N \mathrm{e}^{-\alpha_P x_P^2} = \delta_{N0} \sqrt{\frac{\pi}{\alpha_P}},\tag{V.19}$$

• operators which are given as polynomials of the form $(x_C)^{n_x}(y_C)^{n_y}(z_C)^{n_z}$ can be combined with the corresponding Hermite Gaussians via the the recursion relations.

Using (V.11), the charge distribution in (V.4) can be rewritten into the form

$$\Omega_{BA} = E_{AB} \sum_{N=0}^{n_A + n_B} d_N^{n_A n_B} \Lambda_N(x_P; \alpha_P) e^{-\alpha_P x_P^2}$$
(V.20)

and accordingly for the three-dimensional case

$$\Omega_{BA} = E_{AB} \sum_{N=0}^{n_A + n_B} d_N^{n_A n_B} \Lambda_N(x_P; \alpha_P) \sum_{L=0}^{l_A + l_B} e_L^{l_A l_B} \Lambda_L(y_P; \alpha_P) \sum_{M=0}^{m_A + m_B} f_M^{m_A m_B} \Lambda_M(z_P; \alpha_P) e^{-\alpha_P \mathbf{r}_P^2}$$
(V.21)

$$= E_{AB} \sum_{N=0}^{n_A+n_B} d_N^{n_An_B} \Lambda_N \sum_{L=0}^{l_A+l_B} e_L^{l_Al_B} \Lambda_L \sum_{M=0}^{m_A+m_B} f_M^{m_Am_B} \Lambda_M e^{-\alpha_P \mathbf{r}_P^2}, \qquad (V.22)$$

$$= E_{AB} \sum_{N,L,M} D_{NLM} \Lambda_N \Lambda_L \Lambda_M e^{-\alpha_P \mathbf{r}_P^2}, \qquad (V.23)$$

with

$$D_{NLM} = d_N^{n_A n_B} e_L^{l_A l_B} f_M^{m_A m_B}.$$
 (V.24)

Analog expansions can be established for the other components as well. Whenever the summation is written in the following as a combined sum over N, L and M as in (V.23), the summation ranges from (V.22) are assumed, i.e., for the x component from N = 0 to $n_A + n_B$, for the y component from L = 0 to $l_A + l_B$, and for the z component from M = 0 to $m_A + m_B$. Then, a one-electron integral with a multiplicative operator $\hat{O} = O(\mathbf{r})$ is given by

$$\langle g_B \mid \hat{O} \mid g_A \rangle = E_{AB} \sum_{N,L,M} D_{NLM} [NLM \mid O]$$
(V.25)

with the so-called basic integral

$$[NLM \mid O] = \int d^3 \mathbf{r} \Lambda_N \Lambda_L \Lambda_M O(\mathbf{r}) e^{-\alpha_P \mathbf{r}_P^2}$$
(V.26)

and

$$g_A = g_A^{n_A l_A m_A}, \quad g_B = g_B^{n_B l_B m_B}.$$
 (V.27)

The simplest possible integral in this context is the overlap integral. It is is given as

$$\langle g_B \mid g_A \rangle = \int \mathrm{d}^3 \mathbf{r} \; \Omega_{BA}$$

$$= E_{AB} \sum_{N,L,M} D_{NLM} [NLM \mid 1] \tag{V.28}$$

with

$$[NLM \mid 1] = \int dx \Lambda_N e^{-\alpha_P x_P^2} \int dy \Lambda_L e^{-\alpha_P y_P^2} \int dz \Lambda_M e^{-\alpha_P z_P^2}$$
$$= \delta_{N0} \delta_{L0} \delta_{M0} \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}}.$$
(V.29)

After insertion into (V.28) it follows for the overlap integral:

$$\langle g_B | g_A \rangle = E_{AB} d_0^{n_A n_B} e_0^{l_A l_B} f_0^{m_A m_B} \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}}.$$
 (V.30)

For a x-dipole integral

$$\langle g_B \mid x_C \mid g_A \rangle = \int \mathrm{d}^3 \mathbf{r} \,\Omega_{BA} x_C$$
 (V.31)

$$=E_{AB}\sum_{N,L,M}D_{NLM}[NLM \mid x_C] \tag{V.32}$$

2

the following basic integral is needed

$$[NLM \mid x_C] = \int dx \Lambda_N x_C e^{-\alpha_P x_P^2} \int dy \Lambda_L e^{-\alpha_P y_P^2} \int dz \Lambda_M e^{-\alpha_P z_P^2}$$
(V.33)

$$= \delta_{L0}\delta_{M0} \left\{ \delta_{N1} + \overline{\mathbf{PC}}_x \delta_{N0} \right\} \left(\frac{\pi}{\alpha_P} \right)^{\frac{3}{2}}$$
(V.34)

where the recursion relation for the Hermite Gaussians in (V.14) was used. For the y and z component analog expressions can be derived. Accordingly, the dipole integrals are given as

$$\langle g_B \mid x_C \mid g_A \rangle = E_{AB} \left\{ d_1^{n_A n_B} + \overline{\mathbf{PC}}_x \ d_0^{n_A n_B} \right\} e_0^{l_A l_B} f_0^{m_A m_B} \left(\frac{\pi}{\alpha_P} \right)^{\frac{3}{2}}, \tag{V.35}$$

$$\langle g_B \mid y_C \mid g_A \rangle = E_{AB} \left\{ e_1^{l_A l_B} + \overline{\mathbf{PC}}_y \; e_0^{l_A l_B} \right\} d_0^{n_A n_B} f_0^{m_A m_B} \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}}, \tag{V.36}$$

$$\langle g_B \mid z_C \mid g_A \rangle = E_{AB} \left\{ f_1^{m_A m_B} + \overline{\mathbf{PC}}_z f_0^{m_A m_B} \right\} d_0^{n_A n_B} e_0^{l_A l_B} \left(\frac{\pi}{\alpha_P} \right)^{\frac{1}{2}}.$$
(V.37)

The integrals for the quadrupole moment may be derived in the same manner. Using the recursion relations twice, the expression for the non-diagonal elements is

$$[NLM \mid x_C y_C] = \int \mathrm{d}x \Lambda_N x_C \,\mathrm{e}^{-\alpha_P x_P^2} \int \mathrm{d}y \Lambda_L y_C \,\mathrm{e}^{-\alpha_P y_P^2} \int \mathrm{d}z \Lambda_M \mathrm{e}^{-\alpha_P z_P^2} \tag{V.38}$$

$$= \delta_{M0} \left\{ \delta_{N1} + \overline{\mathbf{PC}}_x \delta_{N0} \right\} \left\{ \delta_{L1} + \overline{\mathbf{PC}}_y \delta_{L0} \right\} \left(\frac{\pi}{\alpha_P} \right)^{\frac{1}{2}}$$
(V.39)

$$\langle g_B \mid x_C y_C \mid g_A \rangle = E_{AB} \{ d_1^{n_A n_B} + \overline{\mathbf{PC}}_x d_0^{n_A n_B} \} \{ e_1^{l_A l_B} + \overline{\mathbf{PC}}_y e_0^{l_A l_B} \} f_0^{m_A m_B} \left(\frac{\pi}{\alpha_P} \right)^{\overline{2}} \quad (V.40)$$

while the diagonal components are, for example, given by

$$[NLM \mid x_C^2] = \int \mathrm{d}x \Lambda_N x_C^2 \,\mathrm{e}^{-\alpha_P x_P^2} \int \mathrm{d}y \Lambda_L \mathrm{e}^{-\alpha_P y_P^2} \int \mathrm{d}z \Lambda_M \mathrm{e}^{-\alpha_P z_P^2} \tag{V.41}$$

$$= \delta_{L0} \delta_{M0} \left\{ 2\delta_{N2} + 2\overline{\mathbf{PC}}_x \delta_{N1} + \left(\overline{\mathbf{PC}}_x^2 + \frac{1}{2\alpha_P}\right) \delta_{N0} \right\} \left(\frac{\pi}{\alpha_P}\right)^{\frac{\pi}{2}} \qquad (V.42)$$
$$\langle g_B \mid x_C^2 \mid g_A \rangle = E_{AB} \left\{ 2d_2^{n_A n_B} + 2\overline{\mathbf{PC}}_x d_1^{n_A n_B} + \left(\overline{\mathbf{PC}}_x^2 + \frac{1}{2\alpha_P}\right) d_0^{n_A n_B} \right\}$$

$$\times e_0^{l_A l_B} f_0^{m_A m_B} \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}}.$$
(V.43)

V.2.4. One-electron integrals with non-factorizable operators

For integrals that contain $|\mathbf{r}_{C}|^{-1}$ in the operator, a factorization and analytic evaluation is impossible. To calculate, for example, the integral over the nuclear-attraction potential

$$\langle g_B \mid |\mathbf{r}_C|^{-1} \mid g_A \rangle = E_{AB} \sum_{N,L,M} D_{NLM} [NLM \mid |\mathbf{r}_C|^{-1}].$$
(V.44)

the basic integral $[NLM \mid |\mathbf{r}_C|^{-1}]$ needs to be evaluated. Using, as was shown by Boys,¹⁰⁸

$$[000 | |\mathbf{r}_{C}|^{-1}] = \int d^{3}\mathbf{r} \ e^{-\alpha_{P}\mathbf{r}_{P}^{2}} \frac{1}{|\mathbf{r}_{C}|} = \frac{2\pi}{\alpha_{P}} F_{0}(T)$$
(V.45)

with the error function

$$F_0(T) = \int_0^1 \exp(-Tu^2) du$$
 (V.46)

and

$$T = \alpha_P (\mathbf{C} - \mathbf{P})^2, \qquad (V.47)$$

as well as (V.10), it follows

$$[NLM \mid |\mathbf{r}_C|^{-1}] = \int \mathrm{d}^3 r \Lambda_N \Lambda_L \Lambda_M \frac{1}{|\mathbf{r}_C|} \mathrm{e}^{-\alpha_P \mathbf{r}_P^2} \tag{V.48}$$

$$= \left(\frac{\partial}{\partial P_x}\right)^N \left(\frac{\partial}{\partial P_y}\right)^L \left(\frac{\partial}{\partial P_z}\right)^M \underbrace{\int \mathrm{d}^3 r \frac{1}{|\mathbf{r}_C|} \mathrm{e}^{-\alpha_P \mathbf{r}_P^2}}_{\frac{2\pi}{\alpha_P} F_0(T)} \tag{V.49}$$

$$=\frac{2\pi}{\alpha_P}\left(\frac{\partial}{\partial P_x}\right)^N \left(\frac{\partial}{\partial P_y}\right)^L \left(\frac{\partial}{\partial P_z}\right)^M F_0(T). \tag{V.50}$$

After introducing

$$R_{NLM} = \left(\frac{\partial}{\partial P_x}\right)^N \left(\frac{\partial}{\partial P_y}\right)^L \left(\frac{\partial}{\partial P_z}\right)^M F_0(T), \qquad (V.51)$$

the basic integral is finally given as

$$[NLM \mid |\mathbf{r}_C|^{-1}] = \frac{2\pi}{\alpha_P} R_{NLM}$$
(V.52)

and the nuclear-attraction integral as

$$\langle g_B \mid |\mathbf{r}_C|^{-1} \mid g_A \rangle = E_{AB} \frac{2\pi}{\alpha_P} \sum_{N,L,M} D_{NLM} R_{NLM}.$$
(V.53)

Thus, the sums in the expression do not vanish and the coefficients are calculated using the recursion relations in (V.15) and (V.16). In order to generate the auxiliary functions R_{NLM} up to the maximal value of N + L + M recursion relations are used which can be derived using the more general integral

$$R_{NLMj} = (-\alpha^{1/2})^{N+L+M} (-2\alpha)^{j} \\ \times \int_{0}^{1} u^{N+L+M+2j} H_{N}(\alpha^{1/2}au) H_{L}(\alpha^{1/2}bu) H_{M}(\alpha^{1/2}cu) e^{-Tu^{2}} du$$
(V.54)

and

$$T = \alpha (a^2 + b^2 + c^2). \tag{V.55}$$

With

$$F_j(T) = \int_0^1 u^{2j} e^{-Tu^2} du$$
 (V.56)

it follows

$$R_{000j} = (-2\alpha)^j F_j(T).$$
 (V.57)

From the recursion relations for the Hermite polynomials (V.13) the recursion relations for R_{NLMj} are derived:

$$R_{00(M+1)j} = cR_{00M(j+1)} + MR_{00(M-1)(j+1)},$$
(V.58)

$$R_{0(L+1)Mj} = bR_{0LM(j+1)} + LR_{0(L-1)M(j+1)},$$
(V.59)

$$R_{(N+1)LMj} = aR_{NLM(j+1)} + NR_{(N-1)LM(j+1)}.$$
(V.60)

Thus, the required R_{NLM} , or accordingly R_{NLM0} , can be generated using a table with the error functions $F_j(T)$ for all values of the index j from 0 to the maximum N + L + M.

V.2.5. Two-electron integrals

In the same manner as the one-electron integrals, the two-electron Coulomb integrals may be expressed using Hermite Gaussians

$$\left\langle g_{B}g_{D} \middle| \frac{1}{r_{12}} \middle| g_{A}g_{C} \right\rangle = E_{AB}E_{CD} \sum_{N=0}^{n_{A}+n_{B}} \sum_{L=0}^{l_{A}+l_{B}} \sum_{M=0}^{m_{A}+n_{B}} \sum_{N'=0}^{n_{C}+n_{D}} \sum_{L'=0}^{l_{C}+l_{D}} \sum_{M'=0}^{m_{C}+m_{D}} d_{N}^{n_{A}n_{B}} e_{L}^{l_{A}l_{B}} f_{M}^{m_{A}m_{B}} d_{N'}^{n_{C}n_{D}} e_{L'}^{l_{C}l_{D}} f_{M'}^{m_{C}m_{D}} \left[NLM \middle| \frac{1}{r_{12}} \middle| N'L'M' \right] \quad (V.61)$$

$$= E_{L'D}E_{CD} \sum_{M'=0}^{m_{A}+n_{B}} \sum_{M'=0}^{n_{C}-n_{D}} \sum_{M'=0}^{l_{C}l_{D}} f_{M'}^{m_{C}m_{D}} \left[NLM \middle| \frac{1}{r_{12}} \middle| N'L'M' \right] \quad (V.62)$$

$$= E_{AB} E_{CD} \sum_{N,L,M} \sum_{N',L',M'} D_{NLM} D_{N'L'M'} \left[NLM \left| \frac{1}{r_{12}} \right| N'L'M' \right] \quad (V.62)$$

with

$$\begin{split} \left[NLM \left| \frac{1}{r_{12}} \right| N'L'M' \right] &= \int \int d^{3}\mathbf{r}_{1} d^{3}\mathbf{r}_{2} \Lambda_{N} \Lambda_{L} \Lambda_{M} e^{-\alpha_{P} \mathbf{r}_{1P}^{2}} \frac{1}{r_{12}} \Lambda_{N'} \Lambda_{L'} \Lambda_{M'} e^{-\alpha_{Q} \mathbf{r}_{2Q}^{2}} \quad (V.63) \\ &= \left(\frac{\partial}{\partial P_{x}} \right)^{N} \left(\frac{\partial}{\partial P_{y}} \right)^{L} \left(\frac{\partial}{\partial P_{z}} \right)^{M} \\ &\times \left(\frac{\partial}{\partial Q_{x}} \right)^{N'} \left(\frac{\partial}{\partial Q_{y}} \right)^{L'} \left(\frac{\partial}{\partial Q_{z}} \right)^{M'} \left[000 \left| \frac{1}{r_{12}} \right| 000 \right] \quad (V.64) \end{split}$$

and the basic integral 108 given as

$$\left[000 \left| \frac{1}{r_{12}} \right| 000 \right] = \lambda_0 F_0(T) \tag{V.65}$$

with F_0 as defined in (V.46) but with

$$T = \frac{\alpha_P \alpha_Q}{\alpha_P + \alpha_Q} \left(\overline{\mathbf{PQ}}_x^2 + \overline{\mathbf{PQ}}_y^2 + \overline{\mathbf{PQ}}_z^2 \right)$$
(V.66)

and

$$\lambda_0 = \frac{2\pi^{\frac{5}{2}}}{\alpha_P \alpha_Q \sqrt{\alpha_P + \alpha_Q}}.$$
(V.67)

As T only depends on $\overline{\mathbf{PQ}}_x, \overline{\mathbf{PQ}}_y$, and $\overline{\mathbf{PQ}}_z$ it follows that

$$\frac{\partial}{\partial P_i} f(T) = -\frac{\partial}{\partial Q_i} f(T), \quad i = x, y, z.$$
 (V.68)

Therefore, the basic integral can be rewritten as

$$\begin{bmatrix} NLM \left| \frac{1}{r_{12}} \right| N'L'M' \end{bmatrix} = (-1)^{N'} \left(\frac{\partial}{\partial P_x} \right)^{N+N'} \\ \times (-1)^{L'} \left(\frac{\partial}{\partial P_y} \right)^{L+L'} (-1)^{M'} \left(\frac{\partial}{\partial P_z} \right)^{M+M'} F_0(T) \lambda_0 \qquad (V.69) \\ = (-1)^{N'+L'+M'} \lambda_0 \times \\ \underbrace{\left(\frac{\partial}{\partial P_x} \right)^{N+N'} \left(\frac{\partial}{\partial P_y} \right)^{L+L'} \left(\frac{\partial}{\partial P_z} \right)^{M+M'} F_0(T)}_{(V.70)} \qquad (V.70)$$

$$R_{N+N^\prime,L+L^\prime,M+M^\prime}$$

leading to

$$\left\langle g_{B}g_{D} \left| \frac{1}{r_{12}} \right| g_{A}g_{C} \right\rangle = E_{AB}E_{CD} \sum_{N,L,M} \sum_{N',L',M'} D_{NLM} D_{N'L'M'} \\ \times (-1)^{N'+L'+M'} \lambda_{0} R_{N+N',L+L',M+M'}.$$
(V.71)

V.3. One-electron integrals for relativistic corrections

In the calculation of relativistic corrections using DPT (see chapter IV) integrals of the form $\langle g_B | \sigma \hat{\mathbf{p}} \hat{O} \sigma \hat{\mathbf{p}} | g_A \rangle$ arise which can be separated using the Dirac identity¹⁷ into

$$\langle g_B \mid \boldsymbol{\sigma} \hat{\mathbf{p}} \hat{O} \boldsymbol{\sigma} \hat{\mathbf{p}} \mid g_A \rangle = \langle g_B \mid \hat{\mathbf{p}} \hat{O} \hat{\mathbf{p}} \mid g_A \rangle + \langle g_B \mid i\boldsymbol{\sigma} (\hat{\mathbf{p}} \hat{O} \times \hat{\mathbf{p}}) \mid g_A \rangle$$
(V.72)

with the general operator \hat{O} , the Pauli spin matrices $\boldsymbol{\sigma}$ and the momentum operators $\hat{\mathbf{p}}$. The first term on the right-hand side corresponds to the scalar-relativistic (SR) contribution and is given by

$$\langle g_B \mid \hat{\mathbf{p}}\hat{O}\hat{\mathbf{p}} \mid g_A \rangle = -\sum_{\nu=x,y,z} \left\langle g_B \left| \frac{\partial}{\partial\nu} \hat{O} \frac{\partial}{\partial\nu} \right| g_A \right\rangle \tag{V.73}$$

$$= -\sum_{\nu=x,y,z} \left\{ \left\langle g_B \left| \frac{\partial \hat{O}}{\partial \nu} \right| \frac{\partial g_A}{\partial \nu} \right\rangle + \left\langle g_B \left| \hat{O} \right| \frac{\partial^2 g_A}{\partial \nu^2} \right\rangle \right\}.$$
 (V.74)

All contributions contain derivatives of g_A and thereby differentiated charge distributions G_{BA}^{ν} and $T_{BA}^{\nu\nu}$ with $\nu = x, y, z$. For the x component they are given as

$$G_{BA}^{x} = g_{B}^{n_{B}l_{B}m_{B}} \frac{\partial}{\partial x} g_{A}^{n_{A}l_{A}m_{A}}.$$
(V.75)

$$=g_{B}^{n_{B}l_{B}m_{B}}\left(-2\alpha_{A}g_{A}^{(n_{A}+1)l_{A}m_{A}}+n_{A}g_{A}^{(n_{A}-1)l_{A}m_{A}}\right)$$
(V.76)

$$= E_{AB} \sum_{N=0}^{n_A+n_B+1} {}^x d_N^{n_A n_B} \Lambda_N \sum_{L=0}^{l_A+l_B} e_L^{l_A l_B} \Lambda_L \sum_{M=0}^{m_A+m_B} f_M^{m_A m_B} \Lambda_M e^{-\alpha_P \mathbf{r}_P^2}$$
(V.77)

and

$$T_{BA}^{xx} = g_B^{n_B l_B m_B} \frac{\partial^2}{\partial x^2} g_A^{n_A l_A m_A} \tag{V.78}$$

$$= E_{AB} \sum_{N=0}^{n_A + n_B + 2} {}^{xx} d_N^{n_A n_B} \Lambda_N \sum_{L=0}^{l_A + l_B} e_L^{l_A l_B} \Lambda_L \sum_{M=0}^{m_A + m_B} f_M^{m_A m_B} \Lambda_M e^{-\alpha_P \mathbf{r}_P^2}$$
(V.79)

with

$${}^{x}d_{N}^{n_{A}n_{B}} = -2\alpha_{A}d_{N}^{(n_{A}+1)n_{B}} + n_{A}d_{N}^{(n_{A}-1)n_{B}},$$
(V.80)

$${}^{xx}d_N^{n_A n_B} = 4\alpha_A^2 d_N^{(n_A+2)n_B} - 2\alpha_A(2n_A+1)d_N^{n_A n_B} + n_A(n_A-1)d_N^{(n_A-2)n_B}.$$
 (V.81)

In the differentiated charge distributions only the corresponding coefficients as well as the summation limit is changed, but the Hermite Gaussians remain unaltered. Analog expressions also hold for coefficients and charge distributions differentiated with respect to y and z.

Using the differentiated charge distributions, the SR contribution may be expressed as

$$\langle g_B \mid \hat{\mathbf{p}}\hat{O}\hat{\mathbf{p}} \mid g_A \rangle = -\sum_{\nu=x,y,z} \left\{ \int \mathrm{d}^3 \mathbf{r} G_{BA}^{\nu} \frac{\partial \hat{O}}{\partial \nu} + \int \mathrm{d}^3 \mathbf{r} \hat{O} T_{BA}^{\nu\nu} \right\}$$
(V.82)
$$= -\sum_{\nu=x,y,z} \sum_{N,L,M} E_{AB} \left\{ D_{NLM}^{\nu} \left[NLM \middle| \frac{\partial \hat{O}}{\partial \nu} \right] + D_{NLM}^{\nu\nu} \left[NLM \middle| \hat{O} \right] \right\}$$
(V.83)

with D_{NLM}^{ν} and $D_{NLM}^{\mu\nu}$ given by

$$D_{NLM}^{\nu} = \begin{cases} x : {}^{x}d_{N}^{nAnB}e_{L}^{lAlB}f_{M}^{mAmB}} \\ y : d_{N}^{nAnB} {}^{y}e_{L}^{lAlB}f_{M}^{mAmB}} \\ z : d_{N}^{nAnB} {}^{y}e_{L}^{lAlB}f_{M}^{mAmB}} \\ z : d_{N}^{nAnB}e_{L}^{lAlB} {}^{z}f_{M}^{mAmB}} \end{cases}, \qquad D_{NLM}^{\mu\nu} = \begin{cases} xx : {}^{xx}d_{N}^{nAnB}e_{L}^{lAlB}f_{M}^{mAmB}} \\ yy : d_{N}^{nAnB} {}^{y}e_{L}^{lAlB}f_{M}^{mAmB}} \\ zz : d_{N}^{nAnB} {}^{y}e_{L}^{lAlB} {}^{z}f_{M}^{mAmB}} \\ xy : {}^{x}d_{N}^{nAnB} {}^{y}e_{L}^{lAlB} {}^{z}f_{M}^{mAmB}} \\ yz : {}^{x}d_{N}^{nAnB} {}^{y}e_{L}^{lAlB} {}^{z}f_{M}^{mAmB}} \end{cases}.$$

$$(V.84)$$

The summation range in the sum over N, L, and M in (V.83) depends on the superscript of D_{NLM} which indicates for which components the differentiated coefficients are present. Without this being denoted further, it is assumed that for these components the summation range is increased by 1 for the singly differentiated coefficients and by 2 for the doubly differentiated ones as shown in the definitions of G_{BA}^{ν} (V.77) and $T_{BA}^{\nu\nu}$ (V.79).

The spin-orbit (SO) contribution, i.e., the second term on the right hand side of (V.72),

may be expressed as

$$\langle g_B \mid i\boldsymbol{\sigma}(\hat{\mathbf{p}}\hat{O} \times \hat{\mathbf{p}}) \mid g_A \rangle = \left\langle g_B \middle| \begin{pmatrix} i\sigma_x(p_y\hat{O}p_z - p_z\hat{O}p_y) \\ i\sigma_y(p_z\hat{O}p_x - p_x\hat{O}p_z) \\ i\sigma_z(p_x\hat{O}p_y - p_y\hat{O}p_x) \end{pmatrix} \middle| g_A \right\rangle$$
(V.85)

where the topmost row corresponds to the spin-orbit x component (SO_x), the central row to the SO_y, and the lowermost row to the SO_z component. Using the Levi-Cività tensor

$$\epsilon_{\mu\nu\sigma} = \begin{cases} +1, & \text{for cyclic permutations of } x, y, z \\ -1, & \text{for non-cyclic permutations of } x, y, z \\ 0, & \text{for repeatedly occurring indices} \end{cases}$$

the SO components $\eta = x, y, z$ can be written as

$$\langle g_B \mid i\boldsymbol{\sigma}(\hat{\mathbf{p}}\hat{O} \times \hat{\mathbf{p}}) \mid g_A \rangle_{\eta} = \sum_{\mu=x,y,z} \sum_{\nu=x,y,z} \epsilon_{\eta\mu\nu} \sigma_\eta \langle g_B \mid ip_\mu \hat{O}p_\nu \mid g_A \rangle \tag{V.86}$$

$$= -i\sigma_{\eta} \left\langle g_{B} \left| \frac{\partial}{\partial \mu} \hat{O} \frac{\partial}{\partial \nu} - \frac{\partial}{\partial \nu} \hat{O} \frac{\partial}{\partial \mu} \right| g_{A} \right\rangle \tag{V.87}$$

$$= -i\sigma_{\eta} \left\{ \int d^{3}\mathbf{r} G_{BA}^{\nu} \frac{\partial \hat{O}}{\partial \mu} + \int d^{3}\mathbf{r} T_{BA}^{\mu\nu} \hat{O} - \int d^{3}\mathbf{r} G_{BA}^{\mu} \frac{\partial \hat{O}}{\partial \nu} - \int d^{3}\mathbf{r} T_{BA}^{\nu\mu} \hat{O} \right\}$$
(V.88)
$$= -i\sigma_{\eta} \sum_{N,L,M} E_{AB} \left\{ D_{NLM}^{\nu} \left[NLM \middle| \frac{\partial \hat{O}}{\partial \mu} \right] - D_{NLM}^{\mu} \left[NLM \middle| \frac{\partial \hat{O}}{\partial \nu} \right] \right\}$$
(V.89)

with η, μ, ν cyclic. It is exploited here that the contributions containing the doubly differentiated charge distributions $T_{BA}^{\mu\nu}$ and $T_{BA}^{\nu\mu}$ cancel as those quantities are defined via

$$T_{BA}^{\mu\nu} = g_B^{n_B l_B m_B} \frac{\partial}{\partial \mu} \frac{\partial}{\partial \nu} g_A^{n_A l_A m_A} \tag{V.90}$$

$$= E_{AB} \sum_{N,L,M} D_{NLM}^{\mu\nu} \Lambda_N \Lambda_L \Lambda_M e^{-\alpha_P \mathbf{r}_P^2}, \qquad (V.91)$$

and therefore it holds that $T^{\mu\nu}_{BA} = T^{\nu\mu}_{BA}$.

V.3.1. Scalar-relativistic nuclear-electron potential integral

The first one-electron integral that is already needed for DPT2 energy calculations and has been worked out by Christine Berger in her Ph.D. thesis¹⁰⁹ involves the nuclearelectron potential

$$V_{ne} = -\sum_{C} Z_C |\mathbf{r}_C|^{-1} \tag{V.92}$$

and, using (V.74), is given as

$$\left\langle g_B \mid \hat{\mathbf{p}} V_{ne} \hat{\mathbf{p}} \mid g_A \right\rangle = -\sum_{\nu=x,y,z} \left\{ \left\langle g_B \middle| \frac{\partial V_{ne}}{\partial \nu} \middle| \frac{\partial g_A}{\partial \nu} \right\rangle + \left\langle g_B \middle| V_{ne} \middle| \frac{\partial^2 g_A}{\partial \nu^2} \right\rangle \right\}$$
(V.93)

with

$$\left\langle g_B \middle| V_{ne} \middle| \frac{\partial^2 g_A}{\partial \nu^2} \right\rangle = -\int \mathrm{d}^3 \mathbf{r} \sum_C \frac{Z_C}{|\mathbf{r}_C|} T_{BA}^{\nu\nu} \tag{V.94}$$

$$= -\sum_{C} Z_{C} E_{AB} \sum_{N,L,M} D_{NLM}^{\nu\nu} [NLM||\mathbf{r}_{C}|^{-1}]$$
(V.95)

$$= -\frac{2\pi}{\alpha_P} \sum_C Z_C E_{AB} \sum_{N,L,M} D_{NLM}^{\nu\nu} R_{NLM}$$
(V.96)

where the result from (V.52) has been used in the last step.

The first term in (V.93) is given by

$$\left\langle g_B \left| \frac{\partial V_{ne}}{\partial \nu} \right| \frac{\partial g_A}{\partial \nu} \right\rangle = -\int d^3 \mathbf{r} \sum_C Z_C \frac{\partial |\mathbf{r}_C|^{-1}}{\partial x} G_{BA}^{\nu} \tag{V.97}$$

$$= -\sum_{C} Z_{C} E_{AB} \sum_{N,L,M} D_{NLM}^{\nu} \left[NLM \left| \frac{\partial |\mathbf{r}_{C}|^{-1}}{\partial x} \right] \right].$$
(V.98)

In the evaluation of the basic integral

$$\left[NLM \left| \frac{\partial |\mathbf{r}_C|^{-1}}{\partial x} \right] = \int d\mathbf{r}^3 \frac{\partial}{\partial x} \left(\frac{\partial}{\partial P_x} \right)^N \left(\frac{\partial}{\partial P_y} \right)^L \left(\frac{\partial}{\partial P_z} \right)^M |\mathbf{r}_C^{-1}| e^{-\alpha_P \mathbf{r}_P^2}$$
(V.99)

$$= \frac{\partial}{\partial P_x} \left(\frac{\partial}{\partial P_x}\right)^N \left(\frac{\partial}{\partial P_y}\right)^L \left(\frac{\partial}{\partial P_z}\right)^M \frac{2\pi}{\alpha_P} F_0(T) \tag{V.100}$$

V.3. One-electron integrals for relativistic corrections

$$=R_{(N+1)LM}\frac{2\pi}{\alpha_P}\tag{V.101}$$

it is exploited that due to (V.2), (V.46), and (V.47) it holds

$$\frac{\partial}{\partial x}R_{NLM} = -\frac{\partial}{\partial C_x}R_{NLM} = \frac{\partial}{\partial P_x}R_{NLM}.$$
 (V.102)

Combining the two types of integrals for all components the SR integral $\langle g_B | \hat{\mathbf{p}} V_{ne} \hat{\mathbf{p}} | g_A \rangle$ is finally evaluated as

$$\langle g_B \mid \hat{\mathbf{p}} V_{ne} \hat{\mathbf{p}} \mid g_A \rangle = \frac{2\pi}{\alpha_P} \sum_C Z_C E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^x R_{(N+1)LM} + D_{NLM}^{xx} R_{NLM} + D_{NLM}^y R_{N(L+1)M} + D_{NLM}^{yy} R_{NLM} + D_{NLM}^z R_{NL(M+1)} + D_{NLM}^{zz} R_{NLM} \right\}$$

$$(V.103)$$

$$2\pi \sum_{n=1}^{\infty} \sum_{n=1$$

$$= \frac{2\pi}{\alpha_P} \sum_C Z_C E_{AB} \sum_{\nu=x,y,z} \sum_{N,L,M} \left\{ D_{NLM}^{\nu} R_{NLM}^{(\nu+1)} + D_{NLM}^{\nu\nu} R_{NLM} \right\}$$
(V.104)

with

$$R_{NLM}^{(\nu+1)} = \begin{cases} x : R_{(N+1)LM} \\ y : R_{N(L+1)M} \\ z : R_{NL(M+1)} \end{cases}$$
(V.105)

V.3.2. Spin-orbit nuclear-electron potential integral

For a full DPT4 treatment (see chapter IV, sections IV.2.2 and IV.3.1), the SO contributions to the nuclear-electron potential integrals $\langle g_B | i\boldsymbol{\sigma}(\hat{\mathbf{p}}V_{ne} \times \hat{\mathbf{p}}) | g_A \rangle_{\eta}$, $\eta = x, y, z$ are needed and have been implemented as part of this work. Using (V.89), the integrals are given by

$$\langle g_B \mid i\boldsymbol{\sigma}(\hat{\mathbf{p}}V_{ne} \times \hat{\mathbf{p}}) \mid g_A \rangle_{\eta} = -i\sigma_{\eta} \left\langle g_B \left| \frac{\partial}{\partial \mu} V_{ne} \frac{\partial}{\partial \nu} - \frac{\partial}{\partial \nu} V_{ne} \frac{\partial}{\partial \mu} \right| g_A \right\rangle$$
(V.106)
$$= -i\sigma_{\eta} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^{\nu} \left[NLM \left| \frac{\partial V_{ne}}{\partial \mu} \right] \right\}$$
(V.107)

with η, μ, ν cyclic. As the (differentiated) charge distributions affect only the summation range and the coefficients, the resulting expression is easily given as

$$\langle g_B \mid i\boldsymbol{\sigma}(\hat{\mathbf{p}}V_{ne} \times \hat{\mathbf{p}}) \mid g_A \rangle_{\eta} = i\sigma_{\eta} \frac{2\pi}{\alpha_P} \sum_C Z_C E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^{\nu} R_{NLM}^{\mu+1} - D_{NLM}^{\mu} R_{NLM}^{\nu+1} \right\}$$
(V.108)

while the basic integral containing the differentiated nuclear-electron potential V_{ne} is already known from (V.101).

V.3.3. Scalar-relativistic dipole-moment integral

In the calculation of SR corrections to electrical properties, integrals of the form

$$\langle \ g_B \ \mid \ \hat{\mathbf{p}} \ \hat{\mathbf{O}} \ \hat{\mathbf{p}} \ \mid \ g_A \ \rangle$$

arise at the DPT2 level^{102,110} with the according operator for the property $\hat{\mathbf{O}}$ (see chapter IV.4). For the dipole moment, these integrals are given by $\langle g_B | \hat{\mathbf{p}} \boldsymbol{\varepsilon}^T \boldsymbol{\mu} \hat{\mathbf{p}} | g_A \rangle$ with the components of the dipole operator $\mu_k = -ek_C, k = x, y, z$, the elementary charge e (=1 in atomic units), and the vector of the electric field $\boldsymbol{\varepsilon}$. As the scalar contribution is given as

$$\sum_{\nu=x,y,z} \langle g_B | p_\nu \varepsilon_x \mu_x p_\nu + p_\nu \varepsilon_y \mu_y p_\nu + p_\nu \varepsilon_z \mu_z p_\nu | g_A \rangle \tag{V.109}$$

the integrals $\langle g_B | \hat{\mathbf{p}} \mu_i \hat{\mathbf{p}} | g_A \rangle$ need to be calculated. Ignoring in the following the factor -e as well as the component of the electric field ε_i and using (V.74) leads to

$$\langle g_B \mid \hat{\mathbf{p}} k_C \hat{\mathbf{p}} \mid g_A \rangle = -\sum_{\nu=x,y,z} \left\langle g_B \left| \frac{\partial}{\partial \nu} k_C \frac{\partial}{\partial \nu} \right| g_A \right\rangle$$

$$= -\sum_{\nu=x,y,z} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^{\nu} \left[NLM \left| \frac{\partial k_C}{\partial \nu} \right] + D_{NLM}^{\nu\nu} \left[NLM | k_C \right] \right\}$$

$$(V.111)$$

with D_{NLM}^{ν} and $D_{NLM}^{\nu\nu}$ as defined in (V.84). The basic integral $[NLM|k_C]$ has already been given in (V.34). For the other basic integral it holds

$$\left[NLM \middle| \frac{\partial k_C}{\partial \nu} \right] = \begin{cases} [NLM|1] = \delta_{N0} \delta_{L0} \delta_{M0} \text{ (see (V.30)), for } k = \nu \\ 0, \text{ otherwise} \end{cases}$$
(V.112)

For the various components, the resulting integrals, abbreviated by D_{ν}^{SR} are then given as

$$\begin{split} \mathbf{D}_{x}^{\mathrm{SR}} &= - E_{AB} \left(\frac{\pi}{\alpha_{P}}\right)^{\frac{3}{2}} \left\{ e_{0}^{l_{A}l_{B}} f_{0}^{m_{A}m_{B}} x d_{0}^{n_{A}n_{B}} \\ &+ e_{0}^{l_{A}l_{B}} f_{0}^{m_{A}m_{B}} \left(x x d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x} x x d_{0}^{n_{A}n_{B}} \right) \\ &+ y y e_{0}^{l_{A}l_{B}} f_{0}^{m_{A}m_{B}} \left(d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x} d_{0}^{n_{A}n_{B}} \right) \\ &+ e_{0}^{l_{A}l_{B}} z z f_{0}^{m_{A}m_{B}} \left(d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x} d_{0}^{n_{A}n_{B}} \right) \\ &+ e_{0}^{l_{A}l_{B}} z z f_{0}^{m_{A}m_{B}} \left(d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x} d_{0}^{n_{A}n_{B}} \right) \\ &+ d_{0}^{n_{A}n_{B}} f_{0}^{m_{A}m_{B}} y e_{0}^{l_{A}l_{B}} \\ &+ d_{0}^{n_{A}n_{B}} f_{0}^{m_{A}m_{B}} y e_{0}^{l_{A}l_{B}} \\ &+ d_{0}^{n_{A}n_{B}} f_{0}^{m_{A}m_{B}} (e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y} y y e_{0}^{l_{A}l_{B}}) \\ &+ d_{0}^{n_{A}n_{B}} z z f_{0}^{m_{A}m_{B}} (e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y} e_{0}^{l_{A}l_{B}}) \\ &+ d_{0}^{n_{A}n_{B}} z z f_{0}^{m_{A}m_{B}} (e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y} e_{0}^{l_{A}l_{B}}) \\ &+ d_{0}^{n_{A}n_{B}} z z f_{0}^{m_{A}m_{B}} (e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y} e_{0}^{l_{A}l_{B}}) \\ &+ d_{0}^{n_{A}n_{B}} y e_{0}^{l_{A}l_{B}} (f_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z} f_{0}^{m_{A}m_{B}}) \\ &+ d_{0}^{n_{A}n_{B}} y e_{0}^{l_{A}l_{B}} (f_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z} z z f_{0}^{m_{A}m_{B}}) \\ &+ d_{0}^{n_{A}n_{B}} e_{0}^{l_{A}l_{B}} (z z f_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z} z z f_{0}^{m_{A}m_{B}}) \\ \end{array} \right\}.$$
(V.115)

V.3.4. Spin-orbit dipole-moment integral

In this work, the SO contributions to the relativistic dipole-moment integrals have been also implemented as they are needed in the full DPT4 property treatment (see chapter IV.4). As seen from (V.85), in principle, for every spin-orbit component there are contributions from all components of the dipole moment:

$$\left\langle g_B \left| \begin{pmatrix} i\sigma_x(p_y \hat{O}p_z - p_z \hat{O}p_y) \\ i\sigma_y(p_z \hat{O}p_x - p_x \hat{O}p_z) \\ i\sigma_z(p_x \hat{O}p_y - p_y \hat{O}p_x) \end{pmatrix} \right| g_A \right\rangle$$
(V.116)

with

$$\hat{O} = \boldsymbol{\varepsilon}^T \boldsymbol{\mu} = \varepsilon_x \mu_x + \varepsilon_y \mu_y + \varepsilon_z \mu_z.$$
(V.117)

The corresponding contributions to the SO dipole-moment integrals, abbreviated in the following as $D_k^{SO_{\eta}}$, $k, \eta = x, y, z$, while ignoring -e, the component of the electric field ε_k , and the Pauli spin matrices, are given as

•

$$D_{k}^{SO_{\eta}} = -i\left\langle g_{B} \middle| \frac{\partial}{\partial \mu} k_{C} \frac{\partial}{\partial \nu} - \frac{\partial}{\partial \nu} k_{C} \frac{\partial}{\partial \mu} \middle| g_{A} \right\rangle$$
(V.118)

$$= -iE_{AB}\sum_{N,L,M} \left(D_{NLM}^{\nu} \left[NLM \left| \frac{\partial k_C}{\partial \mu} \right] - D_{NLM}^{\mu} \left[NLM \left| \frac{\partial k_C}{\partial \nu} \right] \right)$$
(V.119)

with η, μ, ν cyclic. Due to (V.112) only the integrals

$$D_k^{SO_\eta} = -iE_{AB} \epsilon_{\eta k\nu} \sum_{N,L,M} D_{NLM}^{\nu} [NLM \mid 1]$$
(V.120)

need to be evaluated which finally leads to

$$\mathbf{D}_x^{\mathrm{SO}_x} = 0, \tag{V.121}$$

$$D_x^{SO_y} = iE_{AB} \left(\frac{2\pi}{\alpha_P}\right)^{\frac{3}{2}} d_0^{n_A n_B} e_0^{l_A l_B} {}^z f_0^{m_A m_B}, \qquad (V.122)$$

$$D_x^{SO_z} = -iE_{AB} \left(\frac{2\pi}{\alpha_P}\right)^{\frac{3}{2}} d_0^{n_A n_B \ y} e_0^{l_A l_B} \ f_0^{m_A m_B}, \qquad (V.123)$$

$$D_y^{SO_x} = -iE_{AB} \left(\frac{2\pi}{\alpha_P}\right)^{\frac{3}{2}} d_0^{n_A n_B} e_0^{l_A l_B \ z} f_0^{m_A m_B}, \qquad (V.124)$$

$$\mathcal{D}_{y}^{\mathrm{SO}_{y}} = 0, \tag{V.125}$$

$$D_y^{SO_z} = iE_{AB} \left(\frac{2\pi}{\alpha_P}\right)^{\frac{3}{2}} {}^x d_0^{n_A n_B} e_0^{l_A l_B} f_0^{m_A m_B}, \qquad (V.126)$$

V.3. One-electron integrals for relativistic corrections

$$D_{z}^{SO_{x}} = iE_{AB} \left(\frac{2\pi}{\alpha_{P}}\right)^{\frac{3}{2}} d_{0}^{n_{A}n_{B}} \, {}^{y}e_{0}^{l_{A}l_{B}} \, f_{0}^{m_{A}m_{B}}, \qquad (V.127)$$

$$D_z^{SO_y} = -iE_{AB} \left(\frac{2\pi}{\alpha_P}\right)^{\frac{3}{2}} {}^x d_0^{n_A n_B} e_0^{l_A l_B} f_0^{m_A m_B}, \qquad (V.128)$$

$$\mathsf{D}_z^{\mathrm{SO}_z} = 0. \tag{V.129}$$

Note that the SO dipole integrals require only overlap-integral contributions.

V.3.5. Scalar-relativistic quadrupole-moment integral

For the SR contribution to the quadrupole moment which again first arises in a DPT2 property calculation (see chapter IV.4), the integrals to be evaluated are given by

$$\langle g_B \mid \hat{\mathbf{p}} \hat{Q}_{ij} \hat{\mathbf{p}} \mid g_A \rangle = -\sum_{\nu=x,y,z} \left\langle g_B \left| \frac{\partial}{\partial \nu} \hat{Q}_{ij} \frac{\partial}{\partial \nu} \right| g_A \right\rangle$$

$$= -\sum_{\nu=x,y,z} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^{\nu} \left[NLM \left| \frac{\partial \hat{Q}_{ij}}{\partial \nu} \right] + D_{NLM}^{\nu\nu} \left[NLM \left| \hat{Q}_{ij} \right] \right\}$$

$$(V.130)$$

$$(V.131)$$

with

$$\hat{Q}_{ij} = -ei_C j_C, \quad i_C, j_C = x_C, y_C, z_C.$$
 (V.132)

The first basic integral involving the differentiated quadrupole-moment operator \hat{Q}_{ij} leads to a dipole-moment basic integral as given in (V.34) if one of the components of \hat{Q}_{ij} corresponds to the component of the derivative or vanishes otherwise. The second basic integral involving \hat{Q}_{ij} is evaluated as given in (V.39) and (V.42). The resulting expressions, abbreviated as Q_{ij}^{SR} , i, j = x, y, z, are then

$$Q_{xy}^{SR} = -E_{AB}(-e) \sum_{N,L,M} \left\{ D_{NLM}^{x} [NLM \mid y_{C}] + D_{NLM}^{xx} [NLM \mid x_{C}y_{C}] \right. \\ \left. + D_{NLM}^{y} [NLM \mid x_{C}] + D_{NLM}^{yy} [NLM \mid x_{C}y_{C}] \right. \\ \left. + D_{NLM}^{zz} [NLM \mid x_{C}y_{C}] \right\}$$

$$= E_{AB} e \left(\frac{\pi}{\alpha_{P}} \right)^{\frac{3}{2}} \times$$

$$(V.133)$$

$$\begin{cases} f_{0}^{m_{A}m_{B}}(xd_{0}^{n_{A}n_{B}} + xxd_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x} xxd_{0}^{n_{A}n_{B}})(e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y} e_{0}^{l_{A}l_{B}}) \\ + f_{0}^{m_{A}m_{B}}(ye_{0}^{l_{A}l_{B}} + yye_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y} yye_{0}^{l_{A}l_{B}})(d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x} d_{0}^{n_{A}n_{B}}) \\ + z^{zz}f_{0}^{m_{A}m_{B}}(d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x} d_{0}^{n_{A}n_{B}})(e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y} e_{0}^{l_{A}l_{B}})\}, \qquad (V.134) \end{cases}$$

$$Q_{xz}^{SR} = E_{AB} e\left(\frac{\pi}{\alpha_{P}}\right)^{\frac{3}{2}} \times \left\{ e_{0}^{l_{A}l_{B}}(xd_{0}^{n_{A}n_{B}} + xxd_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x} xxd_{0}^{n_{A}n_{B}})(f_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}f_{0}^{m_{A}m_{B}}) \\ + yye_{0}^{l_{A}l_{B}}(d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x}d_{0}^{n_{A}n_{B}})(f_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}f_{0}^{m_{A}m_{B}}) \\ + e_{0}^{l_{A}l_{B}}(d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{x}d_{0}^{n_{A}n_{B}})(zf_{0}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}f_{0}^{m_{A}m_{B}}) \\ + e_{0}^{l_{A}l_{B}}(d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{y}d_{0}^{n_{A}n_{B}})(zf_{0}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}f_{0}^{m_{A}m_{B}}) \\ + e_{0}^{l_{A}l_{B}}(d_{1}^{n_{A}n_{B}} + \overline{\mathbf{PC}}_{y}e_{0}^{l_{A}l_{B}})(zf_{0}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}f_{0}^{m_{A}m_{B}}) \\ + d_{0}^{n_{A}n_{B}}(e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y}e_{0}^{l_{A}l_{B}})(f_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}f_{0}^{m_{A}m_{B}}) \\ + d_{0}^{n_{A}n_{B}}(ye_{0}^{l_{A}l_{B}} + yye_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y}yye_{0}^{l_{A}l_{B}})(f_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}f_{0}^{m_{A}m_{B}}) \\ + d_{0}^{n_{A}n_{B}}(e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y}e_{0}^{l_{A}l_{B}})(zf_{0}^{m_{A}m_{B}} + zzf_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}zzf_{0}^{m_{A}m_{B}}) \\ + d_{0}^{n_{A}n_{B}}(e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y}e_{0}^{l_{A}l_{B}})(zf_{0}^{m_{A}m_{B}} + zzf_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}zzf_{0}^{m_{A}m_{B}}) \\ + d_{0}^{n_{A}n_{B}}(e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y}e_{0}^{l_{A}l_{B}})(zf_{0}^{m_{A}m_{B}} + zzf_{1}^{m_{A}m_{B}} + \overline{\mathbf{PC}}_{z}zzf_{0}^{m_{A}m_{B}}) \\ + d_{0}^{n_{A}n_{B}}(e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y}e_{0}^{l_{A}l_{B}})(zf_{0}^{m_{A}m_{B}} + zzf_{1$$

$$Q_{xx}^{SR} = E_{AB} \ e \sum_{N,L,M} \left\{ D_{NLM}^{x} [NLM \mid 2x_{C}] + (D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) [NLM \mid x_{C}^{2}] \right\}$$
(V.137)
$$= E_{AB} \ e \left(\frac{\pi}{\alpha_{P}}\right)^{\frac{3}{2}} \left\{ e_{0}^{l_{A}l_{B}} f_{0}^{m_{A}m_{B}} \left(2^{x} d_{1}^{n_{A}n_{B}} + 2\overline{\mathbf{PC}}_{x}^{x} d_{0}^{n_{A}n_{B}}\right) + e_{0}^{l_{A}l_{B}} f_{0}^{m_{A}m_{B}} \left(2^{xx} d_{2}^{n_{A}n_{B}} + 2\overline{\mathbf{PC}}_{x}^{xx} d_{1}^{n_{A}n_{B}} + \left(\overline{\mathbf{PC}}_{x}^{2} + \frac{1}{2\alpha_{P}}\right)^{xx} d_{0}^{n_{A}n_{B}}\right)$$

$$= E_{AB} \ e \sum_{N,L,M} \left\{ D_{NLM}^{x} | NLM | 2x_C \right] \\ + \left(D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz} \right) [NLM | x_C^2] \right\}$$
(V.137)

$$\sum_{N,L,M} \left\{ D_{NLM}^{x} [NLM \mid 2x_{C}] \right\}$$

$$(D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) [NLM \mid x_{C}^{2}] \right\}$$

$$(V$$

$$\sum_{N,L,M} \left\{ D_{NLM}^{x} [NLM \mid 2x_{C}] \right. \\ \left. \sum_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz} \right] \right\}$$
(1)

$$\int \left(2d_2^{n_A n_B} + 2\overline{\mathbf{PC}}_x d_1^{n_A n_B} + C \right) dt$$

 $\mathbf{Q}_{yy}^{\mathrm{SR}} = E_{AB} \ e \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} \left\{ d_0^{m_A n_B} f_0^{m_A m_B} \left(2 \ {}^{y} e_1^{l_A l_B} + 2 \overline{\mathbf{PC}}_y \ {}^{y} e_0^{l_A l_B}\right) \right\}$

 $+ {}^{yy}e_0^{l_A l_B}f_0^{m_A m_B} \left(2d_2^{n_A n_B} + 2\overline{\mathbf{PC}}_x d_1^{n_A n_B} + \left(\overline{\mathbf{PC}}_x^2 + \frac{1}{2\alpha_P}\right)d_0^{n_A n_B}\right)$

 $+ e_0^{l_A l_B \ zz} f_0^{m_A m_B} \left(2d_2^{n_A n_B} + 2\overline{\mathbf{PC}}_x d_1^{n_A n_B} + \left(\overline{\mathbf{PC}}_x^2 + \frac{1}{2\alpha_P} \right) d_0^{n_A n_B} \right) \bigg\},$

 $+ d_0^{n_A n_B} f_0^{m_A m_B} \left(2 \,^{yy} e_2^{l_A l_B} + 2 \overline{\mathbf{PC}}_y \,^{yy} e_1^{l_A l_B} + \left(\overline{\mathbf{PC}}_y^2 + \frac{1}{2\alpha_P} \right) \,^{yy} e_0^{l_A l_B} \right)$

 $+ {}^{xx}d_0^{n_An_B}f_0^{m_Am_B}\left(2e_2^{l_Al_B} + 2\overline{\mathbf{PC}}_ye_1^{l_Al_B} + \left(\overline{\mathbf{PC}}_y^2 + \frac{1}{2\alpha_P}\right)e_0^{l_Al_B}\right)$

(V.138)

V.3. One-electron integrals for relativistic corrections

$$+ d_{0}^{n_{A}n_{B}} zz f_{0}^{m_{A}m_{B}} \left(2e_{2}^{l_{A}l_{B}} + 2\overline{\mathbf{PC}}_{y}e_{1}^{l_{A}l_{B}} + \left(\overline{\mathbf{PC}}_{y}^{2} + \frac{1}{2\alpha_{P}}\right)e_{0}^{l_{A}l_{B}} \right) \right\}, \qquad (V.139)$$

$$Q_{zz}^{SR} = E_{AB} e \left(\frac{\pi}{\alpha_{P}}\right)^{\frac{3}{2}} \left\{ d_{0}^{n_{A}n_{B}}e_{0}^{l_{A}l_{B}} \left(2zf_{1}^{m_{A}m_{B}} + 2\overline{\mathbf{PC}}_{z}zf_{0}^{m_{A}m_{B}} \right) + d_{0}^{n_{A}n_{B}}e_{0}^{l_{A}l_{B}} \left(2zzf_{2}^{m_{A}m_{B}} + 2\overline{\mathbf{PC}}_{z}zzf_{1}^{m_{A}m_{B}} + \left(\overline{\mathbf{PC}}_{z}^{2} + \frac{1}{2\alpha_{P}}\right)zzf_{0}^{m_{A}m_{B}} \right) + xxd_{0}^{n_{A}n_{B}}e_{0}^{l_{A}l_{B}} \left(2f_{2}^{m_{A}m_{B}} + 2\overline{\mathbf{PC}}_{z}f_{1}^{m_{A}m_{B}} + \left(\overline{\mathbf{PC}}_{z}^{2} + \frac{1}{2\alpha_{P}}\right)f_{0}^{m_{A}m_{B}} \right) + d_{0}^{n_{A}n_{B}} yye_{0}^{l_{A}l_{B}} \left(2f_{2}^{m_{A}m_{B}} + 2\overline{\mathbf{PC}}_{z}f_{1}^{m_{A}m_{B}} + \left(\overline{\mathbf{PC}}_{z}^{2} + \frac{1}{2\alpha_{P}}\right)f_{0}^{m_{A}m_{B}} \right) \right\}. \qquad (V.140)$$

V.3.6. Spin-orbit quadrupole-moment integral

The SO quadrupole-moment integrals are given according to (V.85) if \hat{O} is replaced by \hat{Q}_{ij} and have been implemented in this work. In this way, the corresponding contributions, abbreviated by $Q_{ij}^{SO_{\eta}}$ with $\eta, \mu, \nu, i, j = x, y, z$ and η, μ, ν cyclic, can be written as

$$Q_{ij}^{SO_{\eta}} = -i \ e\sigma_{\eta} \left\langle g_B \left| \frac{\partial}{\partial \mu} \hat{Q}_{ij} \frac{\partial}{\partial \nu} - \frac{\partial}{\partial \nu} \hat{Q}_{ij} \frac{\partial}{\partial \mu} \right| g_A \right\rangle$$
(V.141)

$$= -i \ e \sigma_{\eta} E_{AB} \sum_{N,L,M} \left(D_{NLM}^{\nu} \left[NLM \left| \frac{\partial \hat{Q}_{ij}}{\partial \mu} \right| - D_{NLM}^{\mu} \left[NLM \left| \frac{\partial \hat{Q}_{ij}}{\partial \nu} \right| \right) \right).$$
(V.142)

As was already discussed for the SR case, the derivative of \hat{Q}_{ij} with respect to x, y or z leads either to a dipole-moment integral or vanishes. Accordingly, there are only dipole-moment contributions present in the SO quadrupole integrals. The resulting contributions are given by

$$\mathbf{Q}_{xx}^{\mathrm{SO}_x} = 0, \tag{V.143}$$

$$Q_{xx}^{SO_y} = -ie\sigma_y \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \ 2 \ e_0^{l_A l_B} \ {}^z f_0^{m_A m_B} \left(d_1^{n_A n_B} + \overline{\mathbf{PC}}_x \ d_0^{n_A n_B}\right), \tag{V.144}$$

$$Q_{xx}^{SO_z} = ie\sigma_z \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \ 2^{y} e_0^{l_A l_B} \ f_0^{m_A m_B} \left(d_1^{n_A n_B} + \overline{\mathbf{PC}}_x \ d_0^{n_A n_B}\right), \tag{V.145}$$

$$Q_{yy}^{SO_x} = ie\sigma_x \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \ 2 \ d_0^{n_A n_B} \ {}^z f_0^{m_A m_B} \left(e_1^{l_A l_B} + \overline{\mathbf{PC}}_y \ e_0^{l_A l_B}\right), \tag{V.146}$$

$$\mathbf{Q}_{yy}^{\mathrm{SO}_y} = 0, \tag{V.147}$$

 $V. \ \ Calculation \ of \ Relativistic \ Integrals$

$$Q_{yy}^{SO_z} = -ie\sigma_z \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \ 2^{x} d_0^{n_A n_B} \ f_0^{m_A m_B} \left(e_1^{l_A l_B} + \overline{\mathbf{PC}}_y \ e_0^{l_A l_B}\right), \tag{V.148}$$

$$Q_{zz}^{SO_x} = -ie\sigma_x \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \ 2 \ d_0^{n_A n_B \ y} e_0^{l_A l_B} \left(f_1^{m_A m_B} + \overline{\mathbf{PC}}_z \ f_0^{m_A m_B}\right), \qquad (V.149)$$

$$Q_{zz}^{SO_y} = ie\sigma_y \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \ 2^{x} d_0^{n_A n_B} \ e_0^{l_A l_B} \left(f_1^{m_A m_B} + \overline{\mathbf{PC}}_z \ f_0^{m_A m_B}\right),$$
(V.150)

$$Q_{zz}^{SO_y} = ie\sigma_y \left(\frac{\pi}{\alpha_P}\right) \quad E_{AB} \ 2^{x} d_0^{n_A n_B} \ e_0^{A t_B} \left(f_1^{m_A m_B} + \mathbf{PC}_z \ f_0^{m_A m_B}\right), \tag{V.150}$$

$$Q_{zz}^{SO_z} = 0, \qquad (V.151)$$

$$\mathbf{Q}_{zz}^{\mathrm{SO}_z} = 0, \tag{V.151}$$

$$\mathbf{Q}_{xy}^{\mathrm{SO}_x} = ie\sigma_x \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \ e_0^{l_A l_B} \ {}^zf_0^{m_A m_B} \left(d_1^{n_A n_B} + \overline{\mathbf{PC}}_x \ d_0^{n_A n_B}\right), \tag{V.152}$$

$$\mathbf{Q}_{xy}^{SO_x} = ie\sigma_x \left(\frac{\pi}{\alpha_P}\right) \quad E_{AB} e_0^{AB} \stackrel{z}{}_{f_0}^{m_Am_B} \left(d_1^{m_Am_B} + \mathbf{PC}_x d_0^{m_Am_B}\right), \tag{V.152}$$

$$\mathbf{Q}_{xy}^{\mathrm{SO}_y} = -ie\sigma_y \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \ d_0^{l_A l_B} \ {}^z f_0^{m_A m_B} \left(e_1^{l_A l_B} + \overline{\mathbf{PC}}_y \ e_0^{l_A l_B}\right), \tag{V.153}$$

$$Q_{xy}^{SO_z} = -ie\sigma_z \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \left\{ e_0^{l_A l_B} f_0^{m_A m_B} \left({}^x d_1^{n_A n_B} + \overline{\mathbf{PC}}_x {}^x d_0^{n_A n_B} \right) \right\}$$

$$(V.154)$$

$$-d_{0}^{n_{A}n_{B}} f_{0}^{m_{A}m_{B}} \left({}^{y}e_{1}^{l_{A}l_{B}} + \overline{\mathbf{PC}}_{y} {}^{y}e_{0}^{l_{A}l_{B}}\right) \Big\},$$
(V.154)

$$Q_{xz}^{SO_x} = -ie\sigma_x \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \, {}^{y}e_0^{l_A l_B} \, f_0^{m_A m_B} \left(d_1^{n_A n_B} + \overline{\mathbf{PC}}_x \, d_0^{n_A n_B}\right), \qquad (V.155)$$

$$Q_{xz}^{SO_y} = -ie\sigma_y \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \left\{ d_0^{n_A n_B} e_0^{l_A l_B} \left({}^z f_1^{m_A m_B} + \overline{\mathbf{PC}}_z \, {}^z f_0^{m_A m_B} \right) - e_0^{l_A l_B} f_0^{m_A m_B} \left({}^x d_1^{n_A n_B} + \overline{\mathbf{PC}}_x \, {}^x d_0^{n_A n_B} \right) \right\},$$
(V.156)

$$Q_{xz}^{SO_z} = ie\sigma_z \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} d_0^{n_A n_B} \, {}^ye_0^{l_A l_B} \left(f_1^{m_A m_B} + \overline{\mathbf{PC}}_z \, f_0^{m_A m_B}\right), \tag{V.157}$$

$$Q_{yz}^{SO_x} = -ie\sigma_x \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \left\{ d_0^{n_A n_B} f_0^{m_A m_B} \left({}^{y}e_1^{l_A l_B} + \overline{\mathbf{PC}}_y {}^{y}e_0^{l_A l_B} \right) \right\}$$

$$(V.158)$$

$$- d_0^{n_A n_B} e_0^{l_A l_B} \left({}^z f_1^{m_A m_B} + \overline{\mathbf{PC}}_z {}^z f_0^{m_A m_B} \right) \Big\},$$
(V.158)

$$\mathbf{Q}_{yz}^{\mathrm{SO}_y} = i e \sigma_y \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \,^x d_0^{n_A n_B} \, f_0^{m_A m_B} \left(e_1^{l_A l_B} + \overline{\mathbf{PC}}_y \, e_0^{l_A l_B}\right), \tag{V.159}$$

$$Q_{yz}^{OOY} = ie\sigma_y \left(\frac{\pi}{\alpha_P}\right) E_{AB} d_0^{AAB} f_0^{BAB} \left(e_1^{AAB} + \mathbf{PC}_y e_0^{AB}\right), \qquad (V.159)$$

$$Q_{yz}^{SO_z} = -i \ e\sigma_z \left(\frac{\pi}{\alpha_P}\right)^{\frac{3}{2}} E_{AB} \ ^{x} d_0^{n_A n_B} \ e_0^{l_A l_B} \left(f_1^{m_A m_B} + \overline{\mathbf{PC}}_z \ f_0^{m_A m_B}\right).$$
(V.160)

V.3.7. Scalar-relativistic electric-field gradient integral

When calculating integrals over the electric-field gradient (efg) operator

$$\hat{q}_{ij} = \frac{3i_C j_C - \delta_{ij} \mathbf{r}_C^2}{\mathbf{r}_C^5}, \quad i_C, j_C = x_C, y_C, z_C,$$
(V.161)

it can be exploited for the non-diagonal elements $(i \neq j)$ that the operator may be rewritten using the derivatives with respect to C_i, C_j or, due to (V.102), with respect to P_i, P_j

$$\frac{3i_C j_C}{\mathbf{r}_C^5} = \frac{\partial}{\partial C_i} \frac{\partial}{\partial C_j} \frac{1}{\mathbf{r}_C} = \frac{\partial}{\partial P_i} \frac{\partial}{\partial P_j} \frac{1}{\mathbf{r}_C}.$$
 (V.162)

The corresponding basic integral for the xy component is thus given as

$$\begin{bmatrix} NLM \middle| \frac{3x_C y_C}{\mathbf{r}_C^5} \end{bmatrix} = \frac{\partial}{\partial P_x} \frac{\partial}{\partial P_y} \left(\frac{\partial}{\partial P_x} \right)^N \left(\frac{\partial}{\partial P_y} \right)^L \left(\frac{\partial}{\partial P_z} \right)^M \int d^3 \mathbf{r} \frac{1}{|\mathbf{r}_C|} e^{-\alpha_P \mathbf{r}_P^2} \quad (V.163)$$
$$= \frac{2\pi}{R} R_{(N+1)(L+1)M} \quad (V.164)$$

$$= \frac{2\pi}{\alpha_P} R_{(N+1)(L+1)M}, \tag{V.164}$$

or, more generally,

$$\left[NLM \left| \frac{3i_C j_C}{\mathbf{r}_C^5} \right] = \frac{2\pi}{\alpha_P} R_{NLM}^{(i+1)(j+1)}.$$
 (V.165)

The non-diagonal SR efg integrals can be written as

$$\left\langle g_B \middle| \hat{\mathbf{p}} \frac{3i_C j_C}{\mathbf{r}_C^5} \hat{\mathbf{p}} \middle| g_A \right\rangle = -\sum_{\nu=x,y,z} \left\langle g_B \middle| \frac{\partial}{\partial \nu} \frac{3i_C j_C}{\mathbf{r}_C^5} \frac{\partial}{\partial \nu} \middle| g_A \right\rangle$$
(V.166)
$$= -\sum_{\nu=x,y,z} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^{\nu} \left[NLM \middle| \frac{\partial}{\partial \nu} \frac{3i_C j_C}{\mathbf{r}_C^5} \right] + D_{NLM}^{\nu\nu} \left[NLM \middle| \frac{3i_C j_C}{\mathbf{r}_C^5} \right] \right\}.$$
(V.167)

To evaluate this expression the first basic integral on the right-hand side needs to be tackled. Using (V.102) it can be rewritten as

$$\left[NLM \left| \frac{\partial}{\partial \nu} \frac{3i_C j_C}{\mathbf{r}_C^5} \right] = \frac{\partial}{\partial \nu} \frac{2\pi}{\alpha_P} R_{NLM}^{(i+1)(j+1)} = \frac{\partial}{\partial P_\nu} \frac{2\pi}{\alpha_P} R_{NLM}^{(i+1)(j+1)}$$
(V.168)

$$= \begin{cases} \nu = i : \frac{2\pi}{\alpha_P} R_{NLM}^{(i+2)(j+1)} \\ \nu = j : \frac{2\pi}{\alpha_P} R_{NLM}^{(i+1)(j+2)} \\ \nu = k : \frac{2\pi}{\alpha_P} R_{NLM}^{(i+1)(j+1)(k+1)} \end{cases}$$
(V.169)

with $\nu, i, j, k = x, y, z$ and $i \neq j \neq k$. Using (V.165) and (V.168), the non-diagonal elements, abbreviated as $q_{ij}^{SR}, i, j = x, y, z$ are given as

$$q_{xy}^{SR} = -\frac{2\pi}{\alpha_P} E_{AB} \sum_{NLM} \left\{ D_{NLM}^x R_{(N+2)(L+1)M} + D_{NLM}^y R_{(N+1)(L+2)M} + D_{NLM}^z R_{(N+1)(L+1)(M+1)} + (D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) R_{(N+1)(L+1)M} \right\}, \quad (V.170)$$

$$q_{xz}^{SR} = -\frac{2\pi}{\alpha_P} E_{AB} \sum_{NLM} \left\{ D_{NLM}^x R_{(N+2)L(M+1)} + D_{NLM}^y R_{(N+1)(L+1)(M+1)} + D_{NLM}^y R_{(N+1)(L+1)(M+1)} + (D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) R_{(N+1)L(M+1)} \right\}, \quad (V.171)$$

$$q_{yz}^{SR} = -\frac{2\pi}{\alpha_P} E_{AB} \sum_{NLM} \left\{ D_{NLM}^x R_{(N+1)(L+1)(M+1)} + D_{NLM}^y R_{N(L+2)(M+1)} + D_{NLM}^z R_{N(L+1)(M+1)} + (D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) R_{N(L+1)(M+1)} + (D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) R_{N(L+1)(M+1)} + (D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) R_{N(L+1)(M+1)} \right\}. \quad (V.172)$$

For the diagonal elements, the Poisson equation 111

$$\nabla^2 \frac{1}{\mathbf{r}_C} = 4\pi \delta(\mathbf{r}_C) \tag{V.173}$$

needs to be fulfilled, i.e., for $\mathbf{r}_{C} = 0$ the contribution from the delta function needs to be accounted for. To avoid this, the diagonal elements may be rewritten into the form

$$\frac{3i_C^2 - \mathbf{r}_C^2}{\mathbf{r}_C^5} = \frac{1}{3} \left(2\frac{\partial^2}{\partial i_C^2} - \frac{\partial^2}{\partial j_C^2} - \frac{\partial^2}{\partial k_C^2} \right) \frac{1}{|\mathbf{r}_C|}, \quad i, j, k = x, y, z \text{ and } i \neq j \neq k$$
(V.174)

as then the contributions mentioned above cancel out and the efg tensor is, as it should be, also at $\mathbf{r}_{C} = 0$ a traceless quantity. The basic integral is then given by

$$\left[NLM \left| \frac{3i_C^2 - \mathbf{r}_C^2}{\mathbf{r}_C^5} \right] = \frac{2\pi}{\alpha_P} \frac{1}{3} \left(2R_{NLM}^{(i+2)} - R_{NLM}^{(j+2)} - R_{NLM}^{(k+2)} \right).$$
(V.175)

The diagonal scalar-relativistic electric-field gradient integrals are thus given as

$$\left\langle g_B \middle| \hat{\mathbf{p}} \frac{3i_C^2 - \mathbf{r}_C^2}{\mathbf{r}_C^5} \hat{\mathbf{p}} \middle| g_A \right\rangle = -\sum_{\nu=x,y,z} \left\langle g_B \middle| \frac{\partial}{\partial \nu} \frac{3i_C^2 - \mathbf{r}_C^2}{\mathbf{r}_C^5} \frac{\partial}{\partial \nu} \middle| g_A \right\rangle$$
(V.176)
$$= -\sum_{\nu=x,y,z} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^{\nu} \left[NLM \middle| \frac{\partial}{\partial \nu} \frac{3i_C^2 - \mathbf{r}_C^2}{\mathbf{r}_C^5} \right] \right.$$
$$\left. + D_{NLM}^{\nu\nu} \left[NLM \middle| \frac{3i_C^2 - \mathbf{r}_C^2}{\mathbf{r}_C^5} \right] \right\}.$$
(V.177)

Analog to (V.168) and (V.169), the basic integral containing the derivative with respect to ν can be written as

$$\begin{bmatrix} NLM \left| \frac{\partial}{\partial \nu} \frac{3i_C^2 - \mathbf{r}_C^2}{\mathbf{r}_C^5} \right] = \frac{\partial}{\partial P_{\nu}} \frac{2\pi}{\alpha_P} \frac{1}{3} \left(2R_{NLM}^{(i+2)} - R_{NLM}^{(j+2)} - R_{NLM}^{(k+2)} \right)$$
(V.178)
$$= \begin{cases} \nu = i : \frac{2\pi}{\alpha_P} \frac{1}{3} \left(2R_{NLM}^{(i+3)} - R_{NLM}^{(i+1)(j+2)} - R_{NLM}^{(i+1)(k+2)} \right) \\ \nu = j : \frac{2\pi}{\alpha_P} \frac{1}{3} \left(2R_{NLM}^{(i+2)(j+1)} - R_{NLM}^{(j+3)} - R_{NLM}^{(j+1)(k+2)} \right) \\ \nu = k : \frac{2\pi}{\alpha_P} \frac{1}{3} \left(2R_{NLM}^{(i+2)(k+1)} - R_{NLM}^{(j+2)(k+1)} - R_{NLM}^{(k+3)} \right) \end{cases}$$
(V.179)

with $\nu, i, j, k = x, y, z$ and $i \neq j \neq k$. Accordingly, the integrals for the diagonal elements are given as

$$q_{xx}^{SR} = -\frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \frac{1}{3} \Big\{ D_{NLM}^x (2R_{(N+3)LM} - R_{(N+1)(L+2)M} - R_{(N+1)L(M+2)}) \\ + D_{NLM}^y (2R_{(N+2)(L+1)M} - R_{N(L+3)M} - R_{N(L+1)(M+2)}) \\ + D_{NLM}^z (2R_{(N+2)L(M+1)} - R_{N(L+2)(M+1)} - R_{NL(M+3)}) \\ + (D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) (2R_{(N+2)LM} - R_{N(L+2)M} - R_{NL(M+2)}) \Big\}, \quad (V.180)$$

$$q_{yy}^{SR} = -\frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \frac{1}{3} \Big\{ D_{NLM}^x (2R_{(N+1)(L+2)M} - R_{(N+3)LM} - R_{(N+1)L(M+2)}) \\ + D_{NLM}^y (2R_{N(L+3)M} - R_{(N+2)(L+1)M} - R_{N(L+1)(M+2)}) \Big\}$$

$$+ D_{NLM}^{z} (2R_{N(L+2)(M+1)} - R_{(N+2)L(M+1)} - R_{NL(M+3)}) + (D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) (2R_{N(L+2)M} - R_{(N+2)LM} - R_{NL(M+2)}) \bigg\}, \quad (V.181)$$
$$q_{zz}^{SR} = -\frac{2\pi}{\alpha_{P}} E_{AB} \sum_{N,L,M} \frac{1}{3} \bigg\{ D_{NLM}^{x} (2R_{(N+1)L(M+2)} - R_{(N+3)LM} - R_{(N+1)(L+2)M}) + D_{NLM}^{y} (2R_{N(L+1)(M+2)} - R_{(N+2)(L+1)M} - R_{N(L+3)M}) + D_{NLM}^{z} (2R_{NL(M+3)} - R_{(N+2)L(M+1)} - R_{N(L+2)(M+1)}) + (D_{NLM}^{xx} + D_{NLM}^{yy} + D_{NLM}^{zz}) (2R_{NL(M+2)} - R_{(N+2)LM} - R_{N(L+2)M}) \bigg\}. \quad (V.182)$$

V.3.8. Spin-orbit electric-field gradient integral

For the SO contributions which are again needed at the full DPT4 level in a corresponding property calculation (see chapter IV.4) and which have been implemented as a part of this work, the required integrals are

$$\langle g_B \mid i\boldsymbol{\sigma}(\hat{\mathbf{p}}\hat{q}_{ij} \times \hat{\mathbf{p}}) \mid g_A \rangle_{\eta} = -i\sigma_{\eta} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^{\nu} \left[NLM \middle| \frac{\partial \hat{q}_{ij}}{\partial \mu} \right] - D_{NLM}^{\mu} \left[NLM \middle| \frac{\partial \hat{q}_{ij}}{\partial \nu} \right] \right\}$$
(V.183)

with η, μ, ν cyclic. The basic integrals have already been evaluated in (V.169) and (V.179). It follows therefore for the SO contributions, abbreviated as $q_{ij}^{SO_{\eta}}$:

$$\begin{aligned} \mathbf{q}_{xx}^{SO_x} &= -i\sigma_x \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^z (2R_{(N+2)(L+1)M} - R_{N(L+3)M} - R_{N(L+1)(M+2)}) \right. \\ &\quad \left. - D_{NLM}^y (2R_{(N+2)L(M+1)} - R_{N(L+2)(M+1)} - R_{NL(M+3)}) \right\}, \qquad (V.184) \\ \mathbf{q}_{xx}^{SO_y} &= -i\sigma_y \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^x (2R_{(N+2)L(M+1)} - R_{N(L+2)(M+1)} - R_{NL(M+3)}) \right. \\ &\quad \left. - D_{NLM}^z (2R_{(N+3)LM} - R_{(N+1)(L+2)M} - R_{(N+1)L(M+2)}) \right\}, \qquad (V.185) \\ \mathbf{q}_{xx}^{SO_z} &= -i\sigma_z \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^y (2R_{(N+3)LM} - R_{(N+1)(L+2)M} - R_{(N+1)L(M+2)}) \right. \\ &\quad \left. - D_{NLM}^x (2R_{(N+2)(L+1)M} - R_{N(L+3)M} - R_{N(L+1)(M+2)}) \right\}, \qquad (V.186) \\ \mathbf{q}_{yy}^{SO_x} &= -i\sigma_x \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^z (2R_{N(L+3)M} - R_{(N+2)(L+1)M} - R_{N(L+1)(M+2)}) \right\}, \qquad (V.186) \\ \mathbf{q}_{yy}^{SO_x} &= -i\sigma_x \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^z (2R_{N(L+3)M} - R_{(N+2)(L+1)M} - R_{N(L+1)(M+2)}) \right\}, \qquad (V.186) \\ \left. - D_{NLM}^y (2R_{N(L+2)(M+1)} - R_{(N+2)L(M+1)} - R_{NL(M+3)}) \right\}, \qquad (V.187) \end{aligned}$$

$$q_{yy}^{SO_y} = -i\sigma_y \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^x (2R_{N(L+2)(M+1)} - R_{(N+2)L(M+1)} - R_{NL(M+3)}) - D_{NLM}^z (2R_{(N+1)(L+2)M} - R_{(N+3)LM} - R_{(N+1)L(M+2)}) \right\},$$
(V.188)

$$q_{yy}^{SO_z} = -i\sigma_z \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^y (2R_{(N+1)(L+2)M} - R_{(N+3)LM} - R_{(N+1)L(M+2)}) \right\}$$

$$-D_{NLM}^{x}(2R_{N(L+3)M} - R_{(N+2)(L+1)M} - R_{N(L+1)(M+2)})\}, \qquad (V.189)$$

$$q_{zz}^{SO_x} = -i\sigma_x \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^z (2R_{N(L+1)(M+2)} - R_{(N+2)(L+1)M} - R_{N(L+3)M}) \right\}$$

$$-D_{NLM}^{y}(2R_{NL(M+3)} - R_{(N+2)L(M+1)} - R_{N(L+2)(M+1)})\}, \qquad (V.190)$$

$$q_{zz}^{SO_y} = -i\sigma_y \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^x (2R_{NL(M+3)} - R_{(N+2)L(M+1)} - R_{N(L+2)(M+1)}) \right\}$$

$$D_{ZZ}^z = \left(2R - R_{NLM} \right) \left\{ D_{NLM}^x (2R_{NL(M+3)} - R_{(N+2)L(M+1)} - R_{N(L+2)(M+1)}) \right\}$$

$$(V.101)$$

$$-D_{NLM}^{z}(2R_{(N+1)L(M+2)} - R_{(N+3)LM} - R_{(N+1)(L+2)M})\},$$
(V.191)

$$q_{zz}^{SO_z} = -i\sigma_z \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^y (2R_{(N+1)L(M+2)} - R_{(N+3)LM} - R_{(N+1)(L+2)M}) \right\}$$

$$D_{NLM}^x = \left(2R - R_{NLM} - R_{(N+1)(L+2)M} \right)$$
(V.102)

$$-D_{NLM}^{x}(2R_{N(L+1)(M+2)} - R_{(N+2)(L+1)M} - R_{N(L+3)M})\}, \qquad (V.192)$$

$$q_{xy}^{SO_x} = -i\sigma_x \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^z R_{(N+1)(L+2)M} - D_{NLM}^y R_{(N+1)(L+1)(M+1)} \right\}, \quad (V.193)$$

$$q_{xy}^{SO_y} = -i\sigma_y \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^x R_{(N+1)(L+1)(M+1)} - D_{NLM}^z R_{(N+2)(L+1)M} \right\}, \quad (V.194)$$

$$q_{xy}^{SO_z} = -i\sigma_z \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^y R_{(N+2)(L+1)M} - D_{NLM}^x R_{(N+1)(L+2)M} \right\},$$
(V.195)

$$q_{xz}^{SO_x} = -i\sigma_x \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^z R_{(N+1)(L+1)(M+1)} - D_{NLM}^y R_{(N+1)L(M+2)} \right\}, \quad (V.196)$$

$$q_{xz}^{SO_y} = -i\sigma_y \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^x R_{(N+1)L(M+2)} - D_{NLM}^z R_{(N+2)L(M+1)} \right\},$$
(V.197)

$$q_{xz}^{SO_z} = -i\sigma_z \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^y R_{(N+2)L(M+1)} - D_{NLM}^x R_{(N+1)(L+1)(M+1)} \right\}, \quad (V.198)$$

$$q_{yz}^{SO_x} = -i\sigma_x \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^z R_{N(L+2)(M+1)} - D_{NLM}^y R_{N(L+1)(M+2)} \right\}, \qquad (V.199)$$

$$q_{yz}^{SO_y} = -i\sigma_y \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^x R_{N(L+1)(M+2)} - D_{NLM}^z R_{(N+1)(L+1)(M+1)} \right\}, \quad (V.200)$$

$$q_{yz}^{SO_z} = -i\sigma_z \frac{2\pi}{\alpha_P} E_{AB} \sum_{N,L,M} \left\{ D_{NLM}^y R_{(N+1)(L+1)(M+1)} - D_{NLM}^x R_{N(L+2)(M+1)} \right\}.$$
 (V.201)

V.4. Two-electron integrals for relativistic corrections

The integrals appearing in the DPT treatment up to DPT4 (see chapter IV) are given by

$$\left\langle g_B g_D \middle| \boldsymbol{\sigma}_i \hat{\mathbf{p}}_i \frac{1}{r_{12}} \boldsymbol{\sigma}_i \hat{\mathbf{p}}_i \middle| g_A g_C \right\rangle, \quad i = 1, 2$$
 (V.202)

and

$$\left\langle g_B g_D \middle| \boldsymbol{\sigma}_1 \hat{\mathbf{p}}_1 \boldsymbol{\sigma}_2 \hat{\mathbf{p}}_2 \frac{1}{r_{12}} \boldsymbol{\sigma}_1 \hat{\mathbf{p}}_1 \boldsymbol{\sigma}_2 \hat{\mathbf{p}}_2 \middle| g_A g_C \right\rangle.$$
 (V.203)

Using the Dirac identity, both integrals may be separated into a SR and a SO contribution leading to

$$\left\langle g_B g_D \middle| \boldsymbol{\sigma}_i \hat{\mathbf{p}}_i \frac{1}{r_{12}} \boldsymbol{\sigma}_i \hat{\mathbf{p}}_i \middle| g_A g_C \right\rangle = \left\langle g_B g_D \middle| \hat{\mathbf{p}}_i \frac{1}{r_{12}} \hat{\mathbf{p}}_i \middle| g_A g_C \right\rangle + \left\langle g_B g_D \middle| i \boldsymbol{\sigma}_i \left(\hat{\mathbf{p}}_i \frac{1}{r_{12}} \times \hat{\mathbf{p}}_i \right) \middle| g_A g_C \right\rangle, \quad i = 1, 2 \quad (V.204)$$

and, due to spin orthogonality, to

$$\left\langle g_B g_D \middle| \boldsymbol{\sigma}_1 \hat{\mathbf{p}}_1 \boldsymbol{\sigma}_2 \hat{\mathbf{p}}_2 \frac{1}{r_{12}} \boldsymbol{\sigma}_1 \hat{\mathbf{p}}_1 \boldsymbol{\sigma}_2 \hat{\mathbf{p}}_2 \middle| g_A g_C \right\rangle =$$

$$\left\langle g_B g_D \middle| \hat{\mathbf{p}}_1 \hat{\mathbf{p}}_2 \frac{1}{r_{12}} \hat{\mathbf{p}}_1 \hat{\mathbf{p}}_2 \middle| g_A g_C \right\rangle + \left\langle g_B g_D \middle| i \boldsymbol{\sigma}_2 \left(\hat{\mathbf{p}}_2 \times i \boldsymbol{\sigma}_1 \left(\hat{\mathbf{p}}_1 \times \frac{1}{r_{12}} \hat{\mathbf{p}}_1 \right) \hat{\mathbf{p}}_2 \right) \middle| g_A g_C \right\rangle$$

$$(V.205)$$

$$(V.206)$$

where in the SO contribution of (V.206) the integral is only non-zero if σ_1 and σ_2 are of the same type, i.e., both have to be either σ_x, σ_y , or σ_z to give a non-vanishing contribution.

For the integrals in (V.204) it should be noted that it is sufficient to evaluate the contributions for i = 1 as the electrons 1 and 2 are interchangeable. Furthermore, unlike for the one-electron integrals where all the operators were evaluated by working to the right, here all operators standing left from r_{12}^{-1} are evaluated by working to the left while all operators to the right of r_{12}^{-1} are acting to the right.

V.4.1. Scalar-relativistic two-electron integrals

The SR part of (V.204) may be written as

$$\left\langle g_{B}g_{D} \middle| \hat{\mathbf{p}}_{1} \frac{1}{r_{12}} \hat{\mathbf{p}}_{1} \middle| g_{A}g_{C} \right\rangle = -\sum_{\nu=x,y,z} \left\langle g_{B}g_{D} \middle| \frac{\partial}{\partial\nu_{1}} \frac{1}{r_{12}} \frac{\partial}{\partial\nu_{1}} \middle| g_{A}g_{C} \right\rangle$$
$$= \sum_{\nu=x,y,z} \int \int \mathrm{d}^{3}\mathbf{r}_{1} \mathrm{d}^{3}\mathbf{r}_{2} G_{BA}^{\nu\nu} G_{DC} \frac{1}{r_{12}} \qquad (V.207)$$

with $G_{DC} = \Omega_{DC}$ and $G_{BA}^{\nu\nu}$ given for the xx component as

$$G_{BA}^{xx} = \frac{\partial g_B}{\partial x_1} \frac{\partial g_A}{\partial x_1} \tag{V.208}$$

$$=E_{AB}\sum_{N=0}^{n_{A}+n_{B}+2}{}^{AB}d_{N}^{n_{A}n_{B}}\Lambda_{N}\sum_{L=0}^{l_{A}+l_{B}}e_{L}^{l_{A}l_{B}}\Lambda_{L}\sum_{M=0}^{m_{A}+m_{B}}f_{M}^{m_{A}m_{B}}\Lambda_{M}e^{-\alpha_{P}\mathbf{r}_{P}^{2}}$$
(V.209)

$$=E_{AB}\sum_{N,L,M}D_{NLM}^{xx_{AB}}\Lambda_N\Lambda_L\Lambda_M e^{-\alpha_P \mathbf{r}_P^2}$$
(V.210)

with the coefficients

$${}^{AB}d_{N}^{n_{A}n_{B}} = 4\alpha_{A}\alpha_{B}d_{N}^{(n_{A}+1)(n_{B}+1)} - 2\alpha_{B}n_{A}d_{N}^{(n_{A}-1)(n_{B}+1)} - 2\alpha_{A}n_{B}d_{N}^{(n_{A}+1)(n_{B}-1)} + n_{A}n_{B}d_{N}^{(n_{A}-1)(n_{B}-1)}$$
(V.211)

and

$$D_{NLM}^{\nu\nu_{AB}} = \begin{cases} \nu = x : {}^{AB} d_N^{n_A n_B} e_L^{l_A l_B} f_M^{m_A m_B} \\ \nu = y : d_N^{n_A n_B} {}^{AB} e_L^{l_A l_B} f_M^{m_A m_B} \\ \nu = z : d_N^{n_A n_B} e_L^{l_A l_B} {}^{AB} f_M^{m_A m_B} \end{cases}$$
(V.212)

Similar expression also hold for G_{BA}^{yy} and G_{BA}^{zz} and the corresponding coefficients. For the integrals in (V.207), abbreviated as g_1^{SR} it follows

$$g_{1}^{SR} = E_{AB}E_{CD}\sum_{N,L,M}\sum_{N',L',M'} \left(D_{NLM}^{xx_{AB}}D_{N'L'M'} + D_{NLM}^{yy_{AB}}D_{N'L'M'} + D_{NLM}^{zz_{AB}}D_{N'L'M'} \right) \\ \times \left[NLM \left| \frac{1}{r_{12}} \right| N'L'M' \right] \\ = \sum_{N,L,M}\sum_{N',L',M'} \lambda_{0} (-1)^{N'+L'+M'} E_{AB}E_{CD} \left(D_{NLM}^{xx_{AB}} + D_{NLM}^{yy_{AB}} + D_{NLM}^{zz_{AB}} \right)$$

$$\times D_{N'L'M'}R_{N+N',L+L',M+M'},$$
 (V.213)

while the SR integrals in (V.206), abbreviated as $g_{12}^{\rm SR}$ are given by

$$g_{12}^{\rm SR} = \sum_{\mu=x,y,z} \sum_{\nu=x,y,z} \left\langle g_B g_D \left| \frac{\partial}{\partial \mu_1} \frac{\partial}{\partial \nu_2} \frac{1}{r_{12}} \frac{\partial}{\partial \mu_1} \frac{\partial}{\partial \nu_2} \right| g_A g_C \right\rangle \tag{V.214}$$

$$= \sum_{\mu=x,y,z} \sum_{\nu=x,y,z} \int \int d^{3}\mathbf{r}_{1} d^{3}\mathbf{r}_{2} G_{BA}^{\mu\mu} G_{DC}^{\nu\nu} \frac{1}{r_{12}}$$
(V.215)
$$= \sum_{\mu=x,y,z} \sum_{\lambda_{0}(-1)^{N'+L'+M'} E_{AB} E_{CD}} (D_{NLM}^{xx_{AB}} + D_{NLM}^{yy_{AB}} + D_{NLM}^{zz_{AB}})$$

$$\sum_{N,L,M} \sum_{N',L',M'} (V.216) = D_{AB} D_{CD} (D_{NLM} + D_{NLM} + D_{NLM}) \times (D_{N'L'M'}^{xx_{CD}} + D_{N'L'M'}^{yy_{CD}} + D_{N'L'M'}^{zz_{CD}}) R_{N+N',L+L',M+M'}.$$
(V.216)

V.4.2. Spin-orbit two-electron integrals

The SO contribution in (V.204) to a specific component $\eta = x, y, z$ is given by

$$\left\langle g_B g_D \middle| i\boldsymbol{\sigma}_1 \left(\hat{\mathbf{p}}_1 \frac{1}{r_{12}} \times \hat{\mathbf{p}}_1 \right) \middle| g_A g_C \right\rangle_{\eta} = -\sigma_{1\eta} i \left\langle g_B g_D \middle| \frac{\partial}{\partial \mu_1} \frac{1}{r_{12}} \frac{\partial}{\partial \nu_1} - \frac{\partial}{\partial \nu_1} \frac{1}{r_{12}} \frac{\partial}{\partial \mu_1} \middle| g_A g_C \right\rangle$$
$$= i\sigma_{1\eta} \int \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 (G_{BA}^{\mu\nu} G_{DC} - G_{BA}^{\nu\mu} G_{DC}) \frac{1}{r_{12}}$$
(V.217)

with η, μ, ν cyclic and $G^{\mu\nu}_{BA}$ given exemplary for the xy component as

$$G_{BA}^{xy} = \frac{\partial g_B}{\partial x} \frac{\partial g_A}{\partial y} \tag{V.218}$$

$$=\sum_{N=0}^{n_A+n_B+1}\sum_{L=0}^{l_A+l_B+1}\sum_{M=0}^{m_A+m_B}{}^B d_N^{n_An_BA} e_L^{l_Al_B} f_M^{m_Am_B} \Lambda_N \Lambda_L \Lambda_M E_{AB} e^{-\alpha_P \mathbf{r}_P^2}, \qquad (V.219)$$

$$=\sum_{N,L,M} D_{NLM}^{y_A x_B} \Lambda_N \Lambda_L \Lambda_M E_{AB} e^{-\alpha_P \mathbf{r}_P^2}$$
(V.220)

with

$${}^{A}d_{N}^{n_{A}n_{B}} = 2\alpha_{A}d_{N}^{(n_{A}+1)n_{B}} - n_{A}d_{N}^{(n_{A}-1)n_{B}} = -{}^{x}d_{N}^{n_{A}n_{B}}$$
(V.221)

$${}^{B}d_{N}^{n_{A}n_{B}} = 2\alpha_{B}d_{N}^{n_{A}(n_{B}+1)} - n_{B}d_{N}^{n_{A}(n_{B}-1)}$$
(V.222)

and

$$D_{NLM}^{\nu_{A}\mu_{B}} = \begin{cases} \nu = x \begin{cases} \mu = y : & {}^{A}d_{N}^{n_{A}n_{B}} & {}^{B}e_{L}^{l_{A}l_{B}} f_{M}^{m_{A}m_{B}} \\ \mu = z : & {}^{A}d_{N}^{n_{A}n_{B}} e_{L}^{l_{A}l_{B}} & {}^{B}f_{M}^{m_{A}m_{B}} \\ \mu = x : & {}^{B}d_{N}^{n_{A}n_{B}} & {}^{A}e_{L}^{l_{A}l_{B}} f_{M}^{m_{A}m_{B}} \\ \mu = z : & {}^{M_{A}n_{B}} & {}^{A}e_{L}^{l_{A}l_{B}} & {}^{B}f_{M}^{m_{A}m_{B}} \\ \nu = z \begin{cases} \mu = x : & {}^{B}d_{N}^{n_{A}n_{B}} & {}^{A}e_{L}^{l_{A}l_{B}} & {}^{B}f_{M}^{m_{A}m_{B}} \\ \mu = x : & {}^{B}d_{N}^{n_{A}n_{B}} & {}^{L}a^{l_{A}l_{B}} & {}^{M}f_{M}^{m_{A}m_{B}} \\ \mu = y : & {}^{M_{A}n_{B}} & {}^{B}e_{L}^{l_{A}l_{B}} & {}^{A}f_{M}^{m_{A}m_{B}} \end{cases} \end{cases}$$
(V.223)

Therefore, the contributions to the SO components, abbreviated as $g_1^{SO_\eta}$, are given by

$$g_{1}^{SO_{x}} = \sum_{N,L,M} \sum_{N',L',M'} i(-1)^{N'+L'+M'} \lambda_{0} E_{AB} E_{CD} (D_{NLM}^{z_{A}y_{B}} - D_{NLM}^{y_{A}z_{B}})$$

$$\times D_{N'L'M'} R_{N+N',L+L',M+M'},$$

$$(V.224)$$

$$g_{1}^{SO_{y}} = \sum_{N,L,M} \sum_{N',L',M'} i(-1)^{N'+L'+M'} \lambda_{0} E_{AB} E_{CD} (D_{NLM}^{x_{A}z_{B}} - D_{NLM}^{z_{A}x_{B}})$$

$$\times D_{N'L'M'} R_{N+N',L+L',M+M'},$$

$$(V.225)$$

$$g_{1}^{SO_{z}} = \sum_{N,L,M} \sum_{N',L',M'} i(-1)^{N'+L'+M'} \lambda_{0} E_{AB} E_{CD} (D_{NLM}^{y_{A}x_{B}} - D_{NLM}^{x_{A}y_{B}})$$

$$\times D_{N'L'M'} R_{N+N',L+L',M+M'}.$$

$$(V.226)$$

As was already mentioned, for the SO contribution in (V.206) the only non-vanishing terms are those for which σ_1 and σ_2 refer to the same spatial component. Consequently, the only contributions, abbreviated as $g_{12}^{SO_{\eta\eta}}$, are

$$g_{12}^{SO_{xx}} = i\sigma_{2x}i\sigma_{1x}\left(\left\langle\frac{\partial g_B}{\partial y}\frac{\partial g_D}{\partial y}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial z}\frac{\partial g_D}{\partial z}\right\rangle - \left\langle\frac{\partial g_B}{\partial z}\frac{\partial g_D}{\partial y}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial y}\frac{\partial g_D}{\partial z}\right\rangle - \left\langle\frac{\partial g_B}{\partial z}\frac{\partial g_D}{\partial y}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial y}\frac{\partial g_D}{\partial z}\right\rangle$$

$$- \left\langle\frac{\partial g_B}{\partial y}\frac{\partial g_D}{\partial z}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial z}\frac{\partial g_D}{\partial y}\right\rangle + \left\langle\frac{\partial g_B}{\partial z}\frac{\partial g_D}{\partial z}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial y}\frac{\partial g_D}{\partial y}\right\rangle\right) \qquad (V.227)$$

$$= \sum_{N,L,M}\sum_{N',L',M'}(-1)\sigma_{2x}\sigma_{1x}(-1)^{N'+L'+M'}\lambda_0E_{AB}E_{CD}$$

$$\times (D_{NLM}^{z_Ay_B}D_{N'L'M'}^{z_Cy_D} - D_{NLM}^{y_Az_B}D_{N'L'M'}^{z_Cy_D}$$

$$- D_{NLM}^{z_Ay_B}D_{N'L'M'}^{y_Cz_D} + D_{NLM}^{y_Az_B}D_{N'L'M'}^{y_Cz_D})R_{N+N',L+L',M+M'} \qquad (V.228)$$

V. Calculation of Relativistic Integrals

$$g_{12}^{SO_{yy}} = i\sigma_{2y}i\sigma_{1y}\left(\left\langle\frac{\partial g_B}{\partial z}\frac{\partial g_D}{\partial z}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial x}\frac{\partial g_D}{\partial x}\right\rangle - \left\langle\frac{\partial g_B}{\partial x}\frac{\partial g_D}{\partial z}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial z}\frac{\partial g_D}{\partial x}\right\rangle - \left\langle\frac{\partial g_B}{\partial x}\frac{\partial g_D}{\partial z}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial z}\frac{\partial g_D}{\partial x}\right\rangle\right)$$
(V.229)
$$= \sum_{N,L,M}\sum_{N',L',M'}(-1)\sigma_{2y}\sigma_{1y}(-1)^{N'+L'+M'}\lambda_0E_{AB}E_{CD} \times \left(D_{NLM}^{x,zB}D_{N'L'M'}^{z,czD} - D_{NLM}^{z,xB}D_{N'L'M'}^{z,czD}\right)$$
(V.230)
$$g_{12}^{SO_{zz}} = i\sigma_{2z}i\sigma_{1z}\left(\left\langle\frac{\partial g_B}{\partial x}\frac{\partial g_D}{\partial x}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial y}\frac{\partial g_D}{\partial y}\right\rangle + \left\langle\frac{\partial g_B}{\partial y}\frac{\partial g_D}{\partial y}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial x}\frac{\partial g_D}{\partial y}\right\rangle - \left\langle\frac{\partial g_B}{\partial y}\frac{\partial g_D}{\partial x}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial x}\frac{\partial g_D}{\partial y}\right\rangle - \left\langle\frac{\partial g_B}{\partial y}\frac{\partial g_D}{\partial x}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial x}\frac{\partial g_D}{\partial y}\right\rangle - \left\langle\frac{\partial g_B}{\partial y}\frac{\partial g_D}{\partial x}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial x}\frac{\partial g_D}{\partial y}\right\rangle - \left\langle\frac{\partial g_B}{\partial y}\frac{\partial g_D}{\partial x}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial x}\frac{\partial g_D}{\partial y}\right\rangle + \left\langle\frac{\partial g_B}{\partial y}\frac{\partial g_D}{\partial y}\Big|\frac{1}{r_{12}}\Big|\frac{\partial g_A}{\partial x}\frac{\partial g_D}{\partial y}\right\rangle \right)$$
(V.231)
$$= \sum_{N,L,M}\sum_{N',L',M'}(-1)\sigma_{2z}\sigma_{1z}(-1)^{N'+L'+M'}\lambda_0E_{AB}E_{CD} \times \left(D_{NLM}^{yA,xB}D_{N'L'M'}^{yC,xD} - D_{NLM}^{xA,yB}D_{N'L'M'}^{yC,xD}\right)R_{N+N',L+L',M+M'}.$$
(V.232)

VI. Implementation

In order to calculate DPT4 corrections for energies and properties, the quantumchemical program package CFOUR⁸⁰ has been extended and modified thereby exploiting the available second-derivative capabilities.⁷⁸ For DPT4 energy calculations at the HF level as well as at the correlated levels (MP2 and CC), an incore implementation has been carried out first ('pilot code') as the simple structure of such a program is less prone to errors and allows for a verification of the later efficient implementation. In the following, the implemented modifications to the CFOUR program package are discussed in some detail.

VI.1. DPT4 energy corrections at the Hartree-Fock level

As the SR and SO parts of the DPT4 energy are fully separable, they are independently calculated and it is possible to determine either the scalar-relativistic contribution (SR-DPT4) or the full DPT4 correction. The necessary steps for the calculation of the DPT4 energy are shown in the flowchart given in figure VI.1.

After the HF-SCF equations are solved, the required integrals for a SR-DPT4 calculation (see equation IV.54), or, if specified, a full DPT4 calculation (see equation IV.67) are evaluated and processed in a Fock-matrix like manner.⁹⁹ As a consequence, no twoelectron integrals need to be stored on disk. The contributions involving the g_{12}^{SR} and g_{12}^{SO} integrals are directly calculated as expectation values without storage. All integral evaluations and manipulations described here are done in the module xvdint.

In the module **xcphf** the CPHF equations are solved, the matrix $S_{pq}^{\lambda_{rel}}$ is inverted, and the DPT4 energy is calculated.

All relativistic integrals (see equations IV.54 and IV.67) are evaluated using the McMurchie-Davidson scheme¹⁰⁷ as discussed in chapter V. While the positive linear combinations $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} + \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$ with atomic orbitals μ, ν, σ, ρ , are already needed for the DPT2 correction,¹⁰⁹ the SR-DPT4 treatment also requires the corresponding negative linear combinations $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} - \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$. As an alternative it is in principle possible to calculate only the integrals $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} \mid \sigma\rho \rangle$ but then the eight-fold permutational symmetry of the integrals can no longer be exploited. A similar procedure, however, does not work



Figure VI.1.: Flowchart for the calculation of the DPT4 energy (see equations IV.54 and IV.67) at the HF level. If only scalar-relativistic corrections are calculated, all steps in dotted boxes are omitted.

for the SO integrals. Therefore, for the SO treatment, the integrals $\langle \mu\nu \mid \hat{g}_2^{\rm SO} \mid \sigma\rho \rangle$ are in all cases evaluated. Concerning the $\langle \mu\nu \mid \hat{g}_{12}^{\rm SR} \mid \sigma\rho \rangle$ and $\langle \mu\nu \mid \hat{g}_{12}^{\rm SO} \mid \sigma\rho \rangle$ integrals, the eight-fold permutational symmetry can again be exploited.

The routines to calculate all the required integrals have been implemented into the module **xvdint**. For the one-electron integrals the driver routine **onedrv.f** invokes the specific subroutines. While the one-electron SR integrals as given in (IV.57) have been implemented by Christine Berger¹⁰⁹ and are calculated in the routine **dptpvp1.f**, the one-electron SO integrals as given in (IV.69) are calculated in the routine **dpt4pvxp.f**. The two-electron integrals are evaluated in the routine **intdpt.f** which is a subroutine of either **twodpt.f** (for all SR two-electron integrals, i.e., $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} + \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$, $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} - \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$ and $\langle \mu\nu \mid \hat{g}_{12}^{\text{SR}} \mid \sigma\rho \rangle$), twodptso.f (for $\langle \mu\nu \mid \hat{g}_2^{\text{SO}} \mid \sigma\rho \rangle$), or twodptso4c.f (for $\langle \mu\nu \mid \hat{g}_{12}^{\text{SO}} \mid \sigma\rho \rangle$). The type of two-electron integral calculated depends on some flags and the routine that calls **intdpt.f**.

The Fock-matrix like contributions are formed in the routines mvdfock.f (for $f_{pq}^{(SR)}$), mvdfock2.f (for $^{Z1}f_{pq}^{(SR)}$), dpt4sofock.f (for $f_{pq}^{(SO)}$), or dpt4soz1fock.f (for $^{Z1}f_{pq}^{(SO)}$). In the case of the \hat{g}_{12}^{SR} and \hat{g}_{12}^{SO} integrals, the expectation values are calculated in intexp.f and intexpso4c.f, respectively.

The calculation of the two-electron integrals is illustrated for the $\langle \mu\nu \mid \hat{g}_1^{\text{SR}} + \hat{g}_2^{\text{SR}} \mid \sigma\rho \rangle$ integrals which are evaluated in the following sequence:



In twodpt.f a loop runs over shells and corresponding basis functions thereby exploiting the eight-fold permutational symmetry. Inside the loop, after the call of intdpt.f, in cldriv0.f and c2driv1.f the integral

$$\left\langle g_B g_D \mid \hat{g}_2^{\mathrm{SR}} \mid g_A g_C \right\rangle = -\sum_{\nu=x,y,z} \left\langle g_B \frac{\partial g_D}{\partial \nu} \left| \frac{1}{r_{12}} \right| g_A \frac{\partial g_C}{\partial \nu} \right\rangle$$

is calculated for a given subset of basis functions. The above equation is analog to (V.213) with the only difference that the coefficients for electron 1 and 2 are interchanged. The subroutine cldriv0.f contracts the unperturbed coefficients for electron 1 with $R_{N+N',L+L',M+M'}$ where the increased summation range for electron 2 is controlled via the parameter 'MAXDER+2' (see chapter V.4). In c2driv1.f the result from cldriv0.f is combined with the perturbed coefficients for electron 2. In the next step the subroutines cldriv1.f and c2driv0.f evaluate

$$\left\langle g_B g_D \mid \hat{g}_1^{\mathrm{SR}} \mid g_A g_C \right\rangle = -\sum_{\nu=x,y,z} \left\langle \frac{\partial g_B}{\partial \nu} g_D \middle| \frac{1}{r_{12}} \middle| \frac{\partial g_A}{\partial \nu} g_C \right\rangle$$

using the formula given in (V.213). This evaluation is analog to the procedure described before, only that electron 1 and 2 are exchanged, i.e., in cldrivl.f the perturbed coefficients for electron 1 are contracted with $R_{N+N',L+L',M+M'}$ and in c2driv0.f the result is combined with the unperturbed coefficients for electron 1, thereby controlling the modified summation range again via 'MAXDER+2'.

The integrals $\langle \mu\nu \mid \hat{g}_{12}^{\text{SR}} \mid \sigma\rho \rangle$ are implemented in a similar manner as the only difference lies in the fact that now both coefficients, i.e., those for electron 1 and for electron 2 are perturbed. Therefore, their calculation requires only a call of cldrivl.f and c2drivl.f both with the parameter 'MAXDER+2'.

VI.2. DPT4 energy corrections at correlated levels of theory

In figure VI.2 the required steps for a closed-shell DPT4 energy calculation at the MP2 level are shown. After solving the HF equations, the amplitudes t_{ij}^{ab} and the MP2 energy are calculated in the modules **xintprc** and **xvcc**, while the one- and two-electron densities D_{pq} and Γ_{pqrs} as well as the Lagrange multipliers Z_{ai} and I_{pq} are evaluated afterwards in **xdens**. In **xvdint** the integrals $f_{\mu\nu}^{(\lambda_{\rm rel})}$, $S_{\mu\nu}^{\lambda_{\rm rel}}$, and $\langle \mu\nu \mid \hat{g}_1^{\lambda_{\rm rel}} \mid \sigma\rho \rangle$ are calculated in the atomic-orbital (AO) representation and stored on disk. Then, in the module **xcphf** the CPHF equations are solved for the relativistic perturbation, the derivative $\partial f_{pq}/\partial\lambda_{\rm rel}$ is evaluated, the overlap matrix $S_{pq}^{\lambda_{\rm rel}}$ is inverted, the $A_{pq}^{\lambda_{\rm rel}}$ coefficients are determined, and the HF contribution to the DPT4 energy is calculated. In the module **xsdcc** the $\langle \mu \nu \mid \hat{g}_1^{\lambda_{\rm rel}} \mid \sigma \rho \rangle$ integrals are transformed into the molecular-orbital (MO) basis and augmented by the $U_{tp}^{\lambda_{\rm rel}} \langle tq \mid rs \rangle$ terms. Furthermore, the perturbed amplitudes $\partial t_{ij}^{ab}/\partial\lambda_{\rm rel}$

and the perturbed density matrices $\partial D_{pq}/\partial \lambda_{rel}$ and $\partial \Gamma_{pqrs}/\partial \lambda_{rel}$ are calculated, the perturbed Z-vector equations are solved yielding $\partial Z_{ai}/\partial \lambda_{rel}$, and the perturbed intermediates $\partial I_{pq}/\partial \lambda_{rel}$ are evaluated. Then, all terms except those involving the g_{12}^{SO} integrals are calculated.

In order to make the code more efficient, the terms involving the two-electron integrals $\langle pq \mid \hat{g}_1^{\text{SR}} \mid rs \rangle$ are in fact evaluated in the following manner; In **xsdcc** the $U_{tp}^{\text{SR}}\Gamma_{tqrs}$ contributions are added to the perturbed two-electron density matrix $\partial \Gamma_{pqrs}/\partial \lambda_{\text{SR}}$, i.e.,

$$\Gamma' \equiv \frac{\partial \Gamma_{pqrs}}{\partial \lambda_{\rm SR}} + \sum_{t} \Big\{ U_{tp}^{\rm SR} \Gamma_{tqrs} + U_{tq}^{\rm SR} \Gamma_{ptrs} + U_{tr}^{\rm SR} \Gamma_{pqts} + U_{ts}^{\rm SR} \Gamma_{pqrt} \Big\}.$$
(VI.1)

This modified two-electron density matrix Γ' is transformed in xanti and xbcktrn from the MO into the AO basis and in xvdint contracted with $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} + \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$ and $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} - \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$, respectively. In a similar manner the quantity $A_{tp}^{\text{SR}}\Gamma_{tprs}$ is set up and transformed into the AO basis. More precisely, as in this contribution only the $\langle \mu\nu \mid \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$ integrals appear, it is calculated as $(A_1 + A_2)\Gamma$ and $(A_1 - A_2)\Gamma$, with A_1 symbolically given as in (IV.43) and A_2 as the same quantity with electron 1 and 2 permuted, i.e.,

$$(A_1 + A_2)\Gamma \equiv \sum_t \left\{ A_{tp}^{\rm SR} \Gamma_{tqrs} + A_{tq}^{\rm SR} \Gamma_{ptrs} + A_{tr}^{\rm SR} \Gamma_{pqts} + A_{ts}^{\rm SR} \Gamma_{pqrt}, \right\}$$
(VI.2)

$$(A_1 - A_2)\Gamma \equiv \sum_t \left\{ A_{tp}^{\rm SR} \Gamma_{tqrs} - A_{tq}^{\rm SR} \Gamma_{ptrs} + A_{tr}^{\rm SR} \Gamma_{pqts} - A_{ts}^{\rm SR} \Gamma_{pqrt} \right\}.$$
 (VI.3)

Then, after transformation of the terms defined in the above equations into the AO basis, $(A_1 + A_2)\Gamma$ is contracted with $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} + \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$ and $(A_1 - A_2)\Gamma$ with $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} - \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$, respectivelyⁱ, leading to a cancellation of the unwanted cross terms. Note that the discussion holds for the SR case whereas for the SO terms all contributions are directly evaluated in the MO representation. Finally, in **xvdint** the so far missing $g_{12}^{\lambda_{\text{rel}}}$ contributions are evaluated.

The difference between the SR and the SO variant of a DPT4 calculation lies in the fact that the perturbed quantities and the spin adaptation are different (see IV.163 and IV.170). In addition, for the SO contributions there is a loop over the SO components x, y, and z in the electron-correlation part.

The MP2-DPT4 energy has first been implemented into an incore program as 'pilot imple-

ⁱIn the actual program, the contributions due to Γ' and $(A_1 + A_2)\Gamma$ are treated together, as all of them have the same permutational symmetry, i.e., the quantity $\Gamma'' \equiv \Gamma' + (A_1 + A_2)\Gamma$ is evaluated

mentation'. Such a program, however, has its limitations as it is not efficient and requires an unnecessary large amount of memory, yet it is simple and less prone to errors. In the next step, the MP2-DPT4 energy has been included into the CFOUR program package using an efficient implementation as discussed above.

In the module xsdcc, which deals with the electron-correlation part, the existing features for the calculation of second derivatives could be exploited. Modifications and additions are mainly needed for the spin adaptation of the SO contributions and all term involving $h^{(4)}, S^{(4)}$, and $g^{(4)}$, see (IV.141), (IV.143), and (IV.144), as these additional terms do not appear for non-relativistic second derivatives. Furthermore, the loop structure for the SO components has to be set up.

VI.3. DPT4 corrections to electrical properties

A procedure to compute DPT4 energies at the HF level in the presence of an external one-electron perturbation has been implemented based on the code for the calculation of DPT4 energies described in section VI.1. For the calculation of the SR corrections, no further implementation of integrals is required as they already have been implemented for the analytic evaluation of DPT2 corrections to electrical properties.^{102,110} These integrals have been discussed in chapters V.3.3, V.3.5, and V.3.7. Regarding the SO contributions, all additional integrals (see chapters V.3.4, V.3.6, and V.3.8) have been implemented using the McMurchie-Davidson scheme.¹⁰⁷

The contributions due to the external perturbation are added to the one-electron Hamiltonian integrals, i.e., to h_{pq} for the usual non-relativistic contributions and to h_{pq}^{SR} and h_{pq}^{SO} in the case of SR- and SO-DPT corrections. No further change in the DPT4 code is necessary for the finite-differences calculations which have been done using two- to eight-point formulas together with a field strength of $10 \cdot 10^{-6}$ a.u. in the case of efgs and of $75 \cdot 10^{-6}$ a.u. for dipole moments (see Appendix IX.7).

VI.4. Validation of the integrals

The implementation of the scalar-relativistic integrals $\langle \mu\nu \mid \hat{g}_2^{\text{SR}} - \hat{g}_1^{\text{SR}} \mid \sigma\rho \rangle$ poses no challenge as the corresponding positive linear combination already has been implemented by Christine Berger.¹⁰⁹ Implementation of the negative linear combination involves only a sign change and the separate parts of the integral could easily be compared.


Figure VI.2.: Flowchart for the calculation of the DPT4 energy (see IV.163 and IV.170) at the MP2 level.

The same holds for the $\langle \mu\nu \mid \hat{g}_{12}^{\text{SR}} \mid \sigma\rho \rangle$ integrals as they are implemented in a similar manner. The only difference lies in the fact that both coefficients, i.e., those for electron 1 and for electron 2 are perturbed as outlined in section VI.1. Further validation was done implicitly via the DPT4 results for rare-gas atoms as published by Ottschofski and Kutzelnigg.⁷³

The g_2^{SO} and g_{12}^{SO} integrals, see chapter V.4.2, have been verified using incore implementations for testing and the g_2^{SO} integrals were compared to those computed using the DALTON program package.¹¹²

Additionally, for the g_{12}^{SO} integrals the contribution to the energy was estimated in the following way: There is a variance between the SF-DHF implementation as done in CFOUR⁴¹ and as done in the program package Dirac04.¹¹³ In Dirac04 the SF-DHF results are calculated by dropping all imaginary parts in the matrices that arise in the DHF procedure. As the g_{12}^{SO} integrals are real, this contribution is consequently present in the SF-DHF results. In CFOUR the SF-DHF results are calculated based on the spin separation of the Dirac equation¹⁰³ and consequently the g_{12}^{SO} contributions do not appear. Therefore, the difference between the SF-DHF results from Dirac04 and CFOUR provides an estimate of the g_{12}^{SO} contribution to the energy. Nevertheless, this difference also includes higher-order contributions and thus does not represent a strict test.

The spin-orbit integrals for electrical properties, as given in (V.3.4), (V.3.6), and (V.3.8) have been tested using the corresponding non-relativistic integrals. This is possible because the integral for a specific SO component can be written as

$$\langle g_{B}^{i_{B},j_{B},k_{B}} | \hat{p}_{i}\hat{O}\hat{p}_{j} | g_{A}^{i_{A},j_{A},k_{A}} \rangle = 4\alpha_{A}\alpha_{B} \langle g_{B}^{(i_{B}+1),j_{B},k_{B}} | \hat{O} | g_{A}^{i_{A},(j_{A}+1),k_{A}} \rangle - 2\alpha_{A}i_{B} \langle g_{B}^{(i_{B}-1),j_{B},k_{B}} | \hat{O} | g_{A}^{i_{A},(j_{A}+1),k_{A}} \rangle - 2\alpha_{B}j_{A} \langle g_{B}^{(i_{B}+1),j_{B},k_{B}} | \hat{O} | g_{A}^{i_{A},(j_{A}-1),k_{A}} \rangle + 4i_{B}j_{A} \langle g_{B}^{(i_{B}-1),j_{B},k_{B}} | \hat{O} | g_{A}^{i_{A},(j_{A}-1),k_{A}} \rangle$$
(VI.4)

with \hat{O} given as the operator of the electrical property under consideration and i, j, k = x, y, z.

VI.5. Validation of the HF-DPT4 energy

The SR-DPT4 and SO-DPT4 results have been verified by comparing results of the incore program with the efficient implementation in the module **xcphf**. Additionally, the

SR-DPT4 results have been tested using the implementation of the SF-DHF approach in CFOUR. As the SF-DHF results correspond to the infinite-order limit of DPT at the HF level, a perturbative expansion of the SF-DHF equations with respect to $\lambda_{\rm rel}$ leads to SR-DPT. The value of $\lambda_{\rm rel}$ is varied in the SF-DHF calculation so that numerical DPT2 and SR-DPT4 results can be obtained using polynomial fittings.¹⁰⁰

The SO-DPT4 contribution was estimated by the difference between the result of a full four-component DHF calculation and a corresponding SF-DHF calculation.

VI.6. Validation of the MP2-DPT4 energy

For SR-DPT4 and full DPT4 energies at the HF level as well as at correlated levels of theory (MP2), the results have been verified using three independent implementations, i.e., two incore programs, one written as part of the present work and one written by J. Gauß, as well as the efficient implementation into the CFOUR program package. The polynomial fit as for the SR-DPT4 energy at the HF level, however, did not provide conclusive results (see chapter VII for further discussion).

VII. Applications

In this chapter, calculations for the relativistic corrections to total energies and electrical properties have been performed with a focus on the DPT4 results. The DPT corrections are compared to results from fully relativistic calculations for both the SR and SO contributions and their accuracy as well as the convergence behaviour of the DPT series is investigated. For the DPT4 energies at the HF level furthermore a term analysis is performed and the basis-set convergence is investigated. In the last part of this chapter, calculations within a joint experimental and theoretical rotational-spectroscopic investigation for the molecules CH₂BrF, CHBrF₂, and CH₂FI is presented with the focus on DPT4 corrections to the halogen quadrupole-coupling tensors.

VII.1. Relativistic corrections to total energies at the Hartree-Fock level

In this section the accuracy of the DPT corrections up to DPT4 is investigated.⁹⁹ For this purpose, calculations were performed for the hydrogen halides HX, X=F, Cl, Br, I, and At. The geometries and basis sets were taken from Ref. 114. The latter consist of large even-tempered sets^{115–119} augmented by additional polarization functions and are well-suited for the treatment of relativistic effects at the HF level.

Beside the total DPT4 corrections, also the SR-DPT4 (and SR-DPT6¹⁰⁰) as well as the SO-DPT4 corrections are analyzed: The SR-DPT results are compared to relativistic corrections obtained from the difference between results from spin-free Dirac-Hartree-Fock (SF-DHF)^{41,103} and non-relativistic HF-SCF calculations and are analyzed further by giving numerical values for the individual contributions to the DPT4 energy. The SO-DPT corrections are compared to SO contributions obtained from the difference between the fully relativistic DHF and SF-DHF results.

Furthermore, the basis-set dependence of the DPT4 contributions is investigated in calculations with basis sets from Dunning's hierarchy of correlation-consistent polarized and core-polarized valence-zeta sets (cc-pVXZ and cc-pCVXZ with X=T, Q, $5^{120-125}$) as well as their uncontracted (unc) counterparts. To avoid linear dependencies in the uncontracted cc-pCVXZ sets, the additional core-polarization functions in the s- and p- and for Br also in the d-shells were eliminated.

The DPT4 and SF-DHF calculations were performed using the CFOUR⁸⁰ program package. The DPT4 results were thereby obtained using those parts of CFOUR that have been developed in this work. The fully relativistic DHF results were obtained with the program package Dirac04.¹²⁶ In all calculations the point-nuclear model was used.

VII.1.1. DPT4 energies at the HF level: Comparison to fully relativistic calculations

Table VII.1 (see p.114) shows the DPT4 energy corrections for the hydrogen halides (HF-HAt). In the upper part, the full DPT4 corrections are listed together with the four-component DHF results while in the middle and lower parts the DPT4 corrections split up into SR and SO contributions are found. Using the relative error

$$\Delta^{\text{DPT2,4}} = 1 - \frac{E^{\text{DPT2,4}}}{E^{\text{DHF}} - E^{\text{HF}}},$$
(VII.1)

with $E^{\text{DPT2},4}$ as the sum of the DPT corrections DPT2 and DPT4, E^{DHF} as the DHF energy from a fully relativistic calculation, and E^{HF} as the non-relativistic HF energy, the overall picture shows that relativistic energies are reproduced within an error of better than 1% up to the fifth row of the periodic table (HI) if DPT4 corrections are included. Concerning the magnitude of the SO corrections it is found that they are for the considered closed-shell systems about two orders of magnitude smaller than the SR-DPT4

contributions. Since the DPT2 contribution is much larger than the DPT4 correction, which in turn exceeds the remaining error, the DPT convergence behavior is found to be smooth. Furthermore, in the so far considered cases, the DPT energy corrections always underestimate the relativistic energies from a full relativistic treatment leading to a monotonous convergence.

Comparing the relative errors of the SO contributions

$$\Delta^{\rm SO} = 1 - \frac{E^{\rm SO-DPT4}}{E^{\rm DHF} - E^{\rm SF-DHF}}$$
(VII.2)

to those of the SR corrections up to SR-DPT4

$$\Delta^{\text{SR-DPT2},4} = 1 - \frac{E^{\text{SR-DPT2},4}}{E^{\text{SF-DHF}} - E^{\text{HF}}}$$
(VII.3)

Table VII.1.: HF energies as well as total DPT, SR-DPT, and SO-DPT4 corrections in comparison to results from four-component DHF, SF-DHF calculations, and fully relativistic SO corrections. All values are given in atomic units (a.u.). Geometries and basis sets were taken from Ref. 114.

	HF	HCl	HBr	HI	HAt		
Full DPT corrections							
$E^{\rm HF}$	-100.0705	-460.1122	-2573.0521	-6918.5743	-21267.4660		
$E^{\rm DPT2}$	-0.0917	-1.4454	-31.5763	-183.8508	-1338.2337		
$E^{\rm DPT4}$	-0.0002	-0.0107	-0.9832	-12.8673	-235.8894		
$E^{\mathrm{DPT2,4}}$	-0.0919	-1.4562	-32.5596	-196.7181	-1574.1231		
$(E^{\rm DHF} - E^{\rm HF})^a$	-0.0919	-1.4563	-32.6011	-198.0437	-1650.7762		
$\Delta^{\mathrm{DPT2,4}}/\%$	$5.7 \cdot 10^{-4}$	$7.1 \cdot 10^{-3}$	0.13	0.67	4.64		
SR-DPT correction	S						
$E^{\text{SR-DPT4}}$	-0.0002	-0.0101	-0.9043	-11.7629	-214.7659		
$E^{\text{SR-DPT6}}$	$-4.9 \cdot 10^{-7}$	$-9.3 \cdot 10^{-5}$	-0.0347	-1.0224	-47.4243		
$E^{\text{SR-DPT2},4}$	-0.0919	-1.4555	-32.4807	-195.6137	-1552.9996		
$E^{\text{SR-DPT2},4,6}$	-0.0919	-1.4556	-32.5153	-196.6362	-1600.4239		
$(E^{\text{SF-DHF}} - E^{\text{HF}})^b$	-0.0919	-1.4556	-32.5163	-196.7524	-1617.6129		
$\Delta^{\text{SR-DPT2},4}/\%$	$5.4 \cdot 10^{-4}$	$6.5 \cdot 10^{-3}$	0.11	0.58	3.99		
$\Delta^{\mathrm{SR-DPT2,4,6}}/\%$	$1.6 \cdot 10^{-6}$	$6.8 \cdot 10^{-5}$	$3.0 \cdot 10^{-3}$	0.06	1.06		
$\Delta_{\mathrm{B2}}^{\mathrm{SR-DPT4}}/\%$	0.26	0.92	3.79	8.83	23.13		
SO-DPT corrections							
$E^{\text{SO-DPT4}}$	$-8.260 \cdot 10^{-6}$	$-6.891 \cdot 10^{-4}$	-0.0789	-1.1044	-21.1235		
$(E^{\rm DHF} - E^{\rm SF-DHF})^c$	$-8.287 \cdot 10^{-6}$	$-6.986 \cdot 10^{-4}$	-0.0848	-1.2913	-33.1633		
$\dot{\Delta}^{\rm SO}/\%$	0.32	1.35	6.94	14.47	36.30		

 a obtained by taking the difference between the DHF and the nonrelativistic HF values

 b obtained by taking the difference between the spin-free DHF¹⁰⁰ and the nonrelativistic HF values

 $^{c}\,$ obtained by taking the difference between the full DHF and spin-free $\rm DHF^{41}$ values

with $E^{\text{SR-DPT2},4}$ as the sum of the SR energy corrections, i.e., DPT2 and SR-DPT4, it is found that the former are about one to two orders of magnitude larger. However, this is easily explained by the fact that there exists already a first-order contribution (DPT2) for the SR correction whereas the SO correction first appears at the DPT4 level. It is probably more meaningful to compare the SO errors to the remaining SR errors at the SR-DPT4 level beyond DPT2, that is

$$\Delta_{\rm B2}^{\rm SR-DPT4} = 1 - \frac{E^{\rm SR-DPT4}}{E^{\rm SF-DHF} - E^{\rm HF} - E^{\rm DPT2}}.$$
 (VII.4)

As anticipated, the errors now are of a similar magnitude though still somewhat larger for the SO contributions.

Concerning HF and HCl, the relativistic contributions are already reproduced within an error smaller than 1% at the DPT2 level, and the SO corrections are negligible. For HBr, inclusion of the SR-DPT4 correction is necessary to get the error down to less than 1%, which then corresponds to a deviation of 0.1 a.u. from the full relativistic contribution. If the SO correction is also included, the deviation decreases to 0.04 a.u. The SR energy correction up to DPT4 for HI recovers the SR energy contribution with an error of less than 1%. However, the SO contribution is here more important than for the compounds containing lighter elements and although the error in the computed SO correction is rather large (about 14 %), its consideration reduces the total error for the relativistic correction to less than 1%. The remaining deviation is about 1.3 a.u.

For HAt, the DPT series cannot be considered to be converged; the error for the SR-DPT4 energy is still about 4% in comparison to the SF-DHF result, whereas the SO correction is even off by 36%. In terms of absolute energies this means that at the DPT4 level the deviation is about 77 a.u. which should be compared to the fully relativistic value of 22918 a.u.

A graphical representation of the SR-DPT convergence including the SR-DPT6 results from Ref. 100 is found in figure VII.1 (see p.116). The corresponding numerical values are given in the middle part of table VII.1 (see p.114). Consideration of the SR-DPT6 energy correction improves the results further, i.e., reduces the relative error

$$\Delta^{\text{SR-DPT2,4,6}} = 1 - \frac{E^{\text{SR-DPT2,4,6}}}{E^{\text{SF-DHF}} - E^{\text{HF}}}$$
(VII.5)

with $E^{\text{SR-DPT2,4,6}}$ as the sum of the SR corrections up to DPT6 for HBr to less than 0.005% (-0.002 a.u.) and to 0.06% (-0.116 a.u.) for HI. Only for HAt, the inclusion of



Figure VII.1.: Convergence of the scalar-relativistic DPT series for the hydrogen halides HX, X=Cl, Br, I, and At.

Table VII.2.: Term analysis of the SR-DPT4 corrections for the hydrogen halides. All values are given in atomic units (a.u.). Geometries and basis sets are taken from Ref. 114. For an explanation of the terms see text.

			1		
Mol.	$E^{\text{SR-DPT4}}$	CPHF	Reorth	2nd Order	$\langle g_{12}^{ m SR} \rangle$
HF	$-1.873 \cdot 10^{-4}$	$-7.326 \cdot 10^{-4}$	$8.353 \cdot 10^{-5}$	$4.618 \cdot 10^{-4}$	$-8.158 \cdot 10^{-6}$
HCl	-0.0101	-0.0387	$4.858 \cdot 10^{-3}$	0.0237	$-6.892 \cdot 10^{-4}$
HBr	-0.9043	-3.3774	0.4603	2.0128	-0.0835
HI	-11.7629	-43.4821	6.1635	25.5557	-1.2843
HAt	-214.7659	-785.6790	115.2634	455.6496	-33.0609

the SR-DPT6 energy correction is not sufficient to reduce the error below 1%, i.e., the remaining error is still 1.1% (-17.189 a.u.). Nevertheless, in all instances the SR-DPT6 results confirm observations made for the DPT4 corrections concerning the convergence behaviour of the DPT series. It should be noted that the SO-DPT4 corrections in all considered cases are larger or at least of the same magnitude as the SR-DPT6 results. Finally, it is noted that the here discussed findings are in line with what Ottschofski and Kutzelnigg⁷³ found earlier for the noble gases.

VII.1.2. Term analysis of the DPT4 correction at the HF level

In table VII.2 (see p.117) the individual contributions from (IV.54) to the SR-DPT4 energy are listed for the hydrogen halides. The major contribution to the energy stems from the CPHF term which corresponds to the first two lines of (IV.54) and has a negative sign, though it heavily overestimates the total energy correction. The other terms have positive signs, with the second-order terms (last two lines of (IV.54)) being of the same order of magnitude but smaller than the CPHF contribution. A further positive correction comes from the reorthonormalization term (third line in (IV.54)) which however is one order of magnitude smaller. The term symbolized by $\langle g_{12}^{SR} \rangle$ is part of the second-order terms and corresponds to the fourth line in (IV.54). It is listed separately because it is evaluated as an expectation value and involves the g_{12}^{SR} two-electron integrals that are not required for all other contributions. Although one might consider to omit this term due to the additional computational cost for the integrals, as for example suggested by Ottschofski and Kutzelnigg in Ref. 73, this cannot be recommended since for all considered cases its contribution is of similar magnitude as the SO correction.

Table VII.3 (see p.118) shows the same term analysis for the SO contribution. Aside

values are given in atomic units (a.a.). Geometries and basis sets are						
	taken from Ref. 114. For an explanation of the terms see text.					
Mol.	$E^{\text{SO-DPT4}}$	CPHF	2nd Order	$\langle g_{12}^{ m SO} \rangle$		
HF	$-8.260 \cdot 10^{-6}$	$-1.308 \cdot 10^{-5}$	$4.820 \cdot 10^{-6}$	$-1.293 \cdot 10^{-7}$		
HCl	$-6.891 \cdot 10^{-4}$	$-1.378 \cdot 10^{-3}$	$6.887 \cdot 10^{-4}$	$-9.353 \cdot 10^{-6}$		
HBr	-0.0789	-0.1734	0.0944	$-6.326 \cdot 10^{-4}$		
HI	-1.1044	-2.5299	1.4255	$-6.463 \cdot 10^{-3}$		
HAt	-21.1235	-50.1595	29.0360	-0.0842		

Table VII.3.: Term analysis of the SO-DPT4 correction for the hydrogen halides. All values are given in atomic units (a.u.). Geometries and basis sets are taken from Ref. 114. For an explanation of the terms see text.

from the fact that there is no reorthonormalization term (see IV.67) the same picture emerges. The negative CPHF term gives the largest contribution which is damped by the second-order terms that are of the same order of magnitude but have opposite sign. Here, the $\langle g_{12}^{\rm SO} \rangle$ term which is part of the second-order contributions is indeed very small and might therefore be neglected to save the computational cost for the involved two-electron integrals.

VII.1.3. Basis-set convergence of the DPT4 correction at the HF level

While there is plenty of experience in choosing basis sets for relativistic calculations (see, for example, Refs. 127–129), the basis-set convergence in the perturbative treatment is somewhat different, as there is a need to comply with the requirements of both the non-relativistic and the subsequent relativistic treatment. In figures VII.2 and VII.3 (see p.119) the basis-set convergence of the SR-DPT4 and the SO-DPT4 energy corrections for HCl and HBr are shown. In all cases the cc-pV**X**Z basis turns out not to be suited for the description of relativistic effects, as it even, except for the calculation of the SO correction of HCl with a cc-pV5Z basis, gives the wrong sign and does not converge for HBr to the proper basis-set limit. The inclusion of core-polarization functions (cc-pCV**X**Z sets) greatly improves the convergence. However, more important is the decontraction of the basis sets, thereby providing the necessary flexibility to account for the changes in the inner shells due to relativistic effects. On the scale of the figures, the difference between the uncontracted cc-pV**X**Z and cc-pCV**X**Z sets is not visible since the results are nearly indistinguishable as it can be also seen from the corresponding table in the Appendix IX.8.



Figure VII.2.: Basis-set convergence for the scalar-relativistic DPT4 correction to the energy (in a.u.) for HCl (left) and HBr (right).



Figure VII.3.: Basis-set convergence for the spin-orbit DPT4 correction to the energy (in a.u.) for HCl (left) and HBr (right).

Both for SR as well as for SO corrections the convergence of the contracted sets is slower for HBr than for HCl thus showing that for heavier elements relativistic effects are more pronounced and the basis-set requirements are more demanding to allow for a correct description. Finally, it is observed that the basis-set convergence of the SO correction is slightly faster than for the SR correction. Due to the fact that the shape of the orbitals is mostly affected by SR effects²⁰ this finding seems plausible.

VII.2. Relativistic corrections to total energies at correlated levels of theory

In this section, the correlation contributions to the DPT4 corrections are investigated for the hydrogen halides HX, X=F-At and the noble gases He to Rn. The geometries for the HX compounds were taken from Ref. 114 and the used basis set were the large uncontracted sets given in Ref. 114, in the following referred to as 'Neese' basis, and the uncontracted ANO-RCC sets from Ref. 129. In case of the SR corrections the investigation is based on a comparison of the MP2 correlation contributions computed within the framework of DPT to those obtained at the SFDC level. The SO correlation corrections are compared to corresponding differences between the results for the correlation energies from DC and SFDC calculations. Both, the SFDC as well as the DPT calculations were performed using the CFOUR program package,⁸⁰ thereby exploiting in the case of DPT4 those parts that were developed in the present work while the DC calculations were carried out with the program package Dirac04.¹²⁶ In all calculations the point-nucleus model was used if not stated otherwise.

VII.2.1. DPT4 energies at MP2 level: Comparison to fully relativistic calculations

Table VII.4 (see p.122) gathers for the hydrogen halides HX the DPT2 as well as the DPT4 correlation corrections obtained at the MP2 level. In the case of DPT4 both the SR and SO contributions are listed. For both basis sets used it is observed that all correlation contributions have the same sign as the corresponding HF values given in table VII.1. This means that inclusion of electron correlation leads to a further, though small, increase in the total relativistic corrections. The error in the correlation energies at the DPT2 level,

defined via

$$\Delta^{\rm DPT2} = 1 - \frac{E_{\rm corr}^{\rm DPT2}}{E_{\rm corr}^{\rm SFDC}} \tag{VII.6}$$

is about 2 % for HF, 6% for HCl, and 9% for HBr. Noting the overall small magnitude of the correlation energy, i.e., typically less than 1% of the total energy, this means that already at the DPT2 level satisfactory results are obtained concerning relativistic effects on the correlation energy. It should be furthermore noted that the correlation corrections to the total relativistic energy contribution are tiny, i.e., less than 1%, and even decrease when going down in the periodic table. For HI and HAt, however, the error in the DPT2 correlation energies increases substantially and amounts to about 15 and 27% when using the Neese basis and to about 40 and 60% in case of the uncontracted ANO-RCC set.

Based on the experience with DPT at the HF level, it is surprising that the SR-DPT4 correlation corrections, calculated with the Neese basis, are for all hydrogen halides except for HF larger than the corresponding DPT2 contributions and at least two orders of magnitude larger than the expected corrections.ⁱ A similar trend is seen in the ANO-RCC(unc) calculations except that the SR-DPT4 correlation corrections are for HI and HAt larger than the DPT2 contributions. Comparison with the SFDC results indicates that DPT4 in all cases overshoots the correlation contributions.

Concerning the SO-DPT4 corrections, no problem seems to appear. For HCl up to HI the errors in the SO-DPT4 values are rather small, i.e., between 8 and 16% (see table VII.4). Significantly larger errors are observed for HF which needs further investigation. However, as the SO correlation contribution for HF is very small this is of no major concern.

For the heavier hydrogen halides a curious trend arises. The relative errors are here smaller for HI than for HBr and in cases of the Neese basis even decrease for HAt compared to HI. Based on the experience with the HF values the reverse was expected. The apparently good performance is probably due to a fortuitous error cancellation.

In table VII.5 (see p.124) a similar analysis is presented for the noble-gas atoms He to Rn. The results in the upper part of the table, i.e., those obtained with the point-nucleus model, are in line with those for the hydrogen halides for all DPT corrections. In the lower part, the calculations have been repeated using a Gaussian-nuclear model.¹³⁰ It is seen that the deterioration of the DPT4 results is avoided in this case and that the SR-DPT4 corrections are within the expected order of magnitude. This effect is analyzed further in

ⁱThe higher-order estimates may be obtained by subtracting the correlated DPT2 contributions from the SFDC values.

Table VII.	4.: MP2 energies and correlation contributions to SR-DPT and SO-DPT4
	corrections in comparison to results from SFDC calculations at the MF2
	level and fully relativistic SO corrections for the hydrogen halides HX,
	X=F-At. All values are given in atomic units (a.u.). Geometries and the
	basis set denoted by 'Neese' were taken from Ref. 114. In the lower part
	of the table the results were calculated with the ANO-RCC(unc) set from
	Ref. 129.

	HF	HCl	HBr	HI	HAt
Neese					
$\mathrm{E}^{\mathrm{MP2}}$	-0.336	-0.423	-1.085	-1.386	-3.007
$\mathrm{E}^{\mathrm{DPT2},a}$	$-2.13 \cdot 10^{-4}$	$-8.24 \cdot 10^{-4}$	$-1.27 \cdot 10^{-2}$	$-3.69 \cdot 10^{-2}$	$-1.29 \cdot 10^{-1}$
$\mathrm{E}^{\mathrm{SR-DPT4},a}$	$-5.48 \cdot 10^{-6}$	$-1.23 \cdot 10^{-3}$	$-1.70 \cdot 10^{-1}$	-2.66	-8.83
$\mathrm{E}^{\mathrm{SR-DPT2}+4,a}$	$-2.19 \cdot 10^{-4}$	$-2.05 \cdot 10^{-3}$	$-1.83 \cdot 10^{-1}$	-2.69	-8.95
$\mathrm{E}^{\mathrm{SFDC},a,b}$	$-2.18 \cdot 10^{-4}$	$-8.79 \cdot 10^{-4}$	$-1.38 \cdot 10^{-2}$	$-4.32 \cdot 10^{-2}$	$-1.76 \cdot 10^{-1}$
$\delta^{ m DPT2}/\%$	1.98	6.26	8.59	14.67	26.46
$\delta^{ ext{SR-DPT2,4}}/\%$	-0.54	-133.17	-1222.89	-6137.55	-4990.43
$\mathrm{E}^{\mathrm{SO-DPT4},a}$	$4.97 \cdot 10^{-9}$	$-6.11 \cdot 10^{-6}$	$-2.49 \cdot 10^{-4}$	$-1.68 \cdot 10^{-3}$	$-1.44 \cdot 10^{-2}$
$\mathrm{E}^{\mathrm{SODC},a,c}$	$1.90 \cdot 10^{-8}$	$-5.64 \cdot 10^{-6}$	$-2.16 \cdot 10^{-4}$	$-1.45 \cdot 10^{-3}$	$-1.43 \cdot 10^{-2}$
$\delta^{\rm SO}/\%$	73.83	-8.19	-15.23	-15.84	-0.37
ANO-RCC(ur	nc)				
$\mathrm{E}^{\mathrm{MP2}}$	-0.355	-0.466	-1.077	-1.693	-3.167
$\mathrm{E}^{\mathrm{DPT2},a}$	$-2.10 \cdot 10^{-4}$	$-7.14 \cdot 10^{-4}$	$-1.25 \cdot 10^{-2}$	$-2.85 \cdot 10^{-2}$	$-6.99 \cdot 10^{-2}$
$\mathrm{E}^{\mathrm{SR-DPT4},a}$	$-3.71 \cdot 10^{-6}$	$-6.28 \cdot 10^{-5}$	$-1.94 \cdot 10^{-3}$	$-1.61 \cdot 10^{-2}$	-6.38
$E^{SR-DPT2+4,a}$	$-2.14 \cdot 10^{-4}$	$-7.76 \cdot 10^{-4}$	$-1.45 \cdot 10^{-2}$	$-4.46 \cdot 10^{-2}$	-6.45
$\mathrm{E}^{\mathrm{SFDC},a,b}$	$-2.13 \cdot 10^{-4}$	$-7.63 \cdot 10^{-4}$	$-1.36 \cdot 10^{-2}$	$-4.60 \cdot 10^{-2}$	$-1.76 \cdot 10^{-1}$
$\delta^{ m DPT2}/\%$	1.56	6.49	7.42	38.08	60.18
$\delta^{\mathrm{SR-DPT2,4}}/\%$	-0.18	-1.75	-6.89	3.13	-3568.87
$\mathrm{E}^{\mathrm{SO-DPT4},a}$	$1.51 \cdot 10^{-8}$	$-5.83 \cdot 10^{-6}$	$-2.13 \cdot 10^{-4}$	$-1.61 \cdot 10^{-3}$	$-1.33 \cdot 10^{-2}$
$\mathrm{E}^{\mathrm{SODC},a,c}$	$2.63 \cdot 10^{-8}$	$-5.41 \cdot 10^{-6}$	$-1.89 \cdot 10^{-4}$	$-1.46 \cdot 10^{-3}$	$-1.35 \cdot 10^{-2}$
$\delta^{\rm SO}/\%$	42.56	-7.78	-12.83	-9.77	1.63

 a only correlation contribution

 $^b\,$ obtained by taking the difference between the SFDC values at the MP2 level and the SF-DHF results and subtracting ${\rm E}^{\rm MP2}$

 $^{c}\,$ obtained by taking the difference between the full DC and SFDC result at the MP2 level

the following section.

VII.2.2. Analysis of the correlated SR-DPT4 correction

As already noted the correlated SR-DPT4 results overshoot and indicate a divergent behaviour of the DPT expansion. The overestimation is mainly due to the $\hat{h}^{(4)}$ contribution (see equation IV.142 where the $\hat{h}^{(4)}$ terms are part of the $\partial f_{pq}^{\lambda_{rel}}/\partial \lambda_{rel}$ matrix elements). In a less pronounced manner also the $\hat{S}^{(4)}$ terms (see equation IV.144) are responsible for the observed divergence. Both contributions are second-order terms which arise due to the elimination of the small component. The structure of these terms is such that problems are expected as soon as high-lying virtual orbitals appear in the calculation. To verify this assumption, for HCl using the Neese basis, additional calculations have been performed with those high-lying orbitals excluded from the correlation treatment. In order to investigate in which manner the singular electron-nucleus potential is responsible for the divergence the calculations have been repeated with the Gaussian-nuclear model. Results of these calculations are given in table VII.6 (see p.126). In figure VII.4 (see p.125), the SR-DPT4 results for HCl are furthermore plotted against the cutoff energy for dropping virtual orbitals in a logarithmic scale.

The results of these additional calculations confirm the aforementioned expectations, i.e., the divergent behaviour is damped as soon as high-lying orbitals are excluded. In this way an estimate for the fourth-order SR correlation correction of about -7 to $-8 \cdot 10^{-5}$ a.u. is obtained. A similar result of $-8.13 \cdot 10^{-5}$ a.u. is obtained if the calculation is repeated with the 5 steepest s-functions omitted in the AO basis. The calculation with the Gaussian-nuclear model yields $-8.19 \cdot 10^{-5}$ a.u. indicating again that high-lying virtual orbitals are the source of the problem as their orbital energies are substantially decreased when using a finite-nuclear model. In the calculations with the ANO-RCC(unc) basis a value of $-6.28 \cdot 10^{-5}$ a.u. is obtained when using either the point-nuclear or the Gaussian-nuclear model. This shows that in this case, in which no divergence is observed, the effect of using a Gaussian-nuclear model is negligible. The estimates obtained in the additional calculations agree with the higher-order SFDC correction of $-5.5 \cdot 10^{-5}$ a.u.

To conclude, the origin of the divergent behaviour of the DPT expansion at correlated levels has been traced back to high-lying virtual orbitals though a more detailed analysis is necessary in the future. First results indicate that there exist several possibilities to control these instabilities in the calculations but so far the use of correlated SR-DPT4

Table VII.5.:	MP2 energies as well as correlation contributions to SR-DPT and SO-
	DPT4 corrections in comparison to results from SFDC calculations at the
	MP2 level and fully relativistic SO corrections for the noble-gas atoms.
	All values are given in atomic units (a.u.). Geometries taken from Ref.
	114. In all calculations the ANO-RCC(unc) set from Ref. 129 was used.

	He	Ne	Ar	Kr	Xe	Rn		
point nucleus								
E^{MP2}	$-3.58 \cdot 10^{-2}$	-0.358	-0.480	-1.078	-1.720	-3.171		
$\mathrm{E}^{\mathrm{DPT2},a}$	$1.64 \cdot 10^{-6}$	$-2.54 \cdot 10^{-4}$	$-7.06 \cdot 10^{-4}$	$-1.26 \cdot 10^{-2}$	$-3.39 \cdot 10^{-2}$	$-1.25 \cdot 10^{-1}$		
$\mathrm{E}^{\mathrm{SR-DPT4},a}$	$-4.48 \cdot 10^{-9}$	$-5.50 \cdot 10^{-6}$	$-8.02 \cdot 10^{-5}$	$-2.09 \cdot 10^{-3}$	$-1.81 \cdot 10^{-2}$	-7.61		
$E^{SR-DPT2+4,a}$	$1.63 \cdot 10^{-6}$	$-2.59 \cdot 10^{-4}$	$-7.86 \cdot 10^{-4}$	$-1.47 \cdot 10^{-2}$	$-5.19 \cdot 10^{-2}$	-7.74		
$\mathrm{E}^{\mathrm{SFDC},a,b}$	$1.63 \cdot 10^{-6}$	$-2.59 \cdot 10^{-4}$	$-7.68 \cdot 10^{-4}$	$-1.38 \cdot 10^{-2}$	$-4.00 \cdot 10^{-2}$	$-1.73 \cdot 10^{-1}$		
$\delta^{ m DPT2}/\%$	-0.27	1.88	8.09	8.09	15.41	27.43		
$\delta^{\mathrm{SR-DPT2,4}}/\%$	ó 0.00	-0.24	-2.35	-7.12	-29.72	-4383.29		
$\mathrm{E}^{\mathrm{SO-DPT4},a}$	$-4.79 \cdot 10^{-10}$	$-2.03 \cdot 10^{-7}$	$-7.89 \cdot 10^{-6}$	$-2.49 \cdot 10^{-4}$	$-1.74 \cdot 10^{-3}$	$-1.39 \cdot 10^{-2}$		
$\mathrm{E}^{\mathrm{SODC},a,c}$	$-4.79 \cdot 10^{-10}$	$-1.86 \cdot 10^{-7}$	$-7.32 \cdot 10^{-6}$	$-2.22 \cdot 10^{-4}$	$-1.59 \cdot 10^{-3}$	$-1.45 \cdot 10^{-2}$		
$\delta^{ m SO}/\%$	0.03	-9.43	-7.72	-12.15	-9.17	4.41		
finite nucleus (Gaussian model)								
E^{MP2}	$-3.58 \cdot 10^{-2}$	-0.358	-0.480	-1.078	-1.720	-3.171		
$\mathbf{E}^{\mathrm{DPT2},a}$	$1.64 \cdot 10^{-6}$	$-2.54 \cdot 10^{-4}$	$-7.06 \cdot 10^{-4}$	$-1.26 \cdot 10^{-2}$	$-3.39 \cdot 10^{-2}$	$-1.26 \cdot 10^{-1}$		
$\mathrm{E}^{\mathrm{SR-DPT4},a}$	$-4.48 \cdot 10^{-9}$	$-5.50 \cdot 10^{-6}$	$-8.02 \cdot 10^{-5}$	$-2.01 \cdot 10^{-3}$	$-1.19 \cdot 10^{-2}$	$-9.31 \cdot 10^{-2}$		
$E^{SR-DPT2+4,a}$	$1.63 \cdot 10^{-6}$	$-2.59 \cdot 10^{-4}$	$-7.86 \cdot 10^{-4}$	$-1.46 \cdot 10^{-2}$	$-4.58 \cdot 10^{-2}$	$-2.19 \cdot 10^{-1}$		

^{*a*} only correlation contribution

 $^b\,$ obtained by taking the difference between the SFDC values at the MP2 level and the SF-DHF results and subtracting ${\rm E}^{\rm MP2}$

 $^{c}\,$ obtained by taking the difference between the full DC and SFDC result at the MP2 level



corrections cannot be recommended.

Figure VII.4.: Correlated part of the SR-DPT4 correction to the energy (in a.u.) for HCl with 'Neese' basis set from Ref. 114 for different cutoffs in the orbital energies (in a.u., logarithmic scale).

VII.3. Relativistic corrections to electrical properties

In the following the improvements in the calculation of efgs and dipole moments provided by the DPT4 corrections¹³¹ are discussed based on results from SF-DHF^{41,103} and DHF calculations. Using the former, the convergence of the SR contribution is investigated while the difference between DHF and SF-DHF results provides the full SO correction thus allowing an investigation of the SO contribution provided by the DPT4 treatment. Table VII.6.: Study of the correlated SR-DPT4 correction at the MP2 level using a cutoff in the orbital energy, different basis sets and nuclear models. All values are given in atomic units (a.u.). Geometries taken from Ref. 114. Basis sets denoted by 'Neese' basis set from Ref. 114 and the uncontracted ANO-RCC set from Ref. 129.

$E^{\text{SR-DPT4}}$	$\varepsilon_p^{\rm Cutoff}$ k	orbital $\#$	$\log \varepsilon_p^{\rm Cutoff}$	
$-1.23 \cdot 10^{-3}$	$7.420 \cdot 10^8$	136	8.87	(full basis)
$-3.69 \cdot 10^{-4}$	$2.466 \cdot 10^8$	135	8.39	
$-1.75 \cdot 10^{-4}$	$7.273 \cdot 10^7$	134	7.86	
$-1.02 \cdot 10^{-4}$	$1.739 \cdot 10^{7}$	133	7.24	
$-8.19 \cdot 10^{-5}$	$4.344 \cdot 10^{6}$	132	6.64	
$-8.14 \cdot 10^{-5}$	$1.201 \cdot 10^{6}$	131	6.08	
$-8.11 \cdot 10^{-5}$	$6.206 \cdot 10^5$	130	5.79	
$-8.11 \cdot 10^{-5}$	$3.670 \cdot 10^5$	129	5.56	
$-8.06 \cdot 10^{-5}$	$2.550 \cdot 10^5$	128	5.41	
$-7.88 \cdot 10^{-5}$	$1.259 \cdot 10^5$	125	5.10	
$-7.79 \cdot 10^{-5}$	$7.098 \cdot 10^4$	123	4.85	
$-7.38 \cdot 10^{-5}$	$4.407 \cdot 10^4$	120	4.64	
$-7.21 \cdot 10^{-5}$	$3.127 \cdot 10^4$	119	4.50	
$-7.21 \cdot 10^{-5}$	$2.175 \cdot 10^4$	118	4.34	
$-6.24 \cdot 10^{-5}$	$9.152 \cdot 10^{3}$	114	3.96	
$-5.32 \cdot 10^{-5}$	$6.735 \cdot 10^3$	110	3.83	
$-4.92 \cdot 10^{-5}$	$3.537 \cdot 10^{3}$	109	3.55	
$E^{\text{h.o. SFDC}a}$	$\overline{E_{\text{Neese,cut}}^{\text{SR-DPT4}b}}$	$E_{\text{Neese,FN}}^{\text{SR-DPT4}c}$	$\overline{E_{\mathrm{ANO}}^{\mathrm{SR-DPT4}d}}$	$E_{\text{ANO,FN}}^{\text{SR-DPT4}e}$
$-5.50 \cdot 10^{-5}$	$-8.13 \cdot 10^{-5}$	$-8.19 \cdot 10^{-5}$	$-6.28 \cdot 10^{-5}$	$-6.28 \cdot 10^{-5}$

^{*a*} obtained by taking the difference between the SFDC values at the MP2 level and the SF-DHF results and subtracting E^{MP2} as well as the correlation contribution from E^{DPT2} , all calculations with Neese basis set

 $^b\,$ correlated SR-DPT4 correction with Neese basis set where the first 5 steep s-functions have been removed from the basis set

- $^{c}\,$ correlated SR-DPT4 correction with Neese basis set and Gaussian nuclear model
- $^{d}\,$ correlated SR-DPT4 correction with ANO-RCC (unc) basis set
- d correlated SR-DPT4 correction with ANO-RCC(unc) basis set and Gaussian nuclear model

Calculations for both dipole moments and efgs were performed for the hydrogen halides HX, X=F, Cl, Br, I, and At using geometries and basis sets from Ref. 114.

Both the DPT4 and SF-DHF calculations were performed using the CFOUR⁸⁰ program package. The DPT4 results were thereby again obtained using those parts of CFOUR that have been developed in this work. The DHF results were obtained with the program package Dirac04. In all calculations the point-nucleus model was used.

VII.3.1. DPT4 properties at the HF level: Comparison to fully relativistic calculations

In this section the DPT4 results for efgs and dipole moments are compared to those from more rigorous SF-DHF and DHF calculations. Table VII.7 (see p.130) shows the scalar-relativistic DPT corrections to efgs and dipole moments for the hydrogen halides together with results from SF-DHF calculations. The relative errors for the properties are defined in an analog manner compared to those discussed for the energies (see equations VII.1, VII.2, VII.3, VII.4, VII.5, VII.6). For both dipole moment and efg, the relative error in comparison to the SF-DHF results decreases by at least one order of magnitude when going from DPT2 to the scalar relativistic DPT4 (SR-DPT4) contributions. This is in agreement with what has already be seen for energies. However, in comparison to the relative errors for the energies as discussed in chapter VII.1, it is found that the errors here are one order of magnitude larger thus showing that the properties considered are more sensitive to relativistic effects.

It was suggested in Ref. 102 that consideration of SR-DPT4 may reduce the relative error for fifth-row elements to a similar magnitude as DPT2 for elements of the fourth row. In fact, the improvement is even better: for both dipole moments and efgs, the remaining relative errors $\Delta^{\text{SR-DPT2},4}$ are smaller than 2%.

For HAt, however, the DPT expansion up to fourth order cannot be considered converged as the errors at the SR-DPT4 level are still of the order of 10% for the efg and dipole moment. These errors affect the second significant digit in the case of the dipole moment and even the first digit in the case of the efg. Higher-order corrections seem to be necessary to obtain more reliable results. This is in fact observed when the DPT6 corrections¹⁰⁰ are accounted for. The error is then reduced for the efg to 3.6% (0.4093 a.u.) and for the dipole moment to 2.0% (0.0029 a.u.).

For all hydrogen halides the remaining relative errors at the SR-DPT4 level are larger for the efgs than for the dipole moments. Since the efg is a so-called "core property", in the

VII. Applications

sense that the efg operator samples in particular the electron density of the inner-shell region, a proper description of this region is mandatory while for the dipole moments it is more important to properly capture the electron density of the outer regions. Because changes due to relativistic effects mostly happen in the inner shells, the efgs are more affected by approximations in the treatment of relativistic effects. This might also be the reason why the SR-DPT series converges faster in the case of dipole moments than for efgs, at least for the heavier elements.

Table VII.7 (see p.130) also contains the SO-DPT4 contributions which are compared to the corresponding differences between four-component DHF and SF-DHF calculations. These differences will be abbreviated in the following by the acronym SO-DHF. As the SO corrections first appear in DPT4, their relative accuracy Δ^{SO} might be expected to be in the same range as the one for the DPT2 corrections. This is more or less what is observed for the dipole moments. However, for the efgs the relative errors in the SO-DPT4 corrections are much larger which again is explained by the fact that for efgs a proper relativistic description of the inner shells is more important than for dipole moments.

For the efgs, the SO corrections have a different sign than the SR contributions at least for the cases considered here. The absolute value of the non-relativistic result is thereby enlarged by the SR corrections and reduced by the SO contributions. Furthermore, the SO corrections are at least one order of magnitude smaller than the contribution coming from the SR part of the DPT4 treatment. They might therefore be neglected for elements up to the fifth row in order to reduce computational cost.

Concerning the dipole moments, both the SO and the SR contributions have for the hydrogen halides a negative sign so that all relativistic corrections decrease the (positive) non-relativistic values. For the lighter compounds (HF to HBr), the SO contributions are at least one order of magnitude smaller than the SR-DPT4 corrections and might thus be neglected. The SO contributions for HI and HAt, however, are larger than the corresponding SR corrections at the DPT4 level. DPT4 predicts them to be about twice as large than the SR contributions whereas in the DHF calculations it is found that they are even larger. Inclusion of SO effects thus appears mandatory for these compounds. For HI, the dipole moment including the full DPT4 correction is 0.2056 a.u. which deviates by about 0.002 a.u. from the DHF result. This corresponds to a relative error of about 1%. For HAt, the dipole moment even changes sign when SO contributions are accounted for. But as already noted for the SR results for HAt, the DPT expansion up to fourth

order cannot be considered converged for this molecule.

VII.4. Relativistic corrections to hyperfine parameters in rotational spectroscopy: Application to CH₂BrF, CHBrF₂, and CH₂FI

In this section, the techniques for calculating relativistic corrections to efgs as developed in this work are applied within a joint experimental and theoretical rotationalspectroscopic investigation of the bromine and iodine quadrupole-coupling tensors for the molecules CH_2BrF , $CHBrF_2$, and CH_2FI^{131} with the focus on the DPT4 corrections. The bromine containing species are potentially of interest in atmospheric chemistry due their important role in stratospheric ozone depletion and global warming¹³² while the investigation of fluoroiodomethane is important as the knowledge of its spectroscopic parameters enables a systematic analysis of their variation along the series CH_3I , CH_2FI , CHF_2I , and CF_3I upon fluorine substitution.¹³³

The corresponding experiments have been carried out at the University of Bologna by G. Cazzoli and C. Puzzarini. Recording and in particular the analysis of the spectra is challenging due to their complicated hyperfine structure. However, using the so-called 'Lamb-Dip' technique,¹³⁴ the hyperfine structure of the rotational spectra can be resolved, but the determination of the hyperfine constants, such as, for example, the quadrupole-coupling constants is often cumbersome. Therefore, highly accurate theoretical predictions play an important role as they yield precise information about the (hyperfine)pattern of the spectra and help in the assignment of specific transitions. Furthermore, they are important to verify the experimental results, i.e., to confirm the accuracy of the determined spectroscopic parameters. Many examples of this fruitful interplay between theory and experiment can be found in the literature.²

For the theoretical prediction of the quadrupole-coupling constants, the following relation to the efg at the nucleus K is used²

$$\chi_{ij} = \frac{(-eQ_K)q_{ij}^K}{\hbar} \tag{VII.7}$$

with $(-eQ_K)$ as the nuclear quadrupole moment for the nucleus K. For the conversion from the effs to quadrupole coupling constants, the nuclear quadrupole moment for ⁷⁹Br has been chosen to 307.5(10) mb¹³⁵ and for ¹²⁷I to -696(12) mb.^{136,137}

Table VII.7.:	Scalar-relativistic DPT corrections to the halogen electric-field gradient
	q_{zz} and to the dipole moments μ_z of the hydrogen halides in comparison
	to results from SF-DHF calculations as well as the corresponding SO-
	DPT4 corrections in comparison to results for the SO contributions from
	four-component DHF calculations. All values are given in atomic units
	(a.u.). Geometries and basis sets were taken from Ref. 114.

	HF	HCl	HBr	HI	HAt
$q^{ m HF-SCF}$	2.8704	3.6095	7.0704	9.7311	15.4088
$q^{\rm DPT2}$	0.0101	0.0496	0.5057	1.7167	7.4555
$q^{\text{SR-DPT2},4a}$	0.0102	0.0501	0.5337	1.9476	10.1437
$q^{\text{SR-DPT2},4,6d}$	0.0102	0.0502	0.5352	1.9765	11.0358
$q^{\text{SF-DHF}b}$	0.0102	0.0502	0.5352	1.9805	11.4451
$\Delta^{\mathrm{DPT2}}/\%$	$2.8 \cdot 10^{-1}$	1.1	5.5	13.3	34.9
$\Delta^{\text{SR-DPT2},4/\%}$	$3.0 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$	$2.9 \cdot 10^{-1}$	1.7	11.4
$\Delta^{\text{SR-DPT2,4,6}/\%}$	$2.3 \cdot 10^{-3}$	$3.4 \cdot 10^{-4}$	$1.4 \cdot 10^{-2}$	0.2	3.6
, HF-SCF	0.7580	0.4707	0 2798	0.2505	0 1004
μ μ DPT2	0.7580	0.4797	0.3728 0.0176	0.2395	0.1904 0.1009
μ USR-DPT2,4 <i>a</i>	-0.0014	-0.0049	-0.0170	-0.0398	-0.1002 0.1321
μ μ SR-DPT2,4,6d	-0.0014	-0.0050	-0.0186	-0.0448	-0.1521
μ USF-DHFb	-0.0014	-0.0050	-0.0186	-0.0455	0.1403
μ $\Lambda^{\rm DPT2}$ /0%	34.10^{-1}	-0.0050	-0.0100	19.3	-0.1400
Δ / 70 Λ SR-DPT2,4/%	$9.4.10^{-4}$	1.2 $1.0.10^{-2}$	23.10^{-1}	1 2.5	8 1
$\Delta^{\text{SR-DPT2},4,6/\%}$	$1.5 \cdot 10^{-4}$	$5.2 \cdot 10^{-4}$	$9.8 \cdot 10^{-3}$	1.5 1.4E-1	2.0
~SO-DPT4	0 100 10-6	6 000 10-5	9 577 10-3	0.0170	0 9195
q _{α} SO-DHF c	-9.109.10 0.200.10-6	$-0.003 \cdot 10$ 7 159 10-5	$-2.077 \cdot 10$ 2 212 10-3	-0.0179	-0.2120
q^{-1} A SO /07	-9.200.10	-7.136.10	-0.010.10	-0.0317	-0.6040
$\Delta^{\prime\prime}$ / 70	1.0	0.0	22.2	43.4	73.1
$\mu^{\text{SO-DPT4}}$	$-6.570 \cdot 10^{-6}$	$-7.610 \cdot 10^{-5}$	-0.001677	-0.00914	-0.0675
$\mu^{\text{SO-DHF}c}$	$-6.603 \cdot 10^{-6}$	$-7.730 \cdot 10^{-5}$	-0.001809	-0.01095	-0.1095
$\Delta^{\rm SO}/\%$	0.6	1.5	7.3	16.5	38.4

 $^a\;$ sum of DPT2 and SR-DPT4 corrections

 $^{b}\,$ difference between SF-DHF and HF-SCF value

 $^{c}\,$ obtained by taking the difference between the full DHF and SF-DHF values

 $^{d}\,$ sum of DPT2, SR-DPT4, and SR-DPT6 corrections



Figure VII.5.: Structure of $CHBrF_2$ as well as a portion of its rotational spectrum. For details see Ref. 139.

For CH₂BrF and CHBrF₂ a detailed account of the experimental and theoretical results including DPT2 corrections computed at the CCSD(T) level is found in Refs. 138 and 139, respectively. Furthermore, for CH₂FI a rotational-spectroscopic investigation has been published in Ref. 140 together with CCSD(T) calculations for the parameters of interest both at the DPT2 and the spin-free Dirac Coulomb (SFDC)⁴¹ level. The geometrical structure as well as a representative portion of the rotational spectra of CHBrF₂ and CH₂FI can be found in the figures VII.5 (p. 131) and VII.6 (p. 132), respectively. All details for the quantum-chemical calculations prior to the DPT4 study discussed in the following as well as the employed geometries are found in the references mentioned before. The emphasis is in the following on the DPT4 corrections which were calculated at the HF level using uncontracted versions of Dunning's correlation-consistent valence polarized basis sets (cc-pV**X**Z) with **X**=T, Q, 5¹²⁰⁻¹²² as well as the uncontracted ANO-RCC basis set.¹²⁹



Figure VII.6.: Structure of CH_2FI as well as a portion of its rotational spectrum. For details see Ref. 140.

VII.4.1. Halogen quadrupole-coupling tensors of CH₂BrF and CHBrF₂

In table VII.8 (see p.133) the computed and experimental bromine quadrupole-coupling constants for CHBrF₂ are shown.¹³⁹ The deviations of the theoretical predictions from experiment are lower than 0.5%. This good agreement is due to the fact that the present calculations include relativistic effects (they range from 15 to 32 MHz, i.e., about 6.5%, as expected from previous investigations of bromine-containing molecules^{102,138}) and that the conversion of the computed efg is based on the most recent values for the bromine quadrupole moments.¹³⁵ On the other hand, vibrational corrections are small, their relative contribution being lower than 1%.

Furthermore, calculations at the DPT4, SF-DHF, as well as DHF level have been carried out in order to compute higher-order relativistic corrections to the diagonal elements of the quadrupole-coupling tensors of the bromine nucleus in $CHBrF_2$ and CH_2BrF . This allows to analyze the convergence of the DPT corrections and to assess the importance of SO effects at least at the HF level.

The results are found in table VII.9 (see p.134). For both CHBrF₂ and CH₂BrF it can be

	quadrupole coupling consol of clipit 2 in third t						
	non- relativistic	relativistic correction	vibrational correction	total	$experiment^b$		
$\chi_{aa} \ \chi_{bb} \ \chi_{cc}$	489.854 -262.496 -227.358	31.827 -17.078 -14.750	-0.328 -0.085 0.413	521.353 -279.659 -241.694	521.257(9) -279.804(40) -241.453(40)		

Table VII.8.: Individual contributions to the diagonal elements of the computed bromine quadrupole-coupling tensor of CHBrF_2 in MHz^a .

^a non-relativistic values obtained at the CCSD(T)/cc-pCVQZ level, the relativistic DPT2 corrections at the CCSD(T)/cc-pVQZ(unc) level, and the vibrational corrections at the MP2/cc-pCVTZ level. Geometries from CCSD(T)/cc-pCVQZ calculations.

 b from Ref. 139

seen that the SR-DPT4 corrections are about 1-2 MHz while the SO contributions are one order of magnitude smaller, i.e., about 0.1-0.3 MHz. Inclusion of the DPT4 corrections does not improve the agreement with the experimental numbers. It should be noted in this context that the error estimate for the bromine quadrupole moment is about 1 mb, so that the remaining uncertainty in the theoretical estimates is up to 1 MHz. Since the SR-DPT4 corrections are of the same order of magnitude as this uncertainty, and since the SO corrections are even smaller, it seems sufficient to limit the treatment of relativistic effects in these cases to the DPT2 level. Furthermore, since correlation and relativistic effects are not additive, we expect, based on previous experience,^{41,102} that the presented corrections computed here at the HF level overestimate the relativistic contribution. Nevertheless, by means of a DPT4 calculation at the HF level, a rough estimate for higher-order relativistic corrections is accessible. In the present case, this estimate justifies the use of and restriction to DPT2.

Regarding the basis-set dependence of the DPT4 corrections, it is seen that they converge rather smoothly when increasing the cardinal number \mathbf{X} in the cc-pV $\mathbf{X}Z(unc)$ sets. For the SR corrections there is a satisfactory agreement between the values calculated using the cc-pV5Z(unc) and the ANO-RCC(unc) basis set while for the SO contributions larger differences are observed. Since the ANO-RCC basis includes more basis functions in the inner-shell region, these numbers are probably more accurate.

Table VII.9.: Higher-order relativistic corrections (beyond DPT2) to the diagonal elements of the bromine quadrupole-coupling tensor of $CHBrF_2$ and CH_2BrF in MHz. Geometries for $CHBrF_2$ from Ref. 139 and for CH_2BrF from Ref. 138.

basis	SR-DPT4	SO-DPT4	h.o. SF-DHF ^{a}	$SO-DHF^b$	$\operatorname{Exp.}^{c}$	$Theory^c$
			$CHBrF_2$			
$\chi_{aa:}$						
cc-pVTZ(unc)	1.74	-0.32	1.82	-0.37	521.257(9)	521.353
cc-pVQZ (unc)	1.84	-0.29	1.93	-0.34		
cc-pV5Z(unc)	1.86	-0.28	1.95	-0.32		
ANO-RCC(unc)	1.87	-0.23	1.97	-0.26		
$\chi_{bb:}$						
cc-pVTZ(unc)	-0.94	0.17	-0.98	0.20	-279.804(40)	-279.659
cc-pVQZ(unc)	-0.99	0.15	-1.04	0.18		
cc-pV5Z(unc)	-1.00	0.15	-1.05	0.17		
ANO-RCC(unc)	-1.01	0.12	-1.06	0.14		
χ_{cc}						
cc-pVTZ(unc)	-0.80	0.15	-0.84	0.18	-241.453(40)	-241.694
cc-pVQZ(unc)	-0.85	0.14	-0.89	0.16	× /	
cc-pV5Z(unc)	-0.86	0.13	-0.90	0.15		
ANO-RCC(unc)	-0.86	0.11	-0.91	0.12		
			CIL D _m E			
			$C \Pi_2 D T F$			
χ_{aa}						
cc-pVTZ(unc)	1.44	-0.23	1.50	-0.27	443.431(8)	441.8
cc-pVQZ(unc)	1.52	-0.21	1.59	-0.25		
cc-pV5Z(unc)	1.53	-0.20	1.61	-0.23		
ANO-RCC(unc)	1.55	-0.15	1.63	-0.19		
$\chi_{bb} - \chi_{cc}$						
cc-pVTZ (unc)	0.45	-0.07	0.47	-0.08	153.566(26)	153.63
cc-pVQZ(unc)	0.47	-0.06	0.50	-0.07		
cc-pV5Z(unc)	0.48	-0.06	0.50	-0.07		
ANO-RCC(unc)	0.48	-0.04	0.51	-0.05		

 a higher-order SF-DHF result defined as the difference between SF-DHF and the total DPT2 value

^b difference between the full DHF and SF-DHF values

^c experimental value and previous theoretical estimate from Ref. 139 in the case of $CHBrF_2$ and from Ref. 138 in the case of CH_2BrF . The non-relativistic values were obtained at the CCSD(T)/cc-pCVQZ level, the relativistic DPT2 corrections at the CCSD(T)/cc-pVQZ-unc level, and the vibrational corrections at the MP2/cc-pCVTZ level.

VII.4.2. Halogen quadrupole-coupling tensor of CH₂FI

The computational results for the iodine quadrupole-coupling tensor of CH₂FI are given in table VII.10 (see p.136) together with the experimental results.¹⁴⁰ Relativistic effects treated at the CCSD(T)/DPT2 level amount here to about 14%. However, the deviation of the theoretical results from experiment is still in the range of 5-26 MHz. These deviations are reduced by inclusion of the DPT4 corrections, i.e., for χ_{aa} from around 26 MHz to 2 MHz, and for χ_{cc} from 21 MHz to 4 MHz. For χ_{bb} the absolute deviation is more or less unchanged, i.e., changes from 5 MHz to -6 MHz. The agreement appears convincing even though the relative error in the SO treatment in comparison to a full DHF calculation is about 36%. However, as seen by the SF-DHF and the full DHF values in table VII.10, relativistic corrections beyond DPT4 are non-negligible. Furthermore, at the HF level, the relativistic contributions are overestimated 41,102 so that the missing higher-order corrections and the HF treatment lead to a fortuitous error compensation. This is confirmed by the SFDC values calculated at the CCSD(T) level.¹⁴⁰ Taking the difference between the SFDC and the DPT2 results yields a higher-order SFDC contribution that is around 2 to 4 MHz smaller than the corresponding higher-order SF-DHF correction and agrees well with the SR-DPT4 results.

Nevertheless, the DPT4 calculations at the HF level provide a useful estimate for missing higher-order relativistic effects beyond the DPT2 treatment. Finally, it is noted that due to the large uncertainty of 12 mb in the iodine nuclear quadrupole moment the comparison to experiment needs to be viewed with some caution.

Table VII.10.: Theoretical predictions and experimental values for the diagonal components of the iodine quadrupole-coupling tensor of CH_2FI in MHz. All theoretical values calculated with the ANO-RCC(unc) basis set¹²⁹ and geometries from CCSD(T)/cc-pwCVQZ¹⁴¹ calculations (see Ref. 140).

Theoretical and experimental results from Ref. 140							
nrl^a		$DPT2^{a}$	total	$\operatorname{Exp.}^{b}$		$\Delta \chi^{ m Exptotal}$	
$\chi_{aa} \ \chi_{bb} \ \chi_{cc}$	-1337.32 497.72 839.60	-218.47 81.58 136.89	-1555.79 579.30 976.49	$\begin{array}{c} -1581.6142(27) \\ 584.1657(52) \\ 997.4485(52) \end{array}$		-25.82 4.87 20.96	
Higher-order relativistic corrections							
$SR-DPT4^{c}$		h.o. SF-DHF ^{d}	h.o. $SFDC^{a,e}$	$SO-DPT4^c$	$\mathrm{SO} ext{-}\mathrm{DHF}^f$	$\Delta\chi^{\rm DPT4}$	$\Delta \chi^{\rm h.o.~DHF}$
$\chi_{aa} \ \chi_{bb} \ \chi_{cc}$	-29.80 11.51 18.29	-33.97 13.12 20.86	-29.77 11.11 18.66	2.46 -0.96 -1.50	3.85 -1.52 -2.33	-27.34 10.54 16.80	-30.12 11.60 18.53

 a Calculated at CCSD(T) level of theory

 b Reference 140

 c Calculated at HF level of theory

 $^{d}\,$ Higher-order SF-DHF result defined as the difference between SF-DHF and the total DPT2 values

 $^{e}\,$ Higher-order SFDC result defined as the difference between SFDC and the total DPT2 values

 $^f\,$ Difference between the full DHF and the SF-DHF values

VIII. Conclusion

In order to reach high-accuracy consideration of relativistic effects in systems containing light elements can be essential. Perturbative schemes represent an attractive and cost-effective option in these cases where relativistic effects are small. Use of the Pauli Hamiltonian, however, is unsatisfactory in the sense that it contains singular operators and can only be applied in lowest order. An alternative route to treat relativistic effects in a perturbative manner is given by Direct Perturbation Theory (DPT). In contrast to schemes based on the Pauli Hamiltonian, DPT can, for example, be applied in arbitrary order. Furthermore, the general theory is systematic and elegant. It can be formulated in terms of energy derivatives based either on the Schrödinger or the Dirac equation making the implementation rather straightforward. The option to calculate higher-order corrections makes it possible to investigate both the convergence of the perturbative expansion as well as spin-orbit contributions for closed-shell systems.

In this work, higher-order relativistic corrections to energies and electrical properties have been investigated in the framework of DPT. A detailed summary of the results is given in the following.

General formulation of DPT in terms of energy derivatives

A general formulation of DPT was presented in terms of analytic-derivative theory. For instance, the DPT4 energy can be expressed as second derivative of the energy with respect to the relativistic perturbation parameter $\lambda_{\rm rel} = c^{-2}$. Using the method of Lagrange multipliers DPT corrections have been derived from two different perspectives, i.e., starting from either the Schrödinger or the Dirac equation.

DPT4 expressions in the framework of HF and MP2

For both Hartree-Fock (HF) and second-order Møller-Plesset perturbation theory (MP2) explicit expressions for the DPT4 correction have been worked out for closed-shell systems. The MP2 formulation is easily extended to other electron-correlation treatments such as coupled-cluster (CC) theory. The spin-orbit corrections which first appear at the DPT4 level have been separated from the scalar-relativistic contributions, thus enabling an independent treatment.

Implementation of the DPT4 corrections

The DPT4 energy corrections at HF and MP2 level have been implemented into the CFOUR program package,⁸⁰ thereby exploiting available second-derivative capabilities.⁷⁸ For the calculation of DPT4 corrections to electrical properties the required numerical differentiation techniques have been set up.

All integrals relevant for DPT4 except for those already implemented for DPT2^{109,110} have been evaluated using the McMurchie-Davidson scheme¹⁰⁷ and implemented into the CFOUR program package.

Convergence of the DPT series at the HF level

The accuracy of the DPT4 corrections as well as the convergence behaviour of the DPT series have been investigated for both the SR and SO contributions at the HF level. The general observation was that the quality of the description degrades for heavier elements. However, the DPT convergence behaviour was found to be smooth and monotonous. For the energies, DPT4 represents a significant improvement over DPT2 and is capable to provide relativistic corrections to the energy with a remaining error in the relativistic description of 1% or less even for molecules containing elements of the fifth row of the periodic table. In the case of even heavier elements, the DPT series could no longer be considered converged in fourth order. In the considered closed-shell cases, the SR contributions were found to be dominant while the SO corrections are about two orders of magnitude smaller. For the DPT4 corrections to electrical properties, the results concerning the convergence were similar except that the relative errors are larger compared to those obtained for the energies.

Concerning the basis-set dependence, it is noted that the chosen basis set needs to comply with requirements of both the non-relativistic and the subsequent relativistic treatment. For the DPT4 energy corrections at the HF level it was found that decontraction of a non-relativistic basis set leads to the fastest convergence.

DPT in electron correlation treatments

At a correlated level of theory the DPT4 contribution tends to overestimate the correlation contribution of the relativistic correction. For the SR contribution, the fourth-order results even indicate a divergence of the DPT expansion. The origin of this problem can be traced back to high-lying virtual s-orbitals together with the use of a point-nucleus model. The correlated SO-DPT4 corrections, however, do not suffer from numerical instabilities and can be used to estimate correlated SO contributions.

Application to rotational spectroscopy

For the molecules CH_2BrF , $CHBrF_2$, and CH_2FI , the importance of higher-order relativistic corrections to the halogen quadrupole-coupling tensors was investigated. Concerning the bromine-containing species, it was found that the restriction to DPT2 is justified while for the iodine quadrupole-coupling tensor higher-order relativistic corrections are important to reach an accuracy of better than 1%.

The present work shows that DPT is an elegant theory for the description of relativistic effects and works well in the framework of HF theory. Furthermore, it enables a detailed analysis of the individual contributions to the relativistic corrections and a formulation in terms of energy derivatives is possible in all orders making the corrections straightforward to implement into quantum-chemical programs. However, DPT in higher orders will probably not become a standard tool for the treatment of relativistic effects in the future because the convergence of the DPT series depends strongly on the atomic number and correlation treatments using higher-order SR-DPT seem to be divergent. Despite these drawbacks, the theory is not to be discarded. DPT2 corrections both at the HF as well as at correlated levels yield excellent results for light elements (up to the fourth row of the periodic table) at low computational cost. Furthermore, understanding the structure and magnitude of all contributions to relativistic corrections is important for the educated application and the development of approaches to treat relativistic effects. Such an analysis is possible only within the framework of DPT. In addition, the SO treatment in DPT can be utilized in other contexts. For example, if the full SR contribution is calculated and only the SO terms are treated perturbatively, the resulting equations are very similar to those used in the present SO-DPT4 treatment rendering their implementation rather straightforward. In this way the insight and computational capabilities resulting from this work will be of advantage in future developments.

IX. Appendix

IX.1. Perturbative expansion of the Dirac-Hartree-Fock equations

Using the modified metric (see chapter IV.1) the Dirac-Hartree-Fock (DHF) equations are given as

$$\hat{\mathbf{f}}_{\mathrm{D}} \boldsymbol{\Psi}_{i} = \varepsilon_{i} \hat{\mathbf{S}}_{\mathrm{D}} \boldsymbol{\Psi}_{i} \tag{IX.1}$$

with

$$\hat{\mathbf{f}}_{\mathrm{D}} = \begin{pmatrix} V + \hat{J}_{\mathrm{LL}} - \hat{K}_{\mathrm{LL}} + \frac{1}{c^2} \hat{J}_{\mathrm{SS}} & \boldsymbol{\sigma} \mathbf{p} - \frac{1}{c^2} \hat{K}_{\mathrm{SL}} \\ \boldsymbol{\sigma} \mathbf{p} - \frac{1}{c^2} \hat{K}_{\mathrm{LS}} & \frac{1}{c^2} V - 2m + \frac{1}{c^2} \hat{J}_{\mathrm{LL}} + \frac{1}{c^4} (\hat{J}_{\mathrm{SS}} - \hat{K}_{\mathrm{SS}}) \end{pmatrix}, \qquad (\mathrm{IX.2})$$

$$\Psi_{i} = \begin{pmatrix} \varphi_{i} \\ \chi_{i} \end{pmatrix}, \quad \hat{\mathbf{S}}_{\mathrm{D}} = \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{c^{2}} \end{pmatrix}, \quad (\mathrm{IX.3})$$

and the Coulomb and Exchange operators defined as

$$\hat{J}_{LL}\phi_i(1) = \int d^3 \mathbf{r}_2 \sum_k \varphi_k^*(2) \frac{1}{r_{12}} \phi_i(1) \varphi_k(2), \quad \phi_i = \varphi_i, \chi_i, \quad (IX.4)$$

$$\hat{J}_{\rm SS}\phi_i(1) = \int d^3 \mathbf{r}_2 \sum_k \chi_k^*(2) \frac{1}{r_{12}} \phi_i(1) \chi_k(2), \quad \phi_i = \varphi_i, \chi_i, \qquad (IX.5)$$

$$\hat{K}_{LL}\phi_i(1) = \int d^3 \mathbf{r}_2 \sum_k \varphi_k^*(2) \frac{1}{r_{12}} \varphi_k(1) \phi_i(2), \quad \phi_i = \varphi_i,$$
(IX.6)

$$\hat{K}_{\rm SS}\phi_i(1) = \int d^3 \mathbf{r}_2 \sum_k \chi_k^*(2) \frac{1}{r_{12}} \chi_k(1)\phi_i(2), \quad \phi_i = \chi_i, \qquad (IX.7)$$

$$\hat{K}_{\rm LS}\phi_i(1) = \int d^3 \mathbf{r}_2 \sum_k \varphi_k^*(2) \frac{1}{r_{12}} \chi_k(1)\phi_i(2), \quad \phi_i = \varphi_i, \qquad (IX.8)$$

$$\hat{K}_{\rm SL}\phi_i(1) = \int d^3 \mathbf{r}_2 \sum_k \chi_k^*(2) \frac{1}{r_{12}} \varphi_k(1)\phi_i(2), \quad \phi_i = \chi_i.$$
(IX.9)

140

Note that in all non-vanishing two-electron integrals both components have to be of the same type for a given electron, i.e., either large or small.

When a perturbative expansion of the DHF equations is carried out in terms of terms of $\lambda_{\rm rel} = c^{-2}$, the zeroth order is given by

$$\hat{\mathbf{f}}_{\rm D}^{(0)} \boldsymbol{\Psi}_i^{(0)} = \varepsilon_i^{(0)} \hat{\mathbf{S}}_{\rm D}^{(0)} \boldsymbol{\Psi}_i^{(0)}$$
(IX.10)

with

$$\hat{\mathbf{f}}_{\mathrm{D}}^{(0)} = \begin{pmatrix} V + \hat{J}_{\mathrm{LL}^{(0)}} - \hat{K}_{\mathrm{LL}}^{(0)} & \boldsymbol{\sigma}\hat{\mathbf{p}} \\ \boldsymbol{\sigma}\hat{\mathbf{p}} & -2m \end{pmatrix}, \boldsymbol{\Psi}_{i}^{(0)} = \begin{pmatrix} \varphi_{i}^{(0)} \\ \chi_{i}^{(0)} \end{pmatrix}, \hat{\mathbf{S}}_{\mathrm{D}}^{(0)} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad (\mathrm{IX.11})$$

and from the second row of (IX.10) it follows

$$\chi_i^{(0)} = \frac{1}{2m} \boldsymbol{\sigma} \hat{\mathbf{p}} \varphi_i^{(0)} \tag{IX.12}$$

which is equivalent to the result from the one-electron Lévy-Leblond equation. The second-order equation is given by

$$\hat{\mathbf{f}}_{\mathrm{D}}^{(0)} \boldsymbol{\Psi}_{i}^{(2)} + \hat{\mathbf{f}}_{\mathrm{D}}^{(2)} \boldsymbol{\Psi}_{i}^{(0)} = \varepsilon_{i}^{(0)} \hat{\mathbf{S}}_{\mathrm{D}}^{(2)} \boldsymbol{\Psi}_{i}^{(0)} + \varepsilon_{i}^{(2)} \hat{\mathbf{S}}_{\mathrm{D}}^{(0)} \boldsymbol{\Psi}_{i}^{(0)} + \varepsilon_{i}^{(0)} \hat{\mathbf{S}}_{\mathrm{D}}^{(0)} \boldsymbol{\Psi}_{i}^{(2)}$$
(IX.13)

which can be rearranged to

$$(\hat{\mathbf{f}}_{\mathrm{D}}^{(0)} - \varepsilon_{i}^{(0)}\hat{\mathbf{S}}_{\mathrm{D}}^{(0)})\boldsymbol{\Psi}_{i}^{(2)} + (\hat{\mathbf{f}}_{\mathrm{D}}^{(2)} - \varepsilon_{i}^{(0)}\hat{\mathbf{S}}_{\mathrm{D}}^{(2)} - \varepsilon_{i}^{(2)}\hat{\mathbf{S}}_{\mathrm{D}}^{(0)})\boldsymbol{\Psi}_{i}^{(0)} = 0 \qquad (\mathrm{IX.14})$$

with

$$\hat{\mathbf{f}}_{\mathrm{D}}^{(2)} = \begin{pmatrix} \hat{J}_{\mathrm{SS}}^{(0)} + \hat{J}_{\mathrm{LL}}^{(2)} - \hat{K}_{\mathrm{LL}}^{(2)} & -\hat{K}_{\mathrm{SL}}^{(0)} \\ -\hat{K}_{\mathrm{LS}}^{(0)} & V + \hat{J}_{\mathrm{LL}}^{(0)} \end{pmatrix}, \quad \hat{\mathbf{S}}_{\mathrm{D}}^{(2)} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$
(IX.15)

The perturbed small component $\chi_i^{(2)}$ is again obtained from the second row of (IX.14)

$$\chi_{i}^{(2)} = \frac{1}{2m} \left\{ (V - \varepsilon_{i}^{(0)} + \hat{J}_{\text{LL}}^{(0)}) \chi_{i}^{(0)} - \hat{K}_{\text{LS}}^{(0)} \varphi_{i}^{(0)} + \boldsymbol{\sigma} \hat{\mathbf{p}} \varphi_{i}^{(2)} \right\}$$
(IX.16)
$$= \frac{1}{2m} \left\{ (V - \varepsilon_{i}^{(0)}) \chi_{i}^{(0)} + \int d^{3} \mathbf{r}_{2} \sum_{k} \varphi_{k}^{(0)}(2) \frac{1}{r_{12}} \left[\chi_{i}^{(0)}(1) \varphi_{k}^{(0)}(2) - \chi_{k}^{(0)}(1) \varphi_{i}^{(0)}(2) \right] + \boldsymbol{\sigma} \hat{\mathbf{p}} \varphi_{i}^{(2)}(1) \right\}$$
(IX.17)

141

$$= \frac{1}{2m} \Big\{ \boldsymbol{\sigma} \mathbf{p} \varphi_i^{(2)} + \Big(V - \varepsilon_i^{(0)} + \sum_k \left[\hat{J}_k^{(0)} - \hat{K}_k^{(0)} \right] \Big) \chi_i^{(0)} \Big\}$$
(IX.18)

with

$$\langle \chi_j^{(0)} \mid \left[\hat{J}_k^{(0)} - \hat{K}_k^{(0)} \right] \mid \chi_i^{(0)} \rangle = \langle \chi_j^{(0)} \varphi_k^{(0)} \mid \chi_i^{(0)} \varphi_k^{(0)} \rangle - \langle \chi_j^{(0)} \varphi_k^{(0)} \mid \chi_k^{(0)} \varphi_i^{(0)} \rangle.$$
(IX.19)

IX.2. CPHF equations for the relativistic perturbation

The CPHF equations for the relativistic perturbation λ_{rel} are obtained by setting the derivative of the virtual-occupied block of the Fock matrix equal to zero

$$0 = \left\{ \frac{\partial \langle \Psi_{a} \mid \hat{\mathbf{f}}_{\mathrm{D}} \mid \Psi_{i} \rangle}{\partial \lambda_{\mathrm{rel}}} \right\}_{\lambda_{\mathrm{rel}}=0}$$
(IX.20)
$$= \left\{ \left\langle \Psi_{a}^{(2)} \mid \hat{\mathbf{f}}_{\mathrm{D}} \mid \Psi_{i}^{(0)} \right\rangle + \left\langle \Psi_{a}^{(0)} \mid \hat{\mathbf{f}}_{\mathrm{D}} \mid \Psi_{i}^{(2)} \right\rangle + \left\langle \Psi_{a}^{(0)} \mid \frac{\partial \hat{\mathbf{f}}_{\mathrm{D}}}{\partial \lambda_{\mathrm{rel}}} \mid \Psi_{i}^{(0)} \right\rangle \right\}_{\lambda_{\mathrm{rel}}=0}$$
(IX.21)
$$= -U_{ia}^{\lambda_{\mathrm{rel}}*} \varepsilon_{i} + U_{ai}^{\lambda_{\mathrm{rel}}} \varepsilon_{a} + f_{ai}^{(\lambda_{\mathrm{rel}})} + \sum_{p,j} U_{pj}^{\lambda_{\mathrm{rel}}*} [\langle \varphi_{a}\varphi_{p} \mid \varphi_{i}\varphi_{j} \rangle - \langle \varphi_{a}\varphi_{p} \mid \varphi_{j}\varphi_{i} \rangle]$$
$$+ \sum_{p,j} U_{pj}^{\lambda_{\mathrm{rel}}} [\langle \varphi_{a}\varphi_{j} \mid \varphi_{i}\varphi_{p} \rangle - \langle \varphi_{a}\varphi_{j} \mid \varphi_{p}\varphi_{i} \rangle]$$
(IX.22)

yielding

$$\sum_{bj} \left(2 \operatorname{Re} U_{bj}^{\lambda_{\mathrm{rel}}} \langle \varphi_a \varphi_b \mid \varphi_i \varphi_j \rangle - U_{bj}^{\lambda_{\mathrm{rel}}*} \langle \varphi_a \varphi_b \mid \varphi_j \varphi_i \rangle - U_{bj}^{\lambda_{\mathrm{rel}}} \langle \varphi_a \varphi_j \mid \varphi_b \varphi_i \rangle \right)$$
$$+ U_{bj}^{\lambda_{\mathrm{rel}}} \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) \right)$$
$$= -\varepsilon_i S_{ai}^{\lambda_{\mathrm{rel}}} - f_{ai}^{(\lambda_{\mathrm{rel}})} + \frac{1}{2} \sum_{jk} S_{kj}^{\lambda_{\mathrm{rel}}} \left(2 \langle \varphi_a \varphi_k \mid \varphi_i \varphi_j \rangle - \langle \varphi_a \varphi_k \mid \varphi_j \varphi_i \rangle \right)$$
$$- \langle \varphi_a \varphi_j \mid \varphi_k \varphi_i \rangle \right).$$
(IX.23)

For the SR part, it follows after spin integration for the closed-shell case

$$\sum_{bj} U_{bj}^{\text{SR}} \Big(4 \langle \phi_a \phi_b \mid \phi_i \phi_j \rangle - \langle \phi_a \phi_b \mid \phi_j \phi_i \rangle - \langle \phi_a \phi_j \mid \phi_b \phi_i \rangle + \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) \Big)$$

= $-\varepsilon_i S_{ai}^{\text{SR}} - f_{ai}^{(\text{SR})} + \frac{1}{2} \sum_{jk} S_{kj}^{\text{SR}} \Big(4 \langle \phi_a \phi_k \mid \phi_i \phi_j \rangle - \langle \phi_a \phi_k \mid \phi_j \phi_i \rangle - \langle \phi_a \phi_j \mid \phi_k \phi_i \rangle \Big) \quad (\text{IX.24})$

142

while for a specific SO component c = x, y, z the spin-integrated CPHF equations are

$$\sum_{bj} U_{bj}^{\text{SOc}} \Big(\langle \phi_a \phi_b \mid \phi_j \phi_i \rangle - \langle \phi_a \phi_j \mid \phi_b \phi_i \rangle + \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) \Big) = -f_{ai}^{(\text{SOc})}.$$
(IX.25)

Note that in this expression for the y component iU_{bj}^{SOy} instead of U_{bj}^{SOy} is determined. The spin cases for the specific components that are evaluated are $U_{b\bar{j}}^{SOx} = U_{\bar{b}j}^{SOx}, iU_{b\bar{j}}^{SOy}$ and U_{bj}^{SOz} .

IX.3. First derivative of the Lagrange multipliers

The second-order Lagrange multipliers $\varepsilon_{ji}^{(2)}$ are given as

$$\varepsilon_{ji}^{(2)} = \left\{ \frac{\partial \langle \Psi_j \mid \hat{\mathbf{f}}_{\mathrm{D}} \mid \Psi_i \rangle}{\partial \lambda_{\mathrm{rel}}} \right\}_{\lambda_{\mathrm{rel}}=0}$$
(IX.26)

$$= \left\{ \left\langle \boldsymbol{\Psi}_{j}^{(2)} \middle| \hat{\mathbf{f}}_{\mathrm{D}} \middle| \boldsymbol{\Psi}_{i}^{(0)} \right\rangle + \left\langle \boldsymbol{\Psi}_{j}^{(0)} \middle| \hat{\mathbf{f}}_{\mathrm{D}} \middle| \boldsymbol{\Psi}_{i}^{(2)} \right\rangle + \left\langle \boldsymbol{\Psi}_{j}^{(0)} \middle| \frac{\partial \hat{\mathbf{f}}_{\mathrm{D}}}{\partial \lambda_{\mathrm{rel}}} \middle| \boldsymbol{\Psi}_{i}^{(0)} \right\rangle \right\}_{\lambda_{\mathrm{rel}}=0}$$
(IX.27)

$$\begin{split} &= \left\{ \left\langle \Psi_{j}^{(2)} \mid \hat{\mathbf{h}}_{\mathrm{D}} \mid \Psi_{i}^{(0)} \right\rangle + \sum_{k} \left[\left\langle \Psi_{j}^{(2)} \Psi_{k}^{(0)} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{i}^{(0)} \Psi_{k}^{(0)} \right\rangle \\ &\quad - \left\langle \Psi_{j}^{(2)} \Psi_{k}^{(0)} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{k}^{(0)} \Psi_{i}^{(0)} \right\rangle \right] \\ &\quad + \left\langle \Psi_{j}^{(0)} \mid \hat{\mathbf{h}}_{\mathrm{D}} \mid \Psi_{i}^{(2)} \right\rangle + \sum_{k} \left[\left\langle \Psi_{j}^{(0)} \Psi_{k}^{(0)} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{i}^{(2)} \Psi_{k}^{(0)} \right\rangle \\ &\quad - \left\langle \Psi_{j}^{(0)} \Psi_{k}^{(0)} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{k}^{(0)} \Psi_{i}^{(2)} \right\rangle \right] \\ &\quad + \sum_{k} \left[2 \operatorname{Re} \langle \Psi_{j}^{(0)} \Psi_{k}^{(2)} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{i}^{(0)} \Psi_{k}^{(0)} \rangle - \left\langle \Psi_{j}^{(0)} \Psi_{k}^{(2)} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{k}^{(0)} \Psi_{i}^{(0)} \right\rangle \\ &\quad - \left\langle \Psi_{j}^{(0)} \Psi_{k}^{(0)} \mid \hat{\mathbf{g}}_{\mathrm{D}} \mid \Psi_{k}^{(2)} \Psi_{i}^{(0)} \right\rangle \right] \\ &\quad + \left\langle \Psi_{j}^{(0)} \mid \frac{\partial \hat{\mathbf{h}}_{\mathrm{D}}}{\partial \lambda_{\mathrm{rel}}} \middle| \Psi_{i}^{(0)} \right\rangle + \sum_{k} \left[\left\langle \Psi_{j}^{(0)} \Psi_{k}^{(0)} \mid \frac{\partial \hat{\mathbf{g}}_{\mathrm{D}}}{\partial \lambda_{\mathrm{rel}}} \middle| \Psi_{i}^{(0)} \Psi_{k}^{(0)} \right\rangle \right] \right\} \\ &\quad - \left\langle \Psi_{j}^{(0)} \Psi_{k}^{(0)} \mid \frac{\partial \hat{\mathbf{g}}_{\mathrm{D}}}{\partial \lambda_{\mathrm{rel}}} \middle| \Psi_{k}^{(0)} \Psi_{i}^{(0)} \right\rangle \right] \right\} \\ \\ &\quad = \left\langle \varphi_{j}^{(2)} \middle| V + \frac{\hat{\mathbf{p}}^{2}}{2m} \middle| \varphi_{i}^{(0)} \right\rangle + \sum_{k} \left[\left\langle \varphi_{j}^{(2)} \varphi_{k}^{(0)} \mid \varphi_{i}^{(0)} \varphi_{k}^{(0)} - \left\langle \varphi_{j}^{(2)} \varphi_{k}^{(0)} \mid \varphi_{k}^{(0)} \varphi_{i}^{(0)} \right\rangle \right] \end{aligned}$$
(IX.28)

$$+ \left\langle \varphi_{j}^{(0)} \middle| V + \frac{\hat{\mathbf{p}}^{2}}{2m} \middle| \varphi_{i}^{(2)} \right\rangle + \sum_{k} \left[\left\langle \varphi_{j}^{(0)} \varphi_{k}^{(0)} \mid \varphi_{i}^{(2)} \varphi_{k}^{(0)} \right\rangle - \left\langle \varphi_{j}^{(0)} \varphi_{k}^{(0)} \mid \varphi_{k}^{(0)} \varphi_{k}^{(2)} \right\rangle \right] \\ + \left\langle \chi_{j}^{(0)} \mid V \mid \chi_{i}^{(0)} \right\rangle + \sum_{k} \left[\left\langle \varphi_{j}^{(0)} \chi_{k}^{(0)} \mid \varphi_{i}^{(0)} \chi_{k}^{(0)} \right\rangle + \left\langle \chi_{j}^{(0)} \varphi_{k}^{(0)} \mid |\chi_{i}^{(0)} \varphi_{k}^{(0)} \right\rangle \right] \\ + \sum_{k} \left[2 \operatorname{Re} \left\langle \varphi_{j}^{(0)} \varphi_{k}^{(2)} \mid \varphi_{i}^{(0)} \varphi_{k}^{(0)} \right\rangle - \left\langle \varphi_{j}^{(0)} \varphi_{k}^{(2)} \mid \varphi_{k}^{(0)} \varphi_{i}^{(0)} \right\rangle - \left\langle \varphi_{j}^{(0)} \varphi_{k}^{(0)} \mid \varphi_{k}^{(2)} \varphi_{i}^{(0)} \right\rangle \right].$$
(IX.29)

With

$$\varphi_q^{(2)} = \sum_p U_{pq}^{\lambda_{\rm rel}} \varphi_p^{(0)} \tag{IX.30}$$

and

$$\hat{f}_{\rm nrl} = \hat{h}_{\rm nrl} + \sum_{k} (\hat{J}_{k}^{(0)} - \hat{K}_{k}^{(0)})$$
(IX.31)

while dropping the superscripts (0), it follows

$$\varepsilon_{ji}^{(2)} = \sum_{p} U_{pj}^{\lambda_{\text{rel}}*} \langle \varphi_{p} \mid \hat{f}_{\text{nrl}} \mid \varphi_{i} \rangle + \sum_{p} U_{pi}^{\lambda_{\text{rel}}} \langle \varphi_{j} \mid \hat{f}_{\text{nrl}} \mid \varphi_{p} \rangle + f_{ji}^{(\lambda_{\text{rel}})} + \sum_{k,p} \left(2 \operatorname{Re} U_{pk}^{\lambda_{\text{rel}}} \langle \varphi_{j}\varphi_{p} \mid \varphi_{i}\varphi_{k} \rangle - U_{pk}^{\lambda_{\text{rel}}*} \langle \varphi_{j}\varphi_{p} \mid \varphi_{k}\varphi_{i} \rangle - U_{pk}^{\lambda_{\text{rel}}} \langle \varphi_{j}\varphi_{k} \mid \varphi_{p}\varphi_{i} \rangle \right)$$
(IX.32)

$$=U_{ij}^{\lambda_{\rm rel}*}\varepsilon_i + U_{ji}^{\lambda_{\rm rel}}\varepsilon_j + f_{ji}^{(\lambda_{\rm rel})} + \sum_{k,p} \left(2\operatorname{Re} U_{pk}^{\lambda_{\rm rel}} \langle \varphi_j \varphi_p \mid \varphi_i \varphi_k \rangle - U_{pk}^{\lambda_{\rm rel}*} \langle \varphi_j \varphi_p \mid \varphi_k \varphi_i \rangle - U_{pk}^{\lambda_{\rm rel}} \langle \varphi_j \varphi_k \mid \varphi_p \varphi_i \rangle \right)$$
(IX.33)

$$= -\frac{1}{2}S_{ji}^{\lambda_{\rm rel}}(\varepsilon_i + \varepsilon_j) + f_{ji}^{(\lambda_{\rm rel})} + \sum_{k,p} \left(2\operatorname{Re} U_{pk}^{\lambda_{\rm rel}} \langle \varphi_j \varphi_p \mid \varphi_i \varphi_k \rangle - U_{pk}^{\lambda_{\rm rel}*} \langle \varphi_j \varphi_p \mid \varphi_k \varphi_i \rangle - U_{pk}^{\lambda_{\rm rel}} \langle \varphi_j \varphi_k \mid \varphi_p \varphi_i \rangle \right)$$
(IX.34)

where it was used that due to (IV.50) it holds

$$0 = \frac{\partial}{\partial \lambda_{\rm rel}} \left\{ \langle \boldsymbol{\Psi}_p \mid \hat{\mathbf{S}}_{\rm D} \mid \boldsymbol{\Psi}_q \rangle \right\}_{\lambda_{\rm rel}=0}$$
(IX.35)
$$= \langle \varphi_p^{(2)} \mid \varphi_q \rangle + \langle \varphi_p^{(0)} \mid \varphi_q^{(2)} \rangle + \langle \chi_p^{(0)} \mid \chi_q^{(0)} \rangle$$
(IX.36)

$$=U_{qp}^{\lambda_{rel}*} + U_{pq}^{\lambda_{rel}} + S_{pq}^{\lambda_{rel}}$$
(IX.37)

IX.4. Spin orthogonality for the g_{12}^{SO} integrals

After separation of the SR and SO parts of the integral

$$\langle pq \mid \boldsymbol{\sigma}_1 \hat{\mathbf{p}}_1 \boldsymbol{\sigma}_2 \hat{\mathbf{p}}_2 r_{12}^{-1} \boldsymbol{\sigma}_1 \hat{\mathbf{p}}_1 \boldsymbol{\sigma}_2 \hat{\mathbf{p}}_2 \mid rs
angle$$

the contributions involving the SO part are given by

$$\langle pq \mid \boldsymbol{\sigma}_{1} \hat{\mathbf{p}}_{1} \boldsymbol{\sigma}_{2} \hat{\mathbf{p}}_{2} r_{12}^{-1} \boldsymbol{\sigma}_{1} \hat{\mathbf{p}}_{1} \boldsymbol{\sigma}_{2} \hat{\mathbf{p}}_{2} \mid rs \rangle \rightarrow \langle pq \mid i\boldsymbol{\sigma}_{1} \hat{\mathbf{p}}_{2} (\hat{\mathbf{p}}_{1} \times r_{12}^{-1} \hat{\mathbf{p}}_{1}) \hat{\mathbf{p}}_{2} \mid rs \rangle + \langle pq \mid i\boldsymbol{\sigma}_{2} (\hat{\mathbf{p}}_{2} \times \hat{\mathbf{p}}_{1} r_{12}^{-1} \hat{\mathbf{p}}_{1} \hat{\mathbf{p}}_{2}) \mid rs \rangle + \langle pq \mid i\boldsymbol{\sigma}_{2} (\hat{\mathbf{p}}_{2} \times i\boldsymbol{\sigma}_{1} (\hat{\mathbf{p}}_{1} \times r_{12}^{-1} \hat{\mathbf{p}}_{1}) \hat{\mathbf{p}}_{2}) \mid rs \rangle.$$
(IX.38)

where the first and second term are of the same type, i.e., $i\boldsymbol{\sigma}_k \cdot R$ with k=1,2 and R as the spin-independent part of the operator. In the DPT4 energy expressions (see IV.51, IV.134) the terms containing the $\hat{g}_{12}^{\lambda_{\text{rel}}}$ integrals are given as

$$\sum_{pq} D_{pq} \sum_{j} \langle pj \mid \mid g_{12}^{\lambda_{\text{rel}}} \mid \mid qj \rangle, \qquad (\text{IX.39})$$

and

$$\sum_{pqrs} \Gamma_{pqrs} \langle pq \mid \mid g_{12}^{\lambda_{rel}} \mid \mid rs \rangle.$$
 (IX.40)

Note that the contribution appearing in (IV.51) is a special case of (IX.39) and therefore does not need a separate discussion.

For the first and second term in (IX.38) it holds that there cannot be a contribution for the SOx and SOy component as the only possible spin cases for D_{pq} and Γ_{pqrs} are those where there is an even number of α and β spins, i.e., D_{pq} , Γ_{pqrs} , $\Gamma_{\bar{p}q\bar{r}s}$, $\Gamma_{\bar{p}q\bar{r}s}$ plus those where α and β spin are exchanged. In the integrals however an odd number of α and β spins is needed to give a non-vanishing contribution as σ_x and σ_y both change the spin case. The SOz component does not change the spin case and therefore contributions of the aforementioned terms are possible. However, they add up to zero for closed-shell systems as shown for the first term in (IX.38)

$$\sum_{pq} D_{pq} \sum_{j} \langle pj \mid | \sigma_{1z}R \mid | qj \rangle$$

$$= \sum_{\rho=\alpha,\beta} \sum_{\omega=\alpha,\beta} \sum_{pq} D_{p_{\rho}q_{\rho}} \sum_{j} (\langle p_{\rho}j_{\omega} \mid \sigma_{1z}R \mid q_{\rho}j_{\omega} \rangle - \langle p_{\rho}j_{\omega} \mid \sigma_{1z}R \mid j_{\omega}q_{\rho} \rangle) \quad (IX.41)$$

$$= \sum_{pq} \sum_{j} \left\{ D_{pq} (\langle pj \mid \sigma_{1z}R \mid qj \rangle + \langle p\overline{j} \mid \sigma_{1z}R \mid q\overline{j} \rangle - \langle pj \mid \sigma_{1z}R \mid jq \rangle) \right\}$$

$$+ D_{\overline{pq}} \underbrace{\left(\langle \overline{pj} \mid \sigma_{1z}R \mid \overline{qj} \rangle + \langle \overline{pj} \mid \sigma_{1z}R \mid \overline{qj} \rangle}_{-\langle pj|R|qj \rangle} - \langle \overline{pj} \mid \sigma_{1z}R \mid \overline{jq} \rangle - \langle \overline{pj} \mid \sigma_{1z}R \mid \overline{jq} \rangle \right) \right\}.$$
(IX.42)

As $D_{pq} = D_{\overline{pq}}$ it follows that

$$\sum_{pq} D_{pq} \sum_{j} \langle pj \mid \mid \sigma_{1z} R \mid \mid qj \rangle = 0.$$
 (IX.43)

When contracted with the two-electron density matrix, these terms add up to zero for closed-shell systems in a similar manner

$$\begin{split} \sum_{pqrs} \Gamma_{pqrs} \langle pq \mid \mid \sigma_{1z}R \mid \mid rs \rangle \\ &= \sum_{pqrs} \sum_{\rho\omega\theta\delta = \alpha,\beta} \Gamma_{p_{\rho}q_{\omega}r_{\theta}s_{\delta}} (\langle p_{\rho}q_{\omega} \mid \sigma_{1z}R \mid r_{\theta}s_{\delta} \rangle - \langle p_{\rho}q_{\omega} \mid \sigma_{1z}R \mid s_{\delta}r_{\theta} \rangle) \qquad (IX.44) \\ &= \sum_{pqrs} \left\{ \Gamma_{pqrs} (\underbrace{\langle pq \mid \sigma_{1z}R \mid rs \rangle}_{\langle pq \mid R \mid rs \rangle} - \underbrace{\langle pq \mid \sigma_{1z}R \mid sr \rangle}_{\langle pq \mid R \mid sr \rangle} \right. \\ &+ \Gamma_{\overline{pqrs}} (\underbrace{\langle \overline{pq} \mid \sigma_{1z}R \mid \overline{rs} \rangle}_{-\langle pq \mid R \mid rs \rangle} - \underbrace{\langle \overline{pq} \mid \sigma_{1z}R \mid \overline{sr} \rangle}_{-\langle pq \mid R \mid sr \rangle} \\ &+ \Gamma_{\overline{p}q\overline{rs}} \underbrace{\langle \overline{pq} \mid \sigma_{1z}R \mid \overline{rs} \rangle}_{-\langle pq \mid R \mid rs \rangle} - \underbrace{\langle p\overline{q} \mid \sigma_{1z}R \mid \overline{sr} \rangle}_{\langle pq \mid R \mid sr \rangle} \\ &+ \Gamma_{\overline{p}q\overline{rs}} \underbrace{\langle \overline{pq} \mid \sigma_{1z}R \mid \overline{rs} \rangle}_{-\langle pq \mid R \mid rs \rangle} - \Gamma_{p\overline{q}\overline{rs}} \underbrace{\langle p\overline{q} \mid \sigma_{1z}R \mid s\overline{r} \rangle}_{\langle pq \mid R \mid rs \rangle} \\ &+ \Gamma_{\overline{p}qr\overline{s}} \underbrace{\langle \overline{pq} \mid \sigma_{1z}R \mid \overline{sr} \rangle}_{-\langle pq \mid R \mid rs \rangle} - \Gamma_{p\overline{q}\overline{rs}} \underbrace{\langle p\overline{q} \mid \sigma_{1z}R \mid s\overline{r} \rangle}_{\langle pq \mid R \mid sr \rangle} \\ \end{array} \right\}.$$
 (IX.45)

As $\Gamma_{pqrs} = \Gamma_{\overline{pqrs}}, \Gamma_{\overline{p}q\overline{r}s} = \Gamma_{p\overline{q}r\overline{s}}$, and $\Gamma_{\overline{p}qr\overline{s}} = \Gamma_{p\overline{q}rs}$ it follows that

$$\sum_{pqrs} \Gamma_{pqrs} \langle pq \mid \mid \sigma_{1z} R \mid \mid rs \rangle = 0.$$
 (IX.46)

In the same manner it can be shown that the second term in (IX.38) vanishes when contracted as given in (IX.39) or (IX.40).

Furthermore, for the third term in (IX.38) it holds that σ_1 and σ_2 have to be of the same type, i.e., both have to be either σ_x, σ_y , or σ_z to give a non-vanishing contribution. For the combinations $(1 + \hat{P}_{1,2})\sigma_{1x}\sigma_{2z}$ and $(1 + \hat{P}_{1,2})\sigma_{1y}\sigma_{2z}$ the reason is again that in the density matrices an even number of α and β spins appear whereas the only non-zero contributions in the integrals would have to involve an odd number of α and β . Concerning the contributions $(1 + \hat{P}_{1,2})\sigma_{1x}\sigma_{2y}$ it holds that similar to the previous discussion, the terms add up to zero in the case of closed-shell systems. As both σ_x and σ_y change the spin case, the only non-vanishing contributions from the integrals can come from terms where the spins for electron 1 and 2 on the left-hand side of the integral and those on the right hand side are exchanged. For the contraction with the one-electron density matrix it follows therefore

$$\sum_{pq} D_{pq} \sum_{j} \langle pq \mid \mid \sigma_{1x} \sigma_{1y} R \mid \mid rs \rangle$$

$$= \sum_{pq} \sum_{j} \left\{ D_{pq} \left(-\underbrace{\langle p\overline{j} \mid \sigma_{1x} \sigma_{1y} R \mid \overline{j}q \rangle}_{i\langle pj \mid R \mid jq \rangle} \right) + D_{\overline{pq}} \left(-\underbrace{\langle \overline{p}j \mid \sigma_{1x} \sigma_{1y} R \mid j\overline{q} \rangle}_{-i\langle pj \mid R \mid jq \rangle} \right) \right\} \quad (IX.47)$$

$$= 0 \quad (IX.48)$$

and for the two-electron density matrix

$$\sum_{pqrs} \Gamma_{pqrs} \langle pq \mid \mid \sigma_{1x} \sigma_{1y} R \mid \mid rs \rangle$$

$$= \sum_{pqrs} \left\{ \Gamma_{\overline{p}q\overline{r}s} \left(-\underbrace{\langle \overline{p}q \mid \sigma_{1x} \sigma_{1y} R \mid s\overline{r} \rangle}_{-i \langle pq \mid R \mid sr \rangle} \right) + \Gamma_{p\overline{q}r\overline{s}} \left(-\underbrace{\langle p\overline{q} \mid \sigma_{1x} \sigma_{1y} R \mid \overline{s}r \rangle}_{i \langle pq \mid R \mid sr \rangle} \right)$$

$$+ \Gamma_{\overline{p}qr\overline{s}} \underbrace{\langle \overline{p}q \mid \sigma_{1x} \sigma_{1y} R \mid r\overline{s} \rangle}_{-i \langle pq \mid R \mid rs \rangle} + \Gamma_{p\overline{q}r\overline{s}} \underbrace{\langle p\overline{q} \mid \sigma_{1x} \sigma_{1y} R \mid \overline{r}s \rangle}_{i \langle pq \mid R \mid rs \rangle} \right\}$$
(IX.49)
$$= 0.$$

$$(IX.50)$$

Obviously the result is the same if electron 1 and 2 are exchanged.

IX.5. Spin integration for the $f_{pq}^{(SO)}$ matrix elements

The spin integration for the spin-orbit components may be exemplary shown for the $f_{pq}^{(SO)}$ matrix elements which are given as

$$f_{pq}^{(\mathrm{SO})} = \frac{1}{4m^2} \Big(\langle p \mid i\boldsymbol{\sigma}(\hat{\mathbf{p}}V \times \hat{\mathbf{p}}) \mid q \rangle + \sum_j \langle pj \mid \mid i(\boldsymbol{\sigma}_1(\hat{\mathbf{p}}_1 r_{12}^{-1} \times \hat{\mathbf{p}}_1) + \boldsymbol{\sigma}_2(\hat{\mathbf{p}}_2 r_{12}^{-1} \times \hat{\mathbf{p}}_2)) \mid \mid qj \rangle \Big)$$
(IX.51)

For the SOx component the only possible spin cases are $f_{p\bar{q}}^{(SOx)}$ and $f_{\bar{p}q}^{(SOx)}$ and therefore it follows

$$f_{p\overline{q}}^{(\mathrm{SO}x)} = \langle p \mid \hat{\sigma}_x \sigma_1^x \mid \overline{q} \rangle + \sum_j \left\{ \langle pj \mid \sigma_{1x} \hat{g}_1^{\mathrm{SO}x} \mid \overline{q}j \rangle + \langle p\overline{j} \mid \sigma_{1x} \hat{g}_1^{\mathrm{SO}x} \mid \overline{q}\overline{j} \rangle - \langle pj \mid \sigma_{2x} \hat{g}_2^{\mathrm{SO}x} \mid j\overline{q} \rangle - \langle p\overline{j} \mid \sigma_{1x} \hat{g}_1^{\mathrm{SO}x} \mid \overline{j}\overline{q} \rangle \right\}$$
(IX.52)

$$=h_{pq}^{\mathrm{SO}x} + \sum_{j} \left\{ 2\langle pj \mid \hat{g}_{1}^{\mathrm{SO}x} \mid qj \rangle - \langle pj \mid \hat{g}_{1}^{\mathrm{SO}x} \mid jq \rangle - \langle pj \mid \hat{g}_{2}^{\mathrm{SO}x} \mid jq \rangle \right\}$$
(IX.53)

with

$$\hat{o}_{1}^{c} = \frac{1}{4m^{2}} \epsilon_{c\mu\nu} i(\hat{p}_{\mu} V \hat{p}_{\nu} - \hat{p}_{\nu} V \hat{p}_{\mu})$$
(IX.54)

and the Levi-Cività tensor as given in (IV.68). For $f_{\overline{p}q}^{(SOx)}$ the same result is found. As σ_y introduces the imaginary unit *i*, the equation is premultiplied by *i*:

$$if_{p\overline{q}}^{(\mathrm{SO}y)} = i\langle p \mid \hat{\sigma}_{y} o_{1}^{y} \mid \overline{q} \rangle + i \sum_{j} \left\{ \langle pj \mid \sigma_{1y} \hat{g}_{1}^{\mathrm{SO}y} \mid \overline{q}j \rangle + \langle p\overline{j} \mid \sigma_{1y} \hat{g}_{1}^{\mathrm{SO}y} \mid \overline{q}\overline{j} \rangle - \langle pj \mid \sigma_{2y} \hat{g}_{2}^{\mathrm{SO}y} \mid j\overline{q} \rangle - \langle p\overline{j} \mid \sigma_{1y} \hat{g}_{1}^{\mathrm{SO}y} \mid \overline{j}\overline{q} \rangle \right\}$$
(IX.55)

$$=h_{pq}^{\mathrm{SO}y} + \sum_{j} \left\{ 2\langle pj \mid \hat{g}_{1}^{\mathrm{SO}y} \mid qj \rangle - \langle pj \mid \hat{g}_{1}^{\mathrm{SO}y} \mid jq \rangle - \langle pj \mid \hat{g}_{2}^{\mathrm{SO}y} \mid jq \rangle \right\}.$$
(IX.56)

Furthermore it holds that $if_{p\bar{q}}^{(\mathrm{SO}y)} = -if_{\bar{p}q}^{(\mathrm{SO}y)}$. The SOz component involves the Pauli spin matrix σ_z . As it does not change the spin case but only the sign, the possible matrix elements are $f_{pq}^{(\mathrm{SO}z)}$ and $f_{\bar{p}q}^{(\mathrm{SO}z)}$. For the $\alpha\alpha$ element it holds

$$f_{pq}^{(\mathrm{SO}z)} = \langle p \mid \hat{\sigma}_z o_1^z \mid \overline{q} \rangle + \sum_j \left\{ \langle pj \mid \sigma_{1z} \hat{g}_1^{\mathrm{SO}z} \mid qj \rangle + \langle p\overline{j} \mid \sigma_{1z} \hat{g}_1^{\mathrm{SO}z} \mid q\overline{j} \rangle \right.$$

148

$$+ \langle pj \mid \sigma_{2z} \hat{g}_{2}^{\mathrm{SO}z} \mid qj \rangle + \langle p\overline{j} \mid \sigma_{2z} \hat{g}_{2}^{\mathrm{SO}z} \mid q\overline{j} \rangle - \langle pj \mid \sigma_{1z} \hat{g}_{1}^{\mathrm{SO}y} \mid jq \rangle - \langle p\overline{j} \mid \sigma_{1z} \hat{g}_{1}^{\mathrm{SO}z} \mid \overline{j}q \rangle - \langle pj \mid \sigma_{2z} \hat{g}_{2}^{\mathrm{SO}y} \mid jq \rangle - \langle p\overline{j} \mid \sigma_{2z} \hat{g}_{2}^{\mathrm{SO}z} \mid \overline{j}q \rangle \Big\}$$
(IX.57)

$$=h_{pq}^{\mathrm{SO}z} + \sum_{j} \left\{ 2\langle pj \mid \hat{g}_{1}^{\mathrm{SO}z} \mid qj \rangle - \langle pj \mid \hat{g}_{1}^{\mathrm{SO}z} \mid jq \rangle - \langle pj \mid \hat{g}_{2}^{\mathrm{SO}z} \mid jq \rangle \right\}$$
(IX.58)

and $f_{pq}^{(SOz)} = -f_{\overline{pq}}^{(SOz)}$. From (IX.53), (IX.56), and (IX.58) it follows that the equations for $f_{p\overline{q}}^{(SOx)}$, $if_{p\overline{q}}^{(SOy)}$ and $f_{pq}^{(SOz)}$ all have the same structure. As this is generally the case for the SO quantities, it is possible to implement their evaluation in form of loop structure over the SOx, SOy, and SOz component.

IX.6. Spin-integrated quantities for SR-DPT4 at the MP2 level

The definitions of the SR perturbed and unperturbed density matrices, Lagrange multipliers and integrals from (IV.163) are given as

$$\frac{\partial t_{i\bar{j}}^{ab}}{\partial \lambda_{\rm SR}} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \left[\frac{\partial \langle ab \mid \hat{g} \mid ij \rangle}{\partial \lambda_{\rm SR}} - \sum_m \frac{\partial f_{mi}}{\partial \lambda_{\rm SR}} t_{m\bar{j}}^{a\bar{b}} - \sum_m \frac{\partial f_{mj}}{\partial \lambda_{\rm SR}} t_{i\bar{m}}^{a\bar{b}} \right] + \sum_e \frac{\partial f_{ae}}{\partial \lambda_{\rm SR}} t_{i\bar{j}}^{e\bar{b}} + \sum_e \frac{\partial f_{be}}{\partial \lambda_{\rm SR}} t_{i\bar{j}}^{a\bar{e}} \right],$$
(IX.59)

$$\frac{\partial f_{pq}}{\partial \lambda_{\rm SR}} = -\frac{1}{2} S_{pq}^{\rm SR}(\varepsilon_p + \varepsilon_q) + f_{pq}^{\rm (SR)} + \sum_{rk} \left\{ U_{rk}^{\rm SR}(4\langle pr \mid qk \rangle - \langle pr \mid kq \rangle - \langle pk \mid rq \rangle) \right\},$$
(IX.60)

$$\begin{split} \frac{\partial \langle ij \mid \frac{\partial \hat{g}}{\partial \lambda_{\text{SR}}} \mid ab \rangle}{\partial \lambda_{\text{SR}}} = &\sum_{p} \left\{ U_{pi}^{\text{SR}} \langle pj \mid \hat{g}_{1}^{\text{SR}} + \hat{g}_{2}^{\text{SR}} \mid ab \rangle + U_{pa}^{\text{SR}} \langle ij \mid \hat{g}_{1}^{\text{SR}} + \hat{g}_{2}^{\text{SR}} \mid pb \rangle \right. \\ &+ U_{pj}^{\text{SR}} \langle ip \mid \hat{g}_{1}^{\text{SR}} + \hat{g}_{2}^{\text{SR}} \mid ab \rangle + U_{pb}^{\text{SR}} \langle ij \mid \hat{g}_{1}^{\text{SR}} + \hat{g}_{2}^{\text{SR}} \mid ap \rangle \\ &+ 2A_{pi}^{\text{SR}} \langle pj \mid \hat{g}_{1}^{\text{SR}} \mid ab \rangle + 2A_{pa}^{\text{SR}} \langle ij \mid \hat{g}_{1}^{\text{SR}} \mid pb \rangle \\ &+ 2A_{pj}^{\text{SR}} \langle ip \mid \hat{g}_{1}^{\text{SR}} \mid ab \rangle + 2A_{pb}^{\text{SR}} \langle ij \mid \hat{g}_{1}^{\text{SR}} \mid ap \rangle \Big\} \end{split}$$

149

$$+2\langle ij \mid \hat{g}_{12}^{\mathrm{SR}} \mid ab\rangle,\tag{IX.61}$$

$$\frac{\partial D_{ij}}{\partial \lambda_{\rm SR}} = -\frac{1}{2} \sum_{ab} \sum_{k} \left\{ \frac{\partial \lambda_{a\bar{b}}^{k\bar{j}}}{\partial \lambda_{\rm SR}} (4t_{k\bar{i}}^{a\bar{b}} - 2t_{i\bar{k}}^{a\bar{b}}) + \lambda_{a\bar{b}}^{k\bar{j}} \left(4\frac{\partial t_{k\bar{i}}^{a\bar{b}}}{\partial \lambda_{\rm SR}} - 2\frac{\partial t_{i\bar{k}}^{a\bar{b}}}{\partial \lambda_{\rm SR}} \right) \right\}, \qquad (IX.62)$$

$$\frac{\partial D_{ab}}{\partial \lambda_{\rm SR}} = \frac{1}{2} \sum_{kj} \sum_{e} \left\{ \frac{\partial \lambda_{e\bar{a}}^{k\bar{j}}}{\partial \lambda_{\rm SR}} (4t_{k\bar{j}}^{e\bar{b}} - 2t_{j\bar{k}}^{e\bar{b}}) + \lambda_{e\bar{a}}^{k\bar{j}} \left(4\frac{\partial t_{k\bar{j}}^{e\bar{b}}}{\partial \lambda_{\rm SR}} - 2\frac{\partial t_{j\bar{k}}^{e\bar{b}}}{\partial \lambda_{\rm SR}} \right) \right\}, \qquad (IX.63)$$

$$\begin{split} \frac{\partial f_{pq}^{(\mathrm{SR})}}{\lambda_{\mathrm{SR}}} &= \frac{\partial}{\partial \lambda_{\mathrm{SR}}} \left(\left\langle p \mid \frac{\partial \hat{h}}{\partial \lambda_{\mathrm{SR}}} \mid q \right\rangle + \sum_{k} \left(2 \left\langle pk \mid \frac{\partial \hat{g}}{\partial \lambda_{\mathrm{SR}}} \mid qk \right\rangle - \left\langle pk \mid \frac{\partial \hat{g}}{\partial \lambda_{\mathrm{SR}}} \mid kq \right\rangle \right) \right) \\ &= \sum_{t} \left[\left(U_{tp}^{\mathrm{SR}} + 2A_{tp}^{\mathrm{SR}} \right) h_{tq}^{\mathrm{SR}} + \left(U_{tq}^{\mathrm{SR}} + 2A_{tq}^{\mathrm{SR}} \right) h_{pt}^{\mathrm{SR}} \right] - 4m \sum_{ts} A_{tp}^{\mathrm{SR}} S_{ts}^{\mathrm{SR}} A_{sq}^{\mathrm{SR}} \\ &+ \sum_{tk} U_{tp}^{\mathrm{SR}} (2 \left\langle tk \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid qk \right\rangle - \left\langle tk \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid kq \right\rangle) \\ &+ \sum_{tk} 2A_{tp}^{\mathrm{SR}} (2 \left\langle tk \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid kk \right) - \left\langle tk \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid kt \right\rangle) \\ &+ \sum_{tk} U_{tq}^{\mathrm{SR}} (2 \left\langle pk \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid tk \right) - \left\langle pk \mid \hat{g}_{2}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid kt \right\rangle) \\ &+ \sum_{tk} 2A_{tp}^{\mathrm{SR}} (2 \left\langle pk \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid qk \right) - \left\langle pt \mid \hat{g}_{2}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid kq \right\rangle) \\ &+ \sum_{tk} U_{tk}^{\mathrm{SR}} (2 \left\langle pt \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid qk \right) - \left\langle pt \mid \hat{g}_{2}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid kq \right\rangle) \\ &+ \sum_{tk} 2A_{tk}^{\mathrm{SR}} (2 \left\langle pt \mid \hat{g}_{2}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid qt \right) - \left\langle pt \mid \hat{g}_{2}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid tq \right\rangle) \\ &+ \sum_{tk} U_{tk}^{\mathrm{SR}} (2 \left\langle pk \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid qt \right) - \left\langle pk \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid tq \right\rangle) \\ &+ \sum_{tk} 2A_{tk}^{\mathrm{SR}} (2 \left\langle pk \mid \hat{g}_{2}^{\mathrm{SR}} \mid qt \right) - \left\langle pk \mid \hat{g}_{1}^{\mathrm{SR}} + \hat{g}_{2}^{\mathrm{SR}} \mid tq \right\rangle) \\ &+ \sum_{tk} 2A_{tk}^{\mathrm{SR}} (2 \left\langle pk \mid \hat{g}_{2}^{\mathrm{SR}} \mid qt \right) - \left\langle pk \mid \hat{g}_{1}^{\mathrm{SR}} \mid tq \right\rangle) \\ &+ 2\sum_{k} (2 \left\langle pk \mid \hat{g}_{12}^{\mathrm{SR}} \mid qk \right) - \left\langle pk \mid \hat{g}_{12}^{\mathrm{SR}} \mid kq \right\rangle), \quad (\mathrm{IX.64})$$

$$I_{ij} + I_{ji} = -\sum_{l} \sum_{ab} t_{i\bar{l}}^{a\bar{b}} (4\langle jl \mid ab \rangle - 2\langle jl \mid ba \rangle) - 2D_{ij}\varepsilon_j -\sum_{kl} D_{kl} (4\langle kj \mid li \rangle - \langle kj \mid il \rangle - \langle ki \mid jl \rangle)$$

$$-\sum_{bc} D_{bc}(4\langle bj \mid ci\rangle - \langle bj \mid ic\rangle - \langle bi \mid jc\rangle) -\sum_{ak} Z_{ak}(4\langle aj \mid ki\rangle - \langle aj \mid ik\rangle - \langle ai \mid jk\rangle),$$
(IX.65)

$$I_{ai} + I_{ia} = -\sum_{kj} \sum_{b} t_{k\bar{j}}^{a\bar{b}} (4\langle kj \mid ib \rangle - 2\langle kj \mid bi \rangle) - Z_{ai}\varepsilon_i, \qquad (IX.66)$$

$$I_{ab} + I_{ba} = -\sum_{ij} \sum_{c} t_{i\bar{j}}^{c\bar{b}} (4\langle ij \mid ca \rangle - 2\langle ij \mid ac \rangle) - 2D_{ab}\varepsilon_b, \qquad (IX.67)$$

$$\begin{split} \frac{\partial (I_{ij} + I_{ji})}{\partial \lambda_{\text{SR}}} &= -\sum_{l} \sum_{ab} \frac{\partial t_{ab}^{\bar{a}\bar{b}}}{\partial \lambda_{\text{SR}}} (4\langle jl \mid ab \rangle - 2\langle jl \mid ba \rangle) \\ &-\sum_{l} \sum_{ab} t_{d}^{\bar{a}\bar{b}} \left(4\frac{\partial \langle jl \mid \hat{g} \mid ab \rangle}{\partial \lambda_{\text{SR}}} - 2\frac{\langle jl \mid \hat{g} \mid ba \rangle}{\partial \lambda_{\text{SR}}} \right) \\ &- 2\left(\frac{\partial D_{ij}}{\partial \lambda_{\text{SR}}} \varepsilon_j + \sum_{k} D_{ik} \frac{\partial f_{jk}}{\partial \lambda_{\text{SR}}} \right) \\ &- \sum_{kl} \frac{\partial D_{kl}}{\partial \lambda_{\text{SR}}} (4\langle kj \mid li \rangle - \langle kj \mid il \rangle - \langle ki \mid jl \rangle) \\ &- \sum_{kl} \frac{\partial D_{kl}}{\partial \lambda_{\text{SR}}} (4\langle kj \mid \hat{g} \mid \hat{g} \mid \hat{g} \rangle - \frac{\partial \langle kj \mid \hat{g} \mid il \rangle}{\partial \lambda_{\text{SR}}} - \frac{\partial \langle ki \mid \hat{g} \mid jl \rangle}{\partial \lambda_{\text{SR}}} \right) \\ &- \sum_{kl} \frac{\partial D_{bc}}{\partial \lambda_{\text{SR}}} (4\langle bj \mid ci \rangle - \langle bj \mid ic \rangle - \langle bi \mid jc \rangle) \\ &- \sum_{bc} \frac{\partial D_{bc}}{\partial \lambda_{\text{SR}}} (4\langle bj \mid ik \rangle - \langle aj \mid ik \rangle - \langle ai \mid jk \rangle) \\ &- \sum_{bc} \frac{\partial Z_{ak}}{\partial \lambda_{\text{SR}}} (4\langle aj \mid ki \rangle - \langle aj \mid ik \rangle - \langle ai \mid jk \rangle) \\ &- \sum_{ak} \frac{\partial Z_{ak}}{\partial \lambda_{\text{SR}}} (4\langle aj \mid ki \rangle - 2\langle kj \mid bi \rangle) \\ &- \sum_{ak} Z_{ak} \left(4\frac{\partial \langle aj \mid \hat{g} \mid ki \rangle}{\partial \lambda_{\text{SR}}} - \frac{\partial \langle aj \mid \hat{g} \mid ik \rangle}{\partial \lambda_{\text{SR}}} - \frac{\partial \langle ai \mid \hat{g} \mid jk \rangle}{\partial \lambda_{\text{SR}}} \right), \quad (\text{IX.68}) \\ \frac{\partial (I_{ai} + I_{ia})}{\partial \lambda_{\text{SR}}} = -\sum_{kj} \sum_{b} \frac{\partial t_{kj}^{ab}}{\partial \lambda_{\text{SR}}} (4\langle kj \mid ib \rangle - 2\langle kj \mid bi \rangle) \\ &- \sum_{kj} \sum_{b} t_{kj}^{ab}} \left(4\frac{\partial \langle kj \mid \hat{g} \mid ib \rangle}{\partial \lambda_{\text{SR}}} - 2\frac{\partial \langle kj \mid \hat{g} \mid bi \rangle}{\partial \lambda_{\text{SR}}} \right) \\ &- \frac{\partial Z_{ai}}{\partial \lambda_{\text{SR}}} \varepsilon_i - \sum_{k} Z_{ak} \frac{\partial f_{ik}}{\partial \lambda_{\text{SR}}}, \quad (\text{IX.69}) \end{split}$$

$$\frac{\partial (I_{ab} + I_{ba})}{\partial \lambda_{\rm SR}} = -\sum_{ij} \sum_{c} \frac{\partial t_{i\bar{j}}^{cb}}{\partial \lambda_{\rm SR}} (4\langle ij \mid ca \rangle - 2\langle ij \mid ac \rangle)$$

$$-\sum_{ij}\sum_{c} t_{ij}^{c\bar{b}} \left(4 \frac{\partial \langle ij \mid \hat{g} \mid ca \rangle}{\partial \lambda_{\rm SR}} - 2 \frac{\partial \langle ij \mid \hat{g} \mid ac \rangle}{\partial \lambda_{\rm SR}} \right) - 2 \left(\frac{\partial D_{ab}}{\partial \lambda_{\rm SR}} \varepsilon_b + \sum_{c} D_{cb} \frac{\partial f_{ca}}{\partial \lambda_{\rm SR}} \right), \qquad (IX.70)$$

while the unperturbed and perturbed Z-vector equations read

$$\sum_{bj} Z_{bj}[(\varepsilon_{a} - \varepsilon_{i})\delta_{ab}\delta_{ij} + 4\langle ba \mid ji \rangle - \langle ba \mid ij \rangle - \langle bi \mid aj \rangle]$$

$$= \sum_{kj} \sum_{b} t_{k\bar{j}}^{a\bar{b}}(4\langle kj \mid ib \rangle - 2\langle kj \mid bi \rangle) - \sum_{j} \sum_{bc} t_{i\bar{j}}^{c\bar{b}}(4\langle aj \mid cb \rangle - 2\langle aj \mid bc \rangle)$$

$$- \sum_{lk} D_{lk}(4\langle la \mid ki \rangle - \langle la \mid ik \rangle - \langle li \mid ak \rangle)$$

$$- \sum_{bc} D_{bc}(4\langle ba \mid ci \rangle - \langle ba \mid ic \rangle - \langle bi \mid ac \rangle), \qquad (IX.71)$$

$$\begin{split} \sum_{bj} \frac{\partial Z_{bj}}{\partial \lambda_{\rm SR}} [(\varepsilon_a - \varepsilon_i) \delta_{ab} \delta_{ij} + 4 \langle ba \mid ji \rangle - \langle ba \mid ij \rangle - \langle bi \mid aj \rangle] \\ &= -\sum_{bj} Z_{bj} \Biggl\{ 4 \frac{\partial \langle ba \mid \hat{g} \mid ji \rangle}{\partial \lambda_{\rm SR}} - \frac{\partial \langle ba \mid \hat{g} \mid ij \rangle}{\partial \lambda_{\rm SR}} - \frac{\partial \langle bi \mid \hat{g} \mid aj \rangle}{\partial \lambda_{\rm SR}} \\ &+ \delta_{ij} \frac{\partial f_{ba}}{\partial \lambda_{\rm SR}} - \delta_{ab} \frac{\partial f_{ij}}{\partial \lambda_{\rm SR}} \Biggr\} \\ &+ \sum_{kj} \sum_{b} \frac{\partial t_{kj}^{\bar{b}}}{\partial \lambda_{\rm SR}} (4 \langle kj \mid ib \rangle - 2 \langle kj \mid bi \rangle) \\ &+ \sum_{kj} \sum_{b} t_{kj}^{a\bar{b}} \left(4 \frac{\partial \langle kj \mid \hat{g} \mid ib \rangle}{\partial \lambda_{\rm SR}} - 2 \frac{\partial \langle kj \mid \hat{g} \mid bi \rangle}{\partial \lambda_{\rm SR}} \right) \\ &- \sum_{j} \sum_{bc} \frac{\partial t_{ij}^{\bar{b}}}{\partial \lambda_{\rm SR}} (4 \langle aj \mid cb \rangle - 2 \langle aj \mid bc \rangle) \\ &- \sum_{j} \sum_{bc} t_{ij}^{c\bar{b}} \left(4 \frac{\partial \langle aj \mid \hat{g} \mid cb \rangle}{\partial \lambda_{\rm SR}} - 2 \frac{\partial \langle aj \mid \hat{g} \mid bc \rangle}{\partial \lambda_{\rm SR}} \right) \\ &- \sum_{lk} \frac{\partial D_{lk}}{\partial \lambda_{\rm SR}} (4 \langle la \mid ki \rangle - \langle la \mid ik \rangle - \langle li \mid ak \rangle) \\ &- \sum_{lk} D_{lk} \left(4 \frac{\partial \langle la \mid \hat{g} \mid ki \rangle}{\partial \lambda_{\rm SR}} - \frac{\partial \langle la \mid \hat{g} \mid ik \rangle}{\partial \lambda_{\rm SR}} - \frac{\partial \langle li \mid \hat{g} \mid ak \rangle}{\partial \lambda_{\rm SR}} \right) \end{split}$$

152

$$-\sum_{bc} \frac{\partial D_{bc}}{\partial \lambda_{\rm SR}} (4\langle ba \mid ci \rangle - \langle ba \mid ic \rangle - \langle bi \mid ac \rangle) -\sum_{bc} D_{bc} \left(4 \frac{\partial \langle ba \mid \hat{g} \mid ci \rangle}{\partial \lambda_{\rm SR}} - \frac{\partial \langle ba \mid \hat{g} \mid ic \rangle}{\partial \lambda_{\rm SR}} - \frac{\partial \langle bi \mid \hat{g} \mid ac \rangle}{\partial \lambda_{\rm SR}} \right).$$
(IX.72)

IX.7. Accuracy of the numerical SR-DPT4 and SO-DPT4 results

The accuracy of the DPT corrections to dipole moments and efgs obtained by numerical differentiation was tested with different field strengths, i.e., $X \cdot 10^{-6}$ a.u., with X = 1, 5, 10, 20, 50, 75, and 100 using two- to eight-point formulas for the calculation of the corresponding corrections. For the efgs, a field strength of $10 \cdot 10^{-6}$ a.u. seems to be well suited as there is a fast convergence when increasing the number of points in the differentiation formula as can be seen in figure IX.1. Larger field strengths result in deterioration of the results. For the dipole moments, as seen in figure IX.2, a field strength of $75 \cdot 10^{-6}$ a.u. appears the best choice, as it shows the most stable convergence pattern. To ensure that the reported digits in the computed DPT corrections are significant, calculations were carried out using different convergence criteria in the SCF procedure.



Figure IX.1.: Convergence of the DPT2, SR-DPT4, and SO-DPT4 corrections to the iodine efg (in a.u.) in HI with different field strengths



Figure IX.2.: Convergence of the DPT2, SR-DPT4, and SO-DPT4 corrections to the dipole moment (in a.u.) of HI with different field strengths

IX.8. Basis-set dependence of DPT4

Table IX.1 provides information about the basis-set dependence of the DPT4 correction at the HF level. The results show that uncontraction of the basis is more important than choosing the cc-pCVXZ instead of the cc-pVXZ set.

Table IX.1.:	Basis-set dependence of the DPT4 correction, see chapter VII.1.2, geomet-
	ries from $CCSD(T)/cc$ -pCVQZ calculations including DPT2 corrections: ¹⁰⁹
	HCl: $R = 1.27351$ Å, HBr: $R = 1.44121$ Å.

SR-DPT4 for HCl						
X	cc-pVXZ	cc-pVXZ(unc)	cc-p $CVXZ$	cc-pCVXZ(unc)		
Т	1.10393E-02	-1.00003E-02	-7.19218E-04	-1.00004E-02		
\mathbf{Q}	1.23711E-02	-1.00317E-02	-7.02785E-03	-1.00317E-02		
5	6.20376E-03	-1.00521E-02	-8.89171E-03	-1.00521E-02		
SR-DPT4 for HBr						
Χ	cc-pVXZ	$\operatorname{cc-pVXZ}(\operatorname{unc})$	cc-p $CVXZ$	cc-pCVXZ(unc)		
Т	1.00137	-9.02804E-01	1.03991	-9.02804E-01		
Q	1.02158	-9.03687E-01	-6.00360E-01	-9.03687E-01		
5	1.04047	-9.04133E-01	-6.15448E-01	-9.04133E-01		
SO-DPT4 for HCl						
SO-E	OPT4 for HCl					
SO-E X	DPT4 for HCl cc-pV X Z	$\operatorname{cc-pV} \mathbf{X} Z(\operatorname{unc})$	cc-p $CVXZ$	cc -p $CV\mathbf{X}Z(unc)$		
SO-E X T	DPT4 for HCl cc-pV X Z 3.86488E-05	cc-pV X Z(unc) -6.58307E-04	cc-pCV X Z -5.04987E-04	cc-pCV X Z(unc) -6.58348E-04		
$\frac{\begin{array}{c} \text{SO-E} \\ \mathbf{X} \end{array}}{\begin{array}{c} T \\ Q \end{array}}$	DPT4 for HCl cc-pV X Z 3.86488E-05 5.18253E-05	cc-pV X Z(unc) -6.58307E-04 -6.77950E-04	cc-pCV X Z -5.04987E-04 -5.98344E-04	cc-pCV X Z(unc) -6.58348E-04 -6.77975E-04		
SO-E X T Q 5	DPT4 for HCl cc-pV X Z 3.86488E-05 5.18253E-05 -6.06518E-04	cc-pV X Z(unc) -6.58307E-04 -6.77950E-04 -6.81965E-04	cc-pCV X Z -5.04987E-04 -5.98344E-04 -6.60495E-04	cc-pCV X Z(unc) -6.58348E-04 -6.77975E-04 -6.81972E-04		
SO-E X T Q 5 SO-E	DPT4 for HCl cc-pV X Z 3.86488E-05 5.18253E-05 -6.06518E-04 DPT4 for HBr	cc-pV X Z(unc) -6.58307E-04 -6.77950E-04 -6.81965E-04	cc-pCV X Z -5.04987E-04 -5.98344E-04 -6.60495E-04	cc-pCV X Z(unc) -6.58348E-04 -6.77975E-04 -6.81972E-04		
SO-E X T Q 5 SO-E X	DPT4 for HCl cc-pV X Z 3.86488E-05 5.18253E-05 -6.06518E-04 DPT4 for HBr cc-pV X Z	cc-pV X Z(unc) -6.58307E-04 -6.77950E-04 -6.81965E-04 cc-pV X Z(unc)	cc-pCV X Z -5.04987E-04 -5.98344E-04 -6.60495E-04 cc-pCV X Z	cc-pCV X Z(unc) -6.58348E-04 -6.77975E-04 -6.81972E-04 cc-pCV X Z(unc)		
SO-I X T Q 5 SO-I X T	DPT4 for HCl cc-pV X Z 3.86488E-05 5.18253E-05 -6.06518E-04 DPT4 for HBr cc-pV X Z 2.95111E-02	cc-pVXZ(unc) -6.58307E-04 -6.77950E-04 -6.81965E-04 cc-pVXZ(unc) -7.77068E-02	cc-pCVXZ -5.04987E-04 -5.98344E-04 -6.60495E-04 cc-pCVXZ -1.65122E-02	cc-pCVXZ(unc) -6.58348E-04 -6.77975E-04 -6.81972E-04 cc-pCVXZ(unc) -7.77067E-02		
SO-I X T Q 5 SO-I X T Q	DPT4 for HCl cc-pV X Z 3.86488E-05 5.18253E-05 -6.06518E-04 DPT4 for HBr cc-pV X Z 2.95111E-02 2.87774E-02	cc-pVXZ(unc) -6.58307E-04 -6.77950E-04 -6.81965E-04 cc-pVXZ(unc) -7.77068E-02 -7.85726E-02	cc-pCV X Z -5.04987E-04 -5.98344E-04 -6.60495E-04 cc-pCV X Z -1.65122E-02 -5.49387E-02	cc-pCVXZ(unc) -6.58348E-04 -6.77975E-04 -6.81972E-04 cc-pCVXZ(unc) -7.77067E-02 -7.85725E-02		

References

- T. Helgaker, P. Jørgensen, and J. Olsen, Molecular Electronic Structure Theory, Wiley, New York, 2002.
- [2] C. Puzzarini, J. F. Stanton, and J. Gauss, Int. Rev. Phys. Chem. 29, 273 (2010).
- [3] W. Koch and M. C. Holthausen, A Chemist's Guide to Density Functional Theory, Wiley-VCH Verlag, Weinheim, second edition, 2001.
- [4] R. G. Parr and W. Yang, Density-Functional Theory of Atoms and Molecules, Science Publications, Oxford, 1994.
- [5] R. M. Martin, *Electronic Structure : Basic Theory and Practical Methods*, Cambridge University Press, Cambridge, UK; New York, 2004.
- [6] W. Thiel, in Modern Methods and Algorithms of Quantum Chemistry, edited by J. Grotendorst, volume 1, p. 233, Neumann Institute for Computing, second edition, 2000.
- [7] C. Møller and M. S. Plesset, *Phys. Rev.* 46, 618 (1934).
- [8] D. Cremer, Wiley Interdisciplinary Reviews: Computational Molecular Science 1, 509 (2011).
- [9] J. Čížek, J. Chem. Phys. 45, 4256 (1966).
- [10] J. Čížek, Adv. Chem. Phys. 14, 35 (1969).
- [11] J. Cížek and J. Paldus, Int. J. Quantum Chem. 5, 359 (1971).
- [12] R. J. Bartlett, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony, p. 1047, World Scientific, Singapore, 1995.
- [13] J. Gauss, in *Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollmann, H. F. Schaefer III, and P. R. Schreiner, p. 615, Wiley, New York, 1998.

- [14] I. Shavitt and R. J. Bartlett, Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory, Cambridge University Press, Cambridge, 2009.
- [15] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. 76, 1910 (1982).
- [16] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* 157, 479 (1989).
- [17] K. G. Dyall and K. Fægri Jr., *Relativistic Quantum Chemistry*, Oxford University Press, New York, 2007, part III.
- [18] P. Strange, *Relativistic Quantum Mechanics*, Cambridge University Press, New York, 1998.
- [19] P. Pyykkö and J. P. Desclaux, Acc. Chem. Res. 12, 276 (1979).
- [20] P. Pyykkö, *Chem. Rev.* 88, 563 (1988).
- [21] A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton, J. Chem. Phys. 121, 11599 (2004).
- [22] I. P. Grant and H. M. Quiney, in *Relativistic Electronic Structure Theory. Part I. Fundamentals*, edited by P. Schwerdtfeger, p. 107, Elsevier, Amsterdam, 2002, chapter 3.
- [23] L. Visscher, in *Relativistic Electronic Structure Theory. Part I. Fundamentals*, edited by P. Schwerdtfeger, p. 291, Elsevier, Amsterdam, 2002, chapter 6.
- [24] T. Saue, K. Fægri, T. Helgaker, and O. Gropen, Mol. Phys. 91, 937 (1997).
- [25] T. Saue and H. J. Aa. Jensen, J. Chem. Phys. 111, 6211 (1999).
- [26] T. Yanai, T. Nakajima, Y. Ishikawa, and K. Hirao, J. Chem. Phys. 114, 6526 (2001).
- [27] W. Liu, G. Hong, D. Dai, L. Li, and M. Dolg, Theor. Chim. Acta 96, 75 (1997).
- [28] T. Yanai, H. Iikura, T. Nakajima, Y. Ishikawa, and K. Hirao, J. Chem. Phys. 115, 8267 (2001).
- [29] H. M. Quiney and P. Belanzoni, J. Chem. Phys. 117, 5550 (2002).

- [30] J. K. Laerdahl, T. Saue, and K. Fægri, *Theor. Chem. Acc.* 97, 117 (1997).
- [31] M. Abe, T. Yanai, T. Nakajima, and K. Hirao, *Chem. Phys. Lett.* **388**, 68 (2004).
- [32] L. Visscher, O. Visser, P. J. C. Aerts, H. Merenga, and W. C. Nieuwport, *Comp. Phys. Comm.* 81, 120 (1994).
- [33] T. Fleig, J. Olsen, and L. Visscher, J. Chem. Phys. 119, 2963 (2003).
- [34] T. Fleig, H. J. Aa. Jensen, J. Olsen, and L. Visscher, J. Chem. Phys. 124, 104106 (2006).
- [35] J. Thyssen, T. Fleig, and H. J. Aa. Jensen, J. Chem. Phys. **129**, 034109 (2008).
- [36] S. Knecht, H. J. Aa. Jensen, and T. Fleig, J. Chem. Phys. 132, 014108 (2010).
- [37] L. Visscher, K. G. Dyall, and T. J. Lee, Int. J. Quantum Chem., Symp. 29, 411 (1995).
- [38] L. Visscher, T. J. Lee, and K. G. Dyall, J. Chem. Phys. 105, 8769 (1996).
- [39] T. Fleig, L. K. Sørensen, and J. Olsen, *Theor. Chim. Acta* **118**, 347 (2007).
- [40] H. S. Nataraj, M. Kállay, and L. Visscher, J. Chem. Phys. 133, 234109 (2010).
- [41] L. Cheng and J. Gauss, J. Chem. Phys. 134, 244112 (2011).
- [42] A. Wolf, M. Reiher, and B. A. Hess, in *Relativistic Electronic Structure Theory. Part I. Fundamentals*, edited by P. Schwerdtfeger, p. 622, Elsevier, Amsterdam, 2002, chapter 11.
- [43] B. A. Hess, *Phys. Rev. A* **33**, 3742 (1986).
- [44] C. Chang, M. Pelissier, and P. Durand, *Phys. Scr.* **34**, 394 (1986).
- [45] J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundqvist, and A.-M. Mårtensson-Pendrill, J. Phys. B 19, 2799 (1986).
- [46] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. 99, 4597 (1993).
- [47] R. van Leeuwen, E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. 101, 1272 (1994).

- [48] E. van Lenthe, R. van Leeuwen, E. J. Baerends, and J. G. Snijders, Int. J. Quantum Chem. 57, 281 (1996).
- [49] K. Dyall, J. Chem. Phys. 106, 9618 (1997).
- [50] W. Liu and D. Peng, J. Chem. Phys. **125**, 044102 (2006).
- [51] M. Iliaš and T. Saue, J. Chem. Phys. **126**, 064102 (2007).
- [52] D. Peng, W. Liu, Y. Xiao, and L. Cheng, J. Chem. Phys. 127, 104106 (2007).
- [53] J. Sikkema, L. Visscher, T. Saue, and M. Iliaš, J. Chem. Phys. 131, 124116 (2009).
- [54] W. Liu and D. Peng, J. Chem. Phys. 131, 031104 (2009).
- [55] W. Liu, Mol. Phys. 108, 1697 (2010).
- [56] T. Saue, Chem. Phys. Chem. 12, 3077 (2011).
- [57] W. Kutzelnigg, Chem. Phys. **395**, 16 (2012).
- [58] L. Visscher and E. van Lenthe, *Chem. Phys. Lett.* **306**, 357 (1999).
- [59] B. A. Hess, R. J. Buenker, and P. Chandra, Int. J. Quantum Chem. 29, 737 (1986).
- [60] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. 101, 9783 (1994).
- [61] W. Kutzelnigg and W. Liu, J. Chem. Phys. 123, 241102 (2005).
- [62] K. G. Dyall and K. Fægri Jr., *Relativistic Quantum Chemistry*, chapter 17, Oxford University Press, New York, 2007, part III.
- [63] W. Kutzelnigg, in *Relativistic Electronic Structure Theory. Part I. Fundamentals*, edited by P. Schwerdtfeger, p. 664, Elsevier, Amsterdam, 2002, chapter 12.
- [64] A. Rutkowski, J. Phys. B 19, 149 (1986).
- [65] A. Rutkowski, J. Phys. B 19, 3431 (1986).
- [66] A. Rutkowski, J. Phys. B 19, 3443 (1986).
- [67] A. Rutkowski, *Phys. Rev. A* 53, 145 (1996).
- [68] W. Kutzelnigg, Z. Phys. D 11, 15 (1989).

- [69] W. Kutzelnigg, Z. Phys. D 15, 27 (1990).
- [70] W. Kutzelnigg, E. Ottschofski, and R. Franke, J. Chem. Phys. 102, 1740 (1995).
- [71] W. Kutzelnigg, *Phys. Rev. A* 54, 1183 (1996).
- [72] J. M. Lévy-Leblond, Commun. math. Phys. 6, 286 (1967).
- [73] E. Ottschofski and W. Kutzelnigg, J. Chem. Phys. 102, 1752 (1995).
- [74] W. Kutzelnigg and W. Liu, *Chem. Phys.* **349**, 133 (2008).
- [75] W. Klopper, J. Comp. Chem. 18, 20 (1997).
- [76] R. Franke, Chem. Phys. Lett. 264, 495 (1997).
- [77] T. Helgaker, in *The Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner, p. 1157, John Wiley & Sons, Chichester, 1998.
- [78] J. F. Stanton and J. Gauss, Int. Rev. Phys. Chem. 19, 61 (2000).
- [79] J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quant. Chem. Symp. 13, 225 (1979).
- [80] Coupled Cluster techniques for Computational Chemistry, a quantum-chemical program package by J. F. Stanton, J. Gauss, M. E. Harding, and P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts, and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.
- [81] M. Born and J. R. Oppenheimer, Ann. Phys. **389**, 457 (1927).
- [82] R. E. Stanton and S. Havriliak, J. Chem. Phys. 81, 1910 (1984).

- [83] J. Sucher, Int. J. Quant. Chem. 25, 3 (1981).
- [84] J. Sucher, *Phys. Rev.* **22**, 348 (1980).
- [85] J. Noga and R. J. Bartlett, J. Chem. Phys. 86, 7041 (1987).
- [86] J. Noga and R. J. Bartlett, J. Chem. Phys. 89, 3401 (1988).
- [87] G. E. Scuseria and H. F. Schaefer III, Chem. Phys. Lett. 152, 382 (1988).
- [88] N. Oliphant and L. Adamowicz, J. Chem. Phys. 95, 6645 (1991).
- [89] S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. 97, 4282 (1992).
- [90] J. Gauss, W. J. Lauderdale, J. F. Stanton, J. D. Watts, and R. J. Bartlett, *Chem. Phys. Lett.* 182, 207 (1991).
- [91] J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. 98, 8718 (1993).
- [92] T. Helgaker, P. Jørgensen, and N. C. Handy, Theor. Chim. Acta 76, 227 (1989).
- [93] T. Helgaker and P. Jørgensen, Theor. Chim. Acta 75, 111 (1989).
- [94] P. Jørgensen and T. Helgaker, J. Chem. Phys. 89, 1560 (1988).
- [95] J. Gerrat and I. M. Mills, J. Chem. Phys. 49, 1719 (1968).
- [96] J. Gauss and J. F. Stanton, Chem. Phys. Lett. 276, 70 (1997).
- [97] R. Pitzer and W. Lipscomb, J. Chem. Phys. 38, 550 (1963).
- [98] P. Pulay, Mol. Phys. 17, 197 (1969).
- [99] S. Stopkowicz and J. Gauss, J. Chem. Phys. 134, 064114 (2011).
- [100] W. Schwalbach, S. Stopkowicz, L. Cheng, and J. Gauss, J. Chem. Phys. 135, 194114 (2011).
- [101] J. Gauss, in Modern Methods and Algorithms of Quantum Chemistry, edited by J. Grotendorst, volume 3, p. 541, Neumann Institute for Computing, second edition, 2000.
- [102] S. Stopkowicz and J. Gauss, J. Chem. Phys. 129, 164119 (2008).

- [103] K. G. Dyall, J. Chem. Phys. 100, 2118 (1994).
- [104] S. Obara and A. Saika, J. Chem. Phys. 84, 3963 (1986).
- [105] S. Obara and A. Saika, J. Chem. Phys. 89, 1540 (1988).
- [106] M. Dupuis, J. Rys, and H. F. King, J. Chem. Phys. 65, 111 (1976).
- [107] L. E. McMurchie and E. R. Davidson, J. Comp. Phys. 26, 218 (1978).
- [108] S. Boys, Proc. Roy. Soc. Lond. Ser. A 200, 542 (1950).
- [109] C. Berger, Störungstheoretische Behandlung relativistischer Korrekturen zu Gleichgewichtsstrukturen im Rahmen der Coupled-Cluster-Theorie, Ph. D. Thesis, Johannes Gutenberg-Universität Mainz, Germany, 2008.
- [110] S. Stopkowicz, Quantenchemische Berechnung relativistischer Korrekturen zu elektrischen Eigenschaften, Diploma Thesis, Johannes Gutenberg-Universität Mainz, Germany, 2008.
- [111] L. C. Evans, Partial Differential Equations, American Mathematical Society, Providence, 1998.
- [112] DALTON, a molecular electronic structure program, Release 2.0 (2005), see http://www.kjemi.uio.no/software/dalton/dalton.html .
- [113] L. Visscher and T. Saue, J. Chem. Phys. 113, 3996 (2000).
- [114] F. Neese, A. Wolf, T. Fleig, M. Reiher, and B. A. Hess, J. Chem. Phys. 122, 204107 (2005).
- [115] C. M. Reeves, J. Chem. Phys. **39**, 1 (1963).
- [116] C. M. Reeves and M. C. Harrison, J. Chem. Phys. **39**, 11 (1963).
- [117] R. C. Raffenetti, J. Chem. Phys. 59, 5936 (1973).
- [118] R. D. Bardo and K. Ruedenberg, **59**, 5956 (1973).
- [119] M. W. Schmidt and K. Ruedenberg, J. Chem. Phys. 71, 3951 (1979).
- [120] T. H. Dunning Jr., J. Chem. Phys. 90, 1007 (1989).

- [121] D. E. Woon and T. H. Dunning Jr., J. Chem. Phys. 98, 1358 (1993).
- [122] A. K. Wilson, D. E. Woon, K. A. Peterson, and T. H. Dunning Jr., J. Chem. Phys. 110, 7667 (1999).
- [123] D. E. Woon and T. H. Dunning Jr., J. Chem. Phys. 103, 4572 (1995).
- [124] K. A. Peterson and T. H. Dunning Jr., J. Chem. Phys. 117, 10548 (2002).
- [125] N. J. DeYonker, K. A. Peterson, and A. K. Wilson, J. Phys. Chem. A 111, 11383 (2007).
- [126] Dirac, a relativistic ab initio electronic structure program, Release DIRAC04.0 (2004), written by H. J. Aa. Jensen, T. Saue, and L. Visscher with contributions from V. Bakken, E. Eliav, T. Enevoldsen, T. Fleig, O. Fossgaard, T. Helgaker, J. Laerdahl, C. V. Larsen, P. Norman, J. Olsen, M. Pernpointner, J. K. Pedersen, K. Ruud, P. Salek, J. N. P. van Stralen, J. Thyssen, O. Visser, and T. Winther, see http://dirac.chem.sdu.dk.
- [127] K. G. Dyall, Theor. Chem. Acc. 99, 366 (1998).
- [128] K. Fægri, Theor. Chem. Acc. 105, 252 (2001).
- [129] B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, and P.-O. Widmark, J. Phys. Chem. A 108, 2851 (2004).
- [130] L. Visscher and K. G. Dyall, Atom. Data Nucl. Data Tabl. 67, 207 (1997).
- [131] S. Stopkowicz and J. Gauss, J. Chem. Phys. 134, 204106 (2011).
- [132] J. S. Daniel, G. J. M. Velders, A. R. Douglass, P. M. D. Forster, D. A. Hauglustaine, I. S. A. Isaksen, L. J. M. Kuijpers, A. McCulloch, and T. J. Wallington, Halocarbon scenarios, ozone depletion potentials, and global warming potentials, in *Scientific Assessment of Ozone Depletion: 2006*, chapter 8, p. 572, Global Ozone Research and Monitoring Project - Report No. 50, World Meteorological Organization, Geneva, Switzerland, 2007.
- [133] C. T. Dewberry, Z. Kisiel, and S. A. Cooke, J. Mol. Spectrosc. 261, 82 (2010).
- [134] G. Cazzoli and L. Dore, J. Mol. Spectrosc. 143, 231 (1990).

- [135] S. Stopkowicz, M. E. Harding, C. Puzzarini, and J. Gauss, to be published.
- [136] J. N. P. van Stralen and L. Visscher, *Mol. Phys.* **101**, 2115 (2003).
- [137] P. Pyykkö, Mol. Phys. 106, 1965 (2008).
- [138] G. Cazzoli, C. Puzzarini, S. Stopkowicz, and J. Gauss, Mol. Phys. 106, 1181 (2008).
- [139] G. Cazzoli, L. Cludi, C. Puzzarini, P. Stoppa, A. P. Charmet, N. Tasinato, A. Baldacci, A. Baldan, S. Giorgianni, R. W. Larsen, S. Stopkowicz, and J. Gauss, J. Phys. Chem. A 115, 453 (2011).
- [140] C. Puzzarini, G. Cazzoli, J. C. López, J. L. Alonso, A. Baldacci, A. Baldan, S. Stopkowicz, L. Cheng, and J. Gauss, J. Chem. Phys. 134, 174312 (2011).
- [141] K. A. Peterson and B. J. Shepler, J. Phys. Chem. A 110, 13877 (2006).

List of publications

Publications resulting from the diploma thesis

- G. Cazzoli, C. Puzzarini, S. Stopkowicz, and J. Gauss. The Hyperfine Structure in the Rotational Spectra of Bromofluoromethane: Lamb-Dip Technique and Quantum-Chemical Calculations. *Mol. Phys.*, 106:1181–1192, 2008.
- S. Stopkowicz and J. Gauss. Relativistic Corrections to Electrical First-Order Properties using Direct Perturbation Theory. J. Chem. Phys., 129:164119/1–9, 2008.

Publications resulting from this work

- S. Stopkowicz and J. Gauss. Direct Perturbation Theory in Terms of Energy Derivatives: Fourth-Order Relativistic Corrections at the Hartree-Fock Level. J. Chem. Phys., 134:064114/1–15, 2011.
- G. Cazzoli, L. Cludi, C. Puzzarini, P. Stoppa, A. Pietropolli Charmet, N. Tasinato, A. Baldacci, A. Baldan, S. Giorgianni, R. W. Larsen, S. Stopkowicz, and J. Gauss. Microwave, High-Resolution Infrared, and Quantum-Chemical Investigations of CHBrF₂: Ground and v₄=1 States. J. Phys. Chem. A, 115:453–459, 2011.
- S. Stopkowicz and J. Gauss. Fourth-Order Relativistic Corrections to Electrical Properties Using Direct Perturbation Theory. J. Chem. Phys., 134:204106/1–9, 2011.
- C. Puzzarini, G. Cazzoli, J. C. López, J. L. Alonso, A. Baldacci, A. Baldan, S. Stopkowicz, L. Cheng, and J. Gauss. Spectroscopic Investigation of Fluoroiodomethane, CH₂FI: Fourier-Transform Microwave and Millimeter-/Submillimeter-Wave Spectroscopy and Quantum-Chemical Calculations. J. Chem. Phys., 134:174312/1–9, 2011.

 W. Schwalbach, S. Stopkowicz, L. Cheng, and J. Gauss. Direct Perturbation Theory in Terms of Energy Derivatives: Scalar-Relativistic Treatment up to Sixth Order. J. Chem. Phys., 135:194114/1–14, 2011.

Other publications

- G. Cazzoli, C. Puzzarini, S. Stopkowicz, and J. Gauss. Hyperfine Structure in the Rotational Spectra of trans-Formic Acid: Lamb-Dip Measurements and Quantum-Chemical Calculations. Astron. & Astrophys., 520:A64/1–6, 2010.
- G. Cazzoli, C. Puzzarini, S. Stopkowicz, and J. Gauss. The Rotational Spectrum of Bi-Deuterated trans-Formic Acid, DCOOD: Lamb-Dip Measurements, THz Spectroscopy and Quantum-Chemical Calculations. *Chem. Phys. Letters*, 502:42–47, 2011.
- G. Cazzoli, C. Puzzarini, S. Stopkowicz, and J. Gauss. Precise Laboratory Measurements for trans-DCOOH and trans-HCOOD for Astrophysical Observations. Astrophys. J. Suppl., 196:10/1–7, 2011.