Molecular Properties

Jürgen Gauss

published in

Modern Methods and Algorithms of Quantum Chemistry,
Proceedings, Second Edition, J. Grotendorst (Ed.),
John von Neumann Institute for Computing, Jülich,
NIC Series, Vol. 3, ISBN 3-00-005834-6, pp. 541-592, 2000.

MOLECULAR PROPERTIES

JÜRGEN GAUSS
Institut für Physikalische Chemie
Universität Mainz
55099 Mainz
Germany
E-mail: gauss@slater.chemie.uni-mainz.de

An introduction is given into the quantum chemical calculation of molecular properties with special emphasis on analytic derivative theory, magnetic properties, and frequency-dependent properties.

1 Introduction

In order to relate results from quantum chemical calculations to experiment, it is essential to compute quantities that are directly available from measurements. Clearly, energies and wavefunctions obtained from the solution of the (electronic) Schrödinger equation are not sufficient for this purpose, and it is necessary to compute further quantities that characterize the atomic or molecular system of interest. In particular, theoretical predictions of structure, spectroscopic quantities, as well as properties such as, for example, dipole moment, polarizability, etc. are important to establish the connection to experiment and to initiate a fruitful interplay between theory and experiment.

It is quite obvious that the routine and efficient computation of the various atomic and molecular properties requires techniques which go beyond the "simple" solution of the Schrödinger equation. Besides theoretical aspects, computational efficiency is – as always in quantum chemistry – the most important issue that needs to be addressed.

Considering a molecule in a given electronic state, quantities of interest are:

a) energy differences, i.e., reaction energies, atomization energies, dissociation energies, energy differences between various isomers or conformers, etc.

b) molecular properties specific for a given electronic state. Examples include the equilibrium structure, dipole moment, polarizability, vibrational frequencies, magnetazibility, NMR chemical shifts, etc.

c) properties that characterize transitions between different electronic states. Examples are here electronic excitation energies, one- and two-photon transition strengths, radiative life times, ionization potentials, electron affinities, etc.

Properties of type a involve energy information at *different* points on the Born-Oppenheimer potential energy surface. For a dissociation energy, for example, the energy of the molecule as well as the energies of the fragments are needed. Properties of type b require information for one electronic state at a *single* point on the potential surface, while properties of type c involve information for *different* electronic states.

The given classification of molecular properties is of computational relevance, as, for example, properties of type a just require energy calculations for different points on the potential energy surface and in this respect are rather straightforward to calculate. Computation of properties of type b and c, however, is more involved and requires techniques such as analytic derivative and/or response theory.

In this lecture, a thorough discussion of the quantum chemical calculations for properties of type b will be given. Special emphasis will be put on analytic derivative theory (section 2), problems inherent to the calculation of magnetic properties (section 3) as well as frequency-dependent properties (section 4).

2 Molecular properties as analytical derivatives

2.1 General discussion

Properties of type b describe the "response" of the molecular system to an external perturbation. Let us consider as an example a molecule in an external electrical field ε. If we treat the field as a weak perturbation, a Taylor expansion around the the "field-free" case is a good description and yields for the energy

$$E(\varepsilon) = E(\varepsilon = 0) + \left.\frac{dE}{d\varepsilon}\right|_{\varepsilon=0} \varepsilon + \frac{1}{2}\left.\frac{d^2E}{d\varepsilon^2}\right|_{\varepsilon=0} \varepsilon^2 + \dots \tag{1}$$

The first-order term in Eq. (1), i.e., the term *linear* in ε, involves the *first derivative* (gradient) of the energy with respect to ε, the second-order term, i.e., the term *quadratic* in ε, the corresponding *second derivative*, etc.

From Eq. (1), it is clear that derivatives of the energy play a key role in describing the response of a molecule to an external perturbation. However, to identify these derivatives with the molecular properties of interest, it is essential to consider also the physical aspect of the interaction with the external field. Doing that, it becomes clear that the first-order interaction with an external electric field involves the molecular dipole moment μ, the second-order interaction the molecular polarizability α, etc.[1] We can therefore make the following identifications

$$\begin{array}{llll} \text{dipole moment } (\mu) & \hat{=} & -\left.\frac{dE}{d\varepsilon}\right|_{\varepsilon=0} & \text{(first derivative)} \\ \text{polarizability } (\alpha) & \hat{=} & -\left.\frac{d^2E}{d\varepsilon^2}\right|_{\varepsilon=0} & \text{(second derivative)} \\ \text{first hyperpolarizability } (\beta) & \hat{=} & -\left.\frac{d^3E}{d\varepsilon^3}\right|_{\varepsilon=0} & \text{(third derivative)} \\ & & \dots & \end{array}$$

and thus already obtain *computational expressions* for these particular molecular properties: they can be determined as the corresponding derivatives of the energy with respect to the components of the external field.

One might ask why a property such as the dipole moment is not just calculated as a simple expectation value, as it should be possible according to the postulates of quantum mechanics[2]. Indeed, the Hellmann-Feynman theorem[3] states the identity of the derivative and expectation value expression for first-order properties:

$$\frac{dE}{dx} = \langle\Psi|\frac{\partial H}{\partial x}|\Psi\rangle \qquad \text{(Hellmann − Feynman Theorem)}. \tag{2}$$

However, it should be noted that the Hellmann-Feynman theorem does not necessarily hold for approximate wavefunctions[a] with which we are generally dealing in quantum chemistry. In such cases, it has been shown that derivative expressions are usually the preferred choice [4].

The derivative ansatz can be generalized to other properties and in this way allows computation of a large variety of atomic and molecular properties. Table 1 gives an overview. The list includes the electrical properties which have been already discussed. Most important for chemical applications, however, are probably properties that are connected to geometrical derivatives. First derivatives with respect to nuclear displacements define the forces on nuclei which are essential for the location of stationary points on the Born-Oppenheimer potential surface and, thus, for the determination of equilibrium and transition state structures[5]. Second derivatives with respect to nuclear coordinates allow a characterization of the stationary points as minima, transition states, etc., but in addition enable a qualitative characterization of vibrational spectra within the harmonic-oscillator approximation. More quantitative treatments of vibrational spectra are possible via higher derivatives (cubic and quartic force constants; see, for example, the discussion given in Ref. 6).

Another important class are magnetic properties. For chemists, certainly NMR chemical shifts and the corresponding spin-spin coupling constants are of greatest interest. However, theory also allows calculation of magnetazibilities, spin-rotation constants, rotational g-tensors (see the book by W.H. Flygare[7] for a detailed account on these properties) as well as parameters that can be obtained from ESR spectroscopy (see the book by W. Weltner[8] for an introduction). A few examples of quantum chemical property calculations will be given later.

2.2 Numerical versus analytical differentiation

In principle, derivatives of the energy can be computed in a rather straightforward manner using finite-differentiation techniques, e.g., the gradient can be obtained via

$$\frac{dE}{dx} \approx \frac{E(\Delta x) - E(-\Delta x)}{2\Delta x} \tag{3}$$

with Δx as an appropriate chosen step size. The main advantage of such a *numerical differentiation* scheme is that it just requires the calculation of energies (though in the presence of the perturbation) and, thus, is rather easily implemented. As a consequence, finite-differentiation techniques have been and are still often used for the calculation of electric properties (so-called “finite-field” calculations). The disadvantages of the numerical differentiation scheme, however, are

a) the limited accuracy (a problem in particular for the computation of higher derivatives),

b) the high computational cost, as numerical differentiation requires for each derivative two additional energy calculations.

---

[a] It should be noted that the Hellmann-Feynman theorem also holds for a few special cases such as, for example, Hartree-Fock theory in the complete basis set limit.

Table 1. List of molecular properties which can be computed as derivatives of energies

Derivative	Observable
$\frac{dE}{d\varepsilon_i}$	dipole moment; in a similar manner also multipole moments, electric field gradients, etc.
$\frac{d^2E}{d\varepsilon_\alpha d\varepsilon_\beta}$	polarizability
$\frac{d^3E}{d\varepsilon_\alpha d\varepsilon_\beta d\varepsilon_\beta}$	(first) hyperpolarizability
$\frac{dE}{dx_i}$	forces on nuclei; stationary points on potential energy surfaces, equilibrium and transition state structures
$\frac{d^2E}{dx_i dx_j}$	harmonic force constants; harmonic vibrational frequencies
$\frac{d^3E}{dx_i dx_j dx_k}$	cubic force constants; vibrational corrections to distances and rotational constants
$\frac{d^4E}{dx_i dx_j dx_k dx_l}$	quartic force constants; anharmonic corrections to vibrational frequencies
$\frac{d^2E}{dx_i d\varepsilon_\alpha}$	dipole derivatives; infrared intensities within the harmonic approximation
$\frac{d^3E}{dx_i d\varepsilon_\alpha d\varepsilon_\beta}$	polarizability derivative; Raman intensities
$\frac{d^2E}{dB_\alpha dB_\beta}$	magnetazibility
$\frac{d^2E}{dm_{Kj} dB_\alpha}$	nuclear magnetic shielding tensor; relative NMR shifts
$\frac{d^2E}{dI_{Ki} dI_{Lj}}$	indirect spin-spin coupling constant
$\frac{d^2E}{dB_\alpha dJ_\beta}$	rotational g-tensor; rotational spectra in magnetic field
$\frac{d^2E}{dI_{Ki} dB_\alpha}$	nuclear spin-rotation tensor; fine structure in rotational spectra
$\frac{dE}{dm_{Kj}}$	spin density; hyperfine interaction constants
$\frac{d^2E}{dS_i dB_\alpha}$	electronic g-tensor

The latter issue is of particular concern if one is interested in the forces on the N nuclei of a molecule within a geometry optimization. The numerical evaluation of gradients requires in this case $2{*}3N$ the cost of the corresponding energy calculation. It is obvious that in this way routine determination of geometries is impossible for larger molecules (see section 2.7).

Further disadvantages of the numerical differentiation scheme are

a) that there is no straightforward extension to the computation of frequency-dependent properties (see section 4) and

b) that handling of magnetic properties is less straightforward (see section 3), as the computation of the latter requires the capability of dealing with complex wavefunction parameters. This capability is in most cases not available.

The alternative to *numerical* differentiation is *analytic* differentiation. This means that first an analytic expression for the corresponding derivative is deduced and then implemented within a computer code for the actual computation of the corresponding property. As we will see later, the use of analytic derivative techniques solves the mentioned problems and, thus, is clearly the preferred choice for the computation of properties.

However, it should be noted that application of analytic derivative techniques is not as straightforward and often requires a complicated computer implementation. The latter often requires substantial programming efforts as well as theoretical work for the derivation of the appropriate derivative expressions. Nevertheless, as the implementation needs in principle to be carried out only once, this cannot be considered a major disadvantage. Analytic derivatives have been in the mean time implemented for most of the standard quantum chemical approaches. For some of the more advanced quantum chemical techniques, however, the task of programming analytic derivatives can become so demanding that the corresponding implementations are still missing[b]. In a similar way, lack of analytic schemes for the calculation of higher derivatives often necessitates the latter to be calculated within mixed analytic-numerical schemes in which lower analytic derivatives are numerically differentiated. A prominent example is here the computation of cubic and quartic force constants which often are obtained by numerical differentiation of analytically evaluated quadratic force constants[9].

2.3 Analytic derivatives: general discussion

We start our discussion of analytic derivatives with a description of the general structure of derivative theory. Naively, one would expect that suitable expressions for the derivatives of the energy can be obtained by simple differentiation of the energy expression with respect to the corresponding parameter(s). While this is in principle true, such an approach, however, does not necessarily lead to computationally efficient expressions. The main problem appears to be the implicit dependence of the energy on the perturbation through the wavefunction parameters.

For our general discussion, it is important to analyze first in which way energy and wavefunction depend on a given external perturbation. For both, we have an *explicit* dependence on the perturbation through either some set of fixed parameters

---

[b] Examples are here CCSDT and CCSDTQ

(e.g., the basis functions which are given at the beginning of a calculation) or the Hamiltonian and an *implicit* dependence through the wavefunction parameters which are determined by some set of equations. Examples for the latter are the molecular orbital (MO) coefficients, the configuration-interaction (CI) coefficients, as well as the coupled-cluster (CC) amplitudes. As long as we are not specifying these parameters further, we will denote them collectively by c.

The energy can be then written in the following convenient form

$$E = E(x, c(x)) \tag{4}$$

and the equations for the wavefunction parameters c in the form

$$g(x, c(x)) = 0 \tag{5}$$

with the function g indicating the structure of the equations for c. Note that Eqs. (4) and (5) are rather general and that various quantum chemical methods just differ in the definition of the set c as well as in the explicit expressions for E and g.

Differentiation of the general energy expression given in Eq. (4) then yields[c]

$$\frac{dE}{dx} = \left(\frac{\partial E}{\partial x}\right) + \left(\frac{\partial E}{\partial c}\right)\left(\frac{\partial c}{\partial x}\right). \tag{6}$$

The first term includes the *explicit* dependence on the perturbation through the Hamiltonian as well as the fixed set of parameters, i.e., the basis functions. This contribution is usually denoted as the *integral derivative* contribution and is easily handled (see section 2.6). The second term is more problematic, as it includes the derivatives of the coefficients c. Contrary to the first term, a straightforward computation is here not possible, as the derivatives $\partial c/\partial x$ are unknown. At a first sight, one might think that these derivatives need to be determined by solving additional equations obtained by differentiation of Eq. (5):

$$\frac{dg}{dx} = h(x, c, \frac{\partial c}{\partial x}) = 0. \tag{7}$$

However, as the determination of c via Eq. (5) usually is the computationally most expensive step of a quantum chemical calculation, solution of Eq. (7) for the perturbed c's would render the analytic scheme rather expensive. The cost would be similar to those of the numerical scheme.

For the following, it is necessary to distinguish between parameters c determined via the variation principle (variational parameters) and those not determined via the variation principle (non-variational parameters). Examples for the first type of parameters are the MO coefficients in Hartree-Fock (HF) theory or the CI coefficients in CI calculations, while CC amplitudes are examples for the second type.

For the variational coefficients, the following condition holds

$$\frac{dE}{dc} = \left(\frac{\partial E}{\partial c}\right) = 0 \tag{8}$$

---

[c] Note that all derivatives are taken here and in the following at the point $x = 0$.

as the variation principle requests minimization of the energy with respect to c. Thus, it is clear that in Eq. (6), i.e., the general expression for the energy gradient, the second term does not contribute and the whole expression simplifies to

$$\frac{dE}{dx} = \left(\frac{\partial E}{\partial x}\right). \tag{9}$$

There is no need to determine the perturbed coefficients $\partial c/\partial x$.

The situation is more complicated for the non-variational parameters, as here the corresponding derivatives $\partial E/\partial c$ do not vanish. Nevertheless, it is possible to eliminate the derivatives of c from the gradient expression. The most elegant way to demonstrate this uses an energy functional $\tilde{E}$ constructed from the energy expression (Eq. (4)) by augmenting it with the equations that determine c (Eq. (5)) multiplied by Lagrangian multipliers λ:

$$\tilde{E}(x, c(x), \lambda(x)) = E(x, c(x)) + \lambda(x) g(x, c(x)). \tag{10}$$

This functional provides the same energy as Eq. (4), as long as Eq. (5) is fulfilled. Furthermore, the energy functional can be made stationary with respect to λ and c by requesting that

$$\left(\frac{d\tilde{E}}{d\lambda}\right) = 0 \tag{11}$$

and

$$\left(\frac{d\tilde{E}}{dc}\right) = 0. \tag{12}$$

The first of the two equations is identical to Eq. (5) for the parameters c, while the second equation allows determination of the Lagrangian multipliers λ. Solution of this additional set is not needed for the determination of the energy but is required to make $\tilde{E}$ stationary with respect to λ.

With Eqs. (11) and (12), the derivative of $\tilde{E}$ with respect to x takes the following rather simple form

$$\frac{d\tilde{E}}{dx} = \left(\frac{\partial \tilde{E}}{\partial x}\right) \tag{13}$$

$$= \left(\frac{\partial E}{\partial x}\right) + \lambda \left(\frac{\partial g}{\partial x}\right) \tag{14}$$

and, as the value of $\tilde{E}$ is identical to E, Eq. (13) also represents the desired gradient expression for E. It can be thus concluded that like for the variational coefficients (see Eq. (9)) there is no need to compute derivatives for the non-variational coefficients c. However, unlike for the variational case, for each non-variational parameter c an additional, though perturbation-independent equation (Eq. (12)) needs to be solved.

Expressions for higher derivatives can be obtained by differentiating the gradient expressions (Eqs. (9) and (13), respectively) with respect to further perturbations.

Derivation of computationally efficient expressions might require some rearrangements, but there are rules which can simplify the derivation. These rules explicitly state that for the coefficients c the knowledge of the nth derivative is sufficient for the calculation of the $(2n+1)$th derivative of the energy ($2n+1$ rule) and for the Lagrangian multipliers λ knowledge of the nth derivative is sufficient to compute the $(2n+2)$th derivative of the energy ($2n+2$ rule). According to these two rules, none of the derivatives is required for the gradient (see discussion above). Knowledge of the derivatives of c suffices for second derivatives, while third derivatives require derivatives of c and for non-variational parameters also of λ. The derivatives of c and λ are determined by solving equations that are obtained by differentiating Eq. (11) and Eq. (12) with respect to the external perturbation, respectively. We illustrate the application of the two rules by some examples.

For the variational case, the expression for the second derivative of the energy takes the following form

$$\frac{d^2E}{dxdy} = \left(\frac{\partial^2 E}{\partial x \partial y}\right) + \left(\frac{\partial^2 E}{\partial x \partial c}\right)\frac{\partial c}{\partial y} + \left(\frac{\partial^2 E}{\partial y \partial c}\right)\frac{\partial c}{\partial x} + \left(\frac{\partial^2 E}{\partial c \partial c}\right)\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}. \tag{15}$$

The contribution due to $\partial^2 c/\partial x \partial y$ vanishes here, as the corresponding prefactor $\partial E/\partial c$ is zero due to Eq. (8).

For non-variational approaches, we obtain for the second derivative of the energy

$$\frac{d^2E}{dxdy} = \left(\frac{\partial^2 \tilde{E}}{\partial x \partial y}\right) + \left(\frac{\partial^2 \tilde{E}}{\partial x \partial c}\right)\frac{\partial c}{\partial y} + \left(\frac{\partial^2 \tilde{E}}{\partial y \partial c}\right)\frac{\partial c}{\partial x} + \left(\frac{\partial^2 \tilde{E}}{\partial c \partial c}\right)\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}. \tag{16}$$

The contributions due to $\partial^2 c/\partial x \partial y$ and $\partial^2 \lambda/\partial x \partial y$ vanish because of Eqs. (11) and (12), i.e., due to the stationarity of the functional $\tilde{E}$ with respect to c and λ. The contributions due to $\partial \lambda/\partial x$ and $\partial \lambda/\partial y$ vanish, because

$$\frac{d}{dx}\left(\frac{\partial \tilde{E}}{\partial \lambda}\right) = \frac{dg}{dx} = 0. \tag{17}$$

The prefactors for the terms involving the first derivatives of λ are just the derivatives of the left-hand side of Eq. (5). As Eq. (5) holds for all values of x and y, the corresponding total derivatives of $g(x, c)$ must vanish.

As another example, we give the expression for the third derivatives of the energy in the non-variational case.

$$
\begin{aligned}
\frac{d^3E}{dxdydz} = & \left(\frac{\partial^3\tilde{E}}{\partial x\partial y\partial z}\right) \\
& + \left(\frac{\partial^3\tilde{E}}{\partial x\partial y\partial c}\right)\frac{\partial c}{\partial z} + \left(\frac{\partial^3\tilde{E}}{\partial x\partial z\partial c}\right)\frac{\partial c}{\partial y} + \left(\frac{\partial^3\tilde{E}}{\partial y\partial z\partial c}\right)\frac{\partial c}{\partial x} \\
& + \left(\frac{\partial^3\tilde{E}}{\partial x\partial c\partial c}\right)\frac{\partial c}{\partial y}\frac{\partial c}{\partial z} + \left(\frac{\partial^3\tilde{E}}{\partial y\partial c\partial c}\right)\frac{\partial c}{\partial x}\frac{\partial c}{\partial z} + \left(\frac{\partial^3\tilde{E}}{\partial z\partial c\partial c}\right)\frac{\partial c}{\partial x}\frac{\partial c}{\partial y} \\
& + \left(\frac{\partial^3\tilde{E}}{\partial c\partial c\partial c}\right)\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}\frac{\partial c}{\partial z} \\
& + \left(\frac{\partial^3\tilde{E}}{\partial x\partial y\partial \lambda}\right)\frac{\partial \lambda}{\partial z} + \left(\frac{\partial^3\tilde{E}}{\partial x\partial z\partial \lambda}\right)\frac{\partial \lambda}{\partial y} + \left(\frac{\partial^3\tilde{E}}{\partial y\partial z\partial \lambda}\right)\frac{\partial \lambda}{\partial x} \\
& + \left(\frac{\partial^3\tilde{E}}{\partial x\partial c\partial \lambda}\right)\frac{\partial c}{\partial y}\frac{\partial \lambda}{\partial z} + \left(\frac{\partial^3\tilde{E}}{\partial y\partial c\partial \lambda}\right)\frac{\partial c}{\partial x}\frac{\partial \lambda}{\partial z} + \left(\frac{\partial^3\tilde{E}}{\partial z\partial c\partial \lambda}\right)\frac{\partial c}{\partial x}\frac{\partial \lambda}{\partial y} \\
& + \left(\frac{\partial^3\tilde{E}}{\partial x\partial c\partial \lambda}\right)\frac{\partial c}{\partial z}\frac{\partial \lambda}{\partial y} + \left(\frac{\partial^3\tilde{E}}{\partial y\partial c\partial \lambda}\right)\frac{\partial c}{\partial z}\frac{\partial \lambda}{\partial x} + \left(\frac{\partial^3\tilde{E}}{\partial z\partial c\partial \lambda}\right)\frac{\partial c}{\partial y}\frac{\partial \lambda}{\partial x} \\
& + \left(\frac{\partial^3\tilde{E}}{\partial c\partial c\partial \lambda}\right)\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}\frac{\partial \lambda}{\partial z} + \left(\frac{\partial^3\tilde{E}}{\partial c\partial c\partial \lambda}\right)\frac{\partial c}{\partial x}\frac{\partial \lambda}{\partial y}\frac{\partial c}{\partial z} + \left(\frac{\partial^3\tilde{E}}{\partial c\partial c\partial \lambda}\right)\frac{\partial \lambda}{\partial x}\frac{\partial c}{\partial y}\frac{\partial c}{\partial z}
\end{aligned}
\tag{18}
$$

Note that Eq. (18) contains no contribution due to higher derivatives of c and λ. Again it can be shown that the corresponding prefactors are identical to zero.

The general approach to analytic derivatives presented here has been first formulated by Helgaker and Jørgensen[10]. Though the corresponding computationally efficient equations can be also obtained in different ways, for example, by using the interchange theorem of perturbation theory[11], the *Lagrangian approach* to analytic derivatives appears to be the simplest as well as the most elegant way to derive computationally efficient expressions. This is also demonstrated in the next section where a few specific examples for analytic energy derivatives are given.

2.4 Analytic derivatives: Specific examples

As first example, we discuss first derivatives (gradients) for standard closed-shell Hartree-Fock self-consistent-field (HF-SCF) calculations. Within the atomic-orbital (AO) notation (Greek indices $\mu, \nu, ...$ are used here and in the following to denote AOs), the following energy expression is obtained for this case

$$
E = \sum_{\mu\nu} P_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} P_{\mu\nu} P_{\sigma\rho} (\langle\mu\sigma|\nu\rho\rangle - \frac{1}{2}\langle\mu\sigma|\rho\nu\rangle) \tag{19}
$$

with $P_{\mu\nu}$ as the closed-shell AO density matrix

$$P_{\mu\nu} = 2\sum_i c^*_{\mu i} c_{\nu i}, \tag{20}$$

$h_{\mu\nu}$ as the one-electron integrals, and $\langle\mu\sigma|\nu\rho\rangle$ as the two-electron integrals in Dirac notation. Indices $i, j, ...$ denote in Eq. (20) as well as in the following occupied molecular orbitals, while indices $a, b, ...$ are reserved for virtual orbitals and indices $p, q, ...$ are used for generic orbitals that are either occupied or unoccupied.

The variational wavefunction parameters are the MO coefficients $c_{\mu i}$. As the orthonormality of the MOs needs to be considered as additional constraint, it is most convenient to start with the following energy functional

$$\begin{aligned}\tilde{E} = &\sum_{\mu\nu} P_{\mu\nu} h_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\rho\sigma} P_{\mu\nu} P_{\sigma\rho}(\langle\mu\sigma|\nu\rho\rangle - \frac{1}{2}\langle\mu\sigma|\rho\nu\rangle)\\ &-2\sum_{ij}\varepsilon_{ij}(\sum_{\mu\nu} c^*_{\mu i} S_{\mu\nu} c_{\nu j} - \delta_{ij})\end{aligned} \tag{21}$$

instead of Eq. (19). The Lagrangian multipliers ε_{ij} can be shown to form a Hermitian matrix. It can be furthermore demonstrated that this matrix can be chosen diagonal which leads to the usual case of canonical HF orbitals (see, for example, Ref. 12). The diagonal element $\varepsilon_i \equiv \varepsilon_{ii}$ can be interpreted as orbital energies (Koopmans' theorem).

Based on the discussion in the previous section, the following gradient expression can be derived[13]

$$\begin{aligned}\frac{dE}{dx} = &\sum_{\mu\nu} P_{\mu\nu}\frac{\partial h_{\mu\nu}}{\partial x} + \frac{1}{2}\sum_{\mu\nu\sigma\rho} P_{\mu\nu} P_{\sigma\rho}(\frac{\partial\langle\mu\sigma|\nu\rho\rangle}{\partial x} - \frac{1}{2}\frac{\partial\langle\mu\sigma|\rho\nu\rangle}{\partial x})\\ &-\sum_{\mu\nu} W_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial x}\end{aligned} \tag{22}$$

with the energy-weighted density matrix defined by

$$W_{\mu\nu} = 2\sum_i c^*_{\mu i}\varepsilon_i c_{\nu i}. \tag{23}$$

From Eq. (22), it is clear that evaluation of HF-SCF gradients consists of a series of contractions of density matrices with the corresponding integral derivatives. For perturbations of the one-electron type, the expression in Eq. (22) takes a particularly simple form, as only the first term needs to be considered:

$$\frac{dE}{dx} = \sum_{\mu\nu} P_{\mu\nu}\frac{\partial h_{\mu\nu}}{\partial x} \quad (\mathrm{one-electron\ perturbation}). \tag{24}$$

For geometrical derivatives, however, the two-electron contribution needs to be considered due to the perturbation dependence of the basis functions. The latter are usually centered at the nuclear positions and thus change with a displacement of the nuclear coordinates. Calculation of the integral derivatives is nowadays a routine task and efficient algorithms have been devised[14]. It should be also noted that calculation of HF-SCF gradients does not require storage of integral derivatives which would be a serious bottleneck.

For second derivatives of the energy, the following expression is obtained at the HF-SCF level[15,16]

$$\begin{aligned}\frac{d^2E}{dxdy} &= \sum_{\mu\nu} P_{\mu\nu}\frac{\partial^2 h_{\mu\nu}}{\partial x\partial y} + \frac{1}{2}\sum_{\mu\nu\sigma\rho} P_{\mu\nu}P_{\sigma\rho}(\frac{\partial^2\langle\mu\sigma|\nu\rho\rangle}{\partial x\partial y} - \frac{1}{2}\frac{\partial^2\langle\mu\sigma|\rho\nu\rangle}{\partial x\partial y}) \\ &\quad -\sum_{\mu\nu} W_{\mu\nu}\frac{\partial^2 S_{\mu\nu}}{\partial x\partial y} + \sum_{\mu\nu}\frac{\partial P_{\mu\nu}}{\partial y}(\frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma\rho} P_{\sigma\rho}(\frac{\partial\langle\mu\sigma|\nu\rho\rangle}{\partial x} - \frac{1}{2}\frac{\partial\langle\mu\sigma|\rho\nu\rangle}{\partial x})) \\ &\quad -\sum_{\mu\nu}\frac{\partial W_{\mu\nu}}{\partial y}\frac{\partial S_{\mu\nu}}{\partial x} \end{aligned} \tag{25}$$

with

$$\frac{\partial P_{\mu\nu}}{\partial x} = 2\sum_i\{\frac{\partial c^*_{\mu i}}{\partial x}c_{\nu i} + c^*_{\mu i}\frac{\partial c_{\nu i}}{\partial x}\} \tag{26}$$

$$\frac{\partial W_{\mu\nu}}{\partial x} = 2\sum_i\{\frac{\partial c^*_{\mu i}}{\partial x}\epsilon_i c_{\nu i} + c^*_{\mu i}\epsilon_i\frac{\partial c_{\nu i}}{\partial x}\} + \sum_{ij} c^*_{\mu i}\frac{\partial\epsilon_{ji}}{\partial x}c_{\nu j}. \tag{27}$$

As a consequence of the $(2n+1)$ rule, the expression given in Eq (25) contains only first derivatives of the MO coefficients. The latter are determined through equations that are obtained by differentiating the HF equations

$$\sum_\nu f_{\mu\nu}c_{\nu i} = \sum_\nu S_{\mu\nu}c_{\nu i}\epsilon_i \tag{28}$$

with $f_{\mu\nu}$ as the Fock matrix

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma\rho} P_{\sigma\rho}(\langle\mu\sigma|\nu\rho\rangle - \frac{1}{2}\langle\mu\sigma|\rho\nu\rangle) \tag{29}$$

or more conveniently by differentiating the equivalent condition

$$\sum_{\mu\nu} c^*_{\mu a}f_{\mu\nu}c_{\nu i} = 0 \tag{30}$$

which is also known as Brillouin's theorem. It is common to parametrize for this purpose the MO coefficient derivatives in the following way

$$\frac{\partial c_{\mu i}}{\partial x} = \sum_p c_{\mu p}U^x_{pi} \tag{31}$$

with the coupled-perturbed HF (CPHF) coefficients U^x_{pi} as the parameters to be determined. The CPHF equations[15,16] obtained from differentiating Eq. (28) or Eq. (30) take then (for real perturbations) the following form[d].

$$\sum_e\sum_m(4\langle ae|im\rangle - \langle ae|mi\rangle - \langle am|ei\rangle + \delta_{ae}\delta_{im}(\varepsilon_a - \varepsilon_i)) = B^x_{ai} \tag{32}$$

---

[d] Note that only the coefficients U^x_{ai} are determined through the CPHF equations, while the coefficients U^x_{ij} can be chosen in any way, as long as the differentiated orthonormality condition

$$U^x_{qp}{}^* + S^x_{pq} + U^x_{pq} = 0$$

with

$$B_{ai}^x = -\sum_{\mu\nu} c_{\mu a}^* c_{\nu i} \left(\frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma\rho} P_{\sigma\rho} \left(\frac{\partial \langle \mu\sigma|\nu\rho \rangle}{\partial x} - \frac{1}{2} \frac{\partial \langle \mu\sigma|\rho\nu \rangle}{\partial x} \right) \right) + \sum_{mn} S_{mn}^x (2\langle am|in \rangle - \langle am|ni \rangle) + S_{ai}^x \epsilon_i \tag{33}$$

with

$$S_{pq}^x = \sum_{\mu\nu} c_{\mu p}^x \frac{\partial S_{\mu\nu}}{\partial x} c_{\nu q}. \tag{34}$$

The CPHF equations are linear and can be solved using iterative algorithms[16].

As another example, first derivatives of the energy in coupled-cluster (CC) theory[17] are discussed. To simplify the discussion, we ignore the dependence of the CC energy on the molecular orbitals and consider only the CC amplitudes as wavefunction parameters. The general CC energy expression is then given by

$$E = \langle 0| \exp(-T) H \exp(T) |0\rangle \tag{35}$$

with T as the cluster operator and $|0\rangle$ denoting the reference determinant, usually provided by the HF wavefunction. The amplitudes in CC theory are determined through equations obtained by projecting the Schrödinger equation on the excitation manifold. Denoting with Φ_p the determinants within this excitation manifold, these equations, usually referred to as coupled-cluster equations, are given by

$$0 = \langle \Phi_p| \exp(-T) H \exp(T) |0\rangle. \tag{36}$$

For the derivatives of the CC gradient expression, we introduce the energy functional

$$\tilde{E} = \langle 0| \exp(-T) H \exp(T) |0\rangle + \sum_p \lambda_p \langle \Phi_p| \exp(-T) H \exp(T) |0\rangle \tag{37}$$

with λ_p as the appropriate Lagrangian multipliers. Eq. (37) is often written in the following short form

$$\tilde{E} = \langle 0|(1+\Lambda) \exp(-T) H \exp(T) |0\rangle \tag{38}$$

where we have introduced the de-excitation operator Λ by

$$\langle 0|\Lambda = \sum_p \lambda_p \langle \Phi_p|. \tag{39}$$

For the CC energy gradient, we then obtain in agreement with the $(2n+1)$ and $(2n+2)$ rules

$$\frac{dE}{dx} = \langle 0|(1+\Lambda) \exp(-T) \frac{\partial H}{\partial x} \exp(T) |0\rangle. \tag{40}$$

---

is fulfilled with the derivatives S_{pq}^x defined as in Eq. (34). The most common choice is

$$U_{ij}^x = -\frac{1}{2} S_{ij}^x.$$

Perturbed T and Λ thus are not required for the evaluation of CC gradients[18]. The λ amplitudes required in Eq. (40) are obtained as solutions to the following equations

$$0 = \langle 0|(1+\Lambda)[\exp(-T)H\exp(T) - E]|\Phi_p\rangle. \tag{41}$$

which are usually referred to as Λ equations.

The actual CC gradient expression is somewhat more involved due to the additional dependence of the CC energy on the MO coefficients. Though the MO coefficients are determined via the variational principle for the HF wavefunction, they are non-variational within CC theory. The reason is that the HF and not the CC energy is made stationary with respect to orbital rotations. Accordingly, the following energy functional represents a suitable starting point

$$\begin{aligned}\tilde{E} = \langle 0|(1+\Lambda)\exp(-T)H\exp(T)|0\rangle + \sum_a\sum_i Z_{ai}\sum_{\mu\nu} c^*_{\mu a} f_{\mu\nu} c_{\nu i} \\ + \sum_{pq} I_{pq}(\sum_{\mu\nu} c^*_{\mu p} S_{\mu\nu} c_{\nu q} - \delta_{pq}),\end{aligned} \tag{42}$$

where we augment the energy functional given in Eq. (37) by the HF condition (Eq. (30), Z_{ai} is the corresponding Lagrangian multiplier) and by the additional orthonormality constraint with I_{pq} as undetermined multiplier.

Differentiating this energy functional yields the complete gradient expression

$$\begin{aligned}\frac{d\tilde{E}}{dx} = \langle 0|(1+\Lambda)\exp(-T)\frac{\partial H}{\partial x}\exp(T)|0\rangle + \sum_a\sum_i Z_{ai}\sum_{\mu\nu} c^*_{\mu a}[\frac{\partial h_{\mu\nu}}{\partial x} \\ + \sum_{\sigma\rho} P_{\sigma\rho}(\frac{\partial\langle\mu\sigma|\nu\rho\rangle}{\partial x} - \frac{1}{2}\frac{\partial\langle\mu\sigma|\rho\nu\rangle}{\partial x})]c_{\nu i} + \sum_{pq} I_{pq}\sum_{\mu\nu} c^*_{\mu p}\frac{\partial S_{\mu\nu}}{\partial x}c_{\nu q},\end{aligned} \tag{43}$$

which is usually cast in the following general form[19,20]

$$\frac{dE}{dx} = \sum_{\mu\nu} D_{\mu\nu}\frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\mu\nu\sigma\rho}\Gamma_{\mu\nu\sigma\rho}\frac{\partial\langle\mu\nu|\sigma\rho\rangle}{\partial x} + \sum_{\mu\nu} I_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial x} \tag{44}$$

with $D_{\mu\nu}$ as an effective one-particle density matrix, $\Gamma_{\mu\nu\sigma\rho}$ as the two-particle density matrix and $I_{\mu\nu}$ as a generalized energy-weighted density matrix. The form given in Eq. (44) for the gradient is rather general and has turned out very convenient for actual computations. Differences between the various quantum chemical approaches just exist in the definition of the corresponding density matrices.

A comment is necessary concerning the additional Lagrangian multipliers introduced in Eq. (43). Z_{ai} leads to an *orbital relaxation* contribution to the one-particle density matrix. It actually is the quantity that has been first introduced by Handy and Schaefer as Z-vector[21]. I_{pq} turns out to be the MO representation of the energy-weighted density matrix $I_{\mu\nu}$ in Eq. (44). Explicit expressions for $D_{\mu\nu}, \Gamma_{\mu\nu\sigma\rho}$, and $I_{\mu\nu}$ for the various CC models have been given in the literature[22−29] and will not be repeated here.

Finally, some basic aspects of the calculation of CC second derivatives are discussed. To emphasize the important aspects, we solely focus on the CC amplitudes and ignore the MO coefficient contributions. A corresponding complete discussion can be found in the literature[30,31].

Differentiation of Eq. (37) with respect to x and y yields[31]

$$\begin{aligned}\frac{d^2E}{dxdy} &= \langle 0|(1+\Lambda)\exp(-T)\frac{\partial^2 H}{\partial x \partial y}\exp(T)|0\rangle \\ &+\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial x}\exp(T),\frac{dT}{dy}]|0\rangle + \\ &+\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial y}\exp(T),\frac{dT}{dx}]|0\rangle + \\ &+\langle 0|(1+\Lambda)[[\exp(-T)H\exp(T),\frac{dT}{dx}],\frac{dT}{dy}]|0\rangle. \end{aligned} \tag{45}$$

As stated by the $(2n+1)$ and $(2n+2)$ rules, the expression given in Eq. (45) contains only first derivatives of the cluster operator (and thus of the CC amplitudes) and no derivative contribution of the Λ operator. The required perturbed amplitudes are determined by solving the first-order CC equations obtained by differentiating the corresponding unperturbed equations given in Eq. (36) with respect to x or y:

$$\langle \Phi_p|\exp(-T)\frac{\partial H}{\partial x}\exp(T)|0\rangle + \langle \Phi_p|[\exp(-T)H\exp(T),\frac{\partial T}{\partial x}]|0\rangle = 0. \tag{46}$$

For some cases, it might be advantageous to rearrange Eq. (45) and to use instead the following expression[31]

$$\begin{aligned}\frac{d^2E}{dxdy} &= \langle 0|(1+\Lambda)\exp(-T)\frac{\partial^2 H}{\partial x \partial y}\exp(T)|0\rangle \\ &+\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial x}\exp(T),\frac{dT}{dy}]|0\rangle + \\ &+\langle 0|\frac{d\Lambda}{dy}\exp(-T)\frac{\partial H}{\partial x}\exp(T)|0\rangle. \end{aligned} \tag{47}$$

In Eq. (47), derivatives of the Lagrangian multipliers appear (at a first sight contrary to the $(2n+2)$ rule), but one should realize that derivative amplitudes in Eq. (47) are only needed for one of the two perturbations, namely y. If the two perturbations belong to different classes, this might be of advantage, as the total number of equations that need to be solved can be lower when using Eq. (47) instead of Eq. (45). The most prominent example is the computation of NMR shielding constants, where with the second, so-called *asymmetric* expression, only 6 perturbed equations for all components of the magnetic field need to be solved, while use of the *symmetric* expression (Eq. (45)) requires solution of a total of $(3N_{atoms}+3)$ equations.

This example shows that different expressions for a derivative are possible. It depends on the circumstances, in particular on the property of interest, which of the deduced expressions is preferred and computationally more efficient.[31]

2.5 Advantages of analytic derivatives

Analytic derivatives are the preferred choice (if available for a quantum chemical approach) for the following reasons:

a) first of all, analytic derivatives generally provide higher accuracy for the calculated derivatives, as they are not affected by rounding errors (too small step sizes in the numerical differentiation) or problems due to contamination by higher derivatives (too large step size in the numerical differentiation). This aspect is of particular importance for higher derivatives, but of lesser concern for first derivatives;

b) the cost of analytic gradients is independent of the number of perturbations. Considering expressions Eq. (22) or Eq. (44), it is clear that the perturbation dependence only appears through the integral derivative contribution. As can be shown, computation of integral derivatives can be carried out with cost independent of the number of perturbations. The same computational advantage is not necessarily as pronounced as for higher derivatives. For example, analytic computation of CC second derivatives scales with the number of perturbations[31]. The same dependence is seen for the calculation of second derivatives based on numerical differentiation of analytically evaluated gradients;

c) magnetic properties can be easily treated, as all quantities in the analytic approach are either purely imaginary or real and, thus, can be handled using real arithmetic. The only complication arises due to the fact that for magnetic properties some matrices are antisymmetric instead of symmetric.

d) extension to frequency-dependent properties is possible in the framework of response theory.

2.6 Availability of analytic derivatives

The use of analytic derivatives in quantum chemistry started in 1969 with the classic work of Pulay[13] on HF gradients[e]. As soon as their applicability and efficiency for geometry optimizations and force constant calculations[33] had been realized, a lot of effort was devoted to theory as well as implementation of analytic derivatives. Important contributions to analytic derivatives were made by many groups; noteworthy probably in particular those of the groups of Pople, Schaefer, Handy as well as Bartlett. Landmarks in the development of analytic derivative techniques have been the implementation of second derivatives at the HF level and MP2 gradients in 1979 by Pople *et al.*[16], the formulation and implementation of MP2 second derivatives by Handy and Bartlett *et al.*[34−36] in 1985, and the implementation of CCSD gradients by Schaefer *et al.*[22] in 1987.

A more general important contribution to derivative theory has been the introduction of the Z-vector method by Handy and Schaefer[21] which had a large impact on the theory of gradients for correlated quantum chemical approaches. Though computation of integral derivatives is nowadays considered a routine issue, it should not be forgotten that the availability of integral derivative packages has been an important prerequisite for all of the advances mentioned above.

---

[e] It might be of interest to note that papers on analytic derivatives (though within a one-center basis set expansion) have been published as early as 1958 by Bratoz[32].

Table 2. Implementation of analytic geometrical derivatives within standard quantum chemical approaches

First derivatives		Ref.
HF	Pulay (1969)	13
DFT	Ziegler *et al.* (1988), Salahub *et al.* (1989),	37,38
	Delley (1991)	39
MCSCF	Kato and Morokuma (1979),	40
	Goddard, Handy, Schaefer (1979)	41
MP2	Pople *et al.*(1979)	16
MP3	Bartlett *et al.* (1985)	42
MP4(SDQ)	Gauss and Cremer (1987)	43
MP4	Gauss and Cremer (1988),	44
	Bartlett *et al.* (1988)	45
CID, CISD	Schaefer *et al.*, Pople *et al.* (1980)	46,47
CPF	Rice, Lee, Handy (1980)	48
QCISD	Gauss and Cremer (1988)	49
QCISD(T)	Gauss and Cremer (1989)	50
CCSD	Schaefer *et al.* (1987)	22
CCSD(T)	Scuseria(1990), Lee and Rendell (1990)	26,27
CCSDT-n	Gauss and Stanton (2000)	29
MR-CI, MR-ACPF	Shepard *et al.* (1991)	51
Second derivatives		
HF	Pople *et al.* (1979)	16
DFT	Handy *et al.* (1993), Johnson, Frisch (1994)	52,53
MCSCF	Schaefer, Handy *et al.* (1984)	54
MP2	Handy *et al.* (1985), Bartlett *et al.* (1986)	34,35,36
MP3, MP4	Gauss and Stanton (1997)	31
CISD	Schaefer *et al.* (1983)	55
CCSD	Koch, Jørgensen, Schaefer *et al.* (1990)	56
CCSD(T)	Gauss and Stanton (1997)	31
CCSDT-n	Gauss and Stanton (2000)	29
Third derivatives		
HF	Schaefer *et al.* (1984)	57

Table 2 gives an overview about the available analytic derivative techniques within the *standard* quantum chemical approaches. The list of references given there, however, must remain incomplete, as it is impossible to mention all papers in the area of analytic derivatives. Often, initial implementations were followed up by extensions to open-shell systems or in case of correlated approaches to other type of reference functions. In addition, there have been many papers considering algorithmic advances. For example, a number of papers have been published reporting direct or semi-direct implementations of MP2 gradients[58−60], thus significantly extending the range of the applicability of MP2 gradients.

With the increasing popularity of density functional theory (DFT) in quantum chemistry, interest very soon focused on analytic DFT derivatives and implementation of first and second derivatives were reported[37−39,52,53]. While analytic derivatives are no more complicated for DFT than for HF-SCF, it should be noted that differentiation of the exchange-correlation contribution can pose some problems due to the usually employed numerical integration schemes[61].

2.7 Application of analytic derivatives: examples for geometrical derivatives

A few illustrative examples for the application of analytic (geometrical) derivatives will be given in the following. Fig. 1 shows a dimer of a hexabenzocoronene derivative (HBC-*t*Bu) which has been synthesized by Müllen *et al.*[62] The structure has been investigated by X-ray analysis[62] as well as by solid-state NMR spectroscopy in the group of Spiess[62]. These experimental studies have been supplemented by quantum chemical calculations[63]. We do not discuss the chemical aspects of these calculations rather focus on their computational aspects. The dimer of HBC-tBu consists of 264 atoms and the corresponding calculations using the 3-21G basis involved 1452 basis functions and 786 degrees of freedom in the geometry optimization.

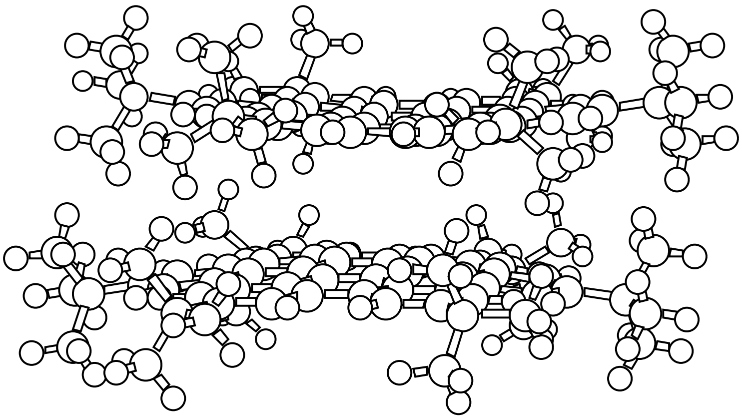


Fig. 1: Optimized structure of HBC-*t*Bu dimer

Using linear-scaling gradient techniques[64] the energy calculation (all calculations have been carried out in C_1 symmetry) required 4 hours and the corresponding gradient required 2.3 hours on a DEC PW 433au workstation. This clearly demonstrates that geometry optimizations for rather large systems are nowadays feasible. The important prerequisite is that the computational costs do not scale with the number of degrees of freedom.

As a second example, we discuss a quantum chemical study of the cubic and quartic force field of propadienylidene (C_3H_2) using analytic derivative techniques at the CC level[28,31]. Propadienylidene is the smallest stable cumulene carbene. It has been investigated using various spectroscopic techniques and attracted a lot of interest as *interstellar* molecule[65]. Computation of the cubic and quartic force

Table 3. Comparison of computed harmonic and fundamental frequencies for C_3H_2 with the experimental data from Ref. 66. All computational results have been obtained at the CCSD(T)/cc-pVTZ level.

	Harmonic Frequency (cm^{-1})	Infrared Intensity (km mol^{-1})	Fundamental Frequency (cm^{-1})	Experimental Fundamental (cm^{-1})
a_1 symmetry				
ν_1	3123	5	2997	3050–3060
ν_2	1998	250	1956	1952–1963
ν_3	1495	10	1458	1447–1449
ν_4	1119	2	1111	—
b_1 symmetry				
ν_5	217	3	211	—
b_2 symmetry				
ν_6	3212	0	3069	—
ν_7	1052	3	1034	—
ν_8	1020	19	996	999–1005
ν_9	275	114	287	—

fields were needed for a rigorous assignment of the matrix IR spectrum measured by Maier *et al.*[66] and for a theoretical determination of vibrational corrections to the rotational constants of C_3H_2. The latter are needed to deduce an equilibrium structure (r_e structure) for propadienylidene from the experimental vibrationally averaged rotational constants[67]. The calculation of the anharmonic force field was carried out by numerical differentiation of analytically evaluated force constants along the normal coordinates (for a detailed description, see Ref. 9). In this way, computation of anharmonic force fields is a rather *routine* matter, while the same cannot be stated for anharmonic force field calculations based on a numerical differentiation of energies. The computation of the semi-diagonal quartic force field at the CCSD(T)/cc-pVTZ level required about 45 days CPU time on a DEC PW 433au workstation. A single energy calculation requires less than half an hour, a gradient calculation about one hour and a complete second derivative calculations about 1.5 days.

The results from our calculations for C_3H_2 are summarized in Fig. 2 and Table 3. Fig. 2 compares the equilibrium geometry obtained from a least-squares fit to the experimental rotational constants corrected for vibrational effects (computed at the CCSD(T)/cc-pCVTZ level) with a structure determined at the CCSD(T)/cc-pCVQZ level (for further details, see Ref. 68). The agreement is excellent and differences amount to less than 0.001 Å. Table 3 compares the computed fundamental frequencies with those obtained in the matrix IR study[66]. Again the agreement is good, except that the calculation sheds some doubt on the assignment of the band at 3050-3060 cm^{-1} to the symmetric CH stretching mode. According to the calculations, an assigment of this band to the antisymmetric CH stretching mode seems to be more plausible.

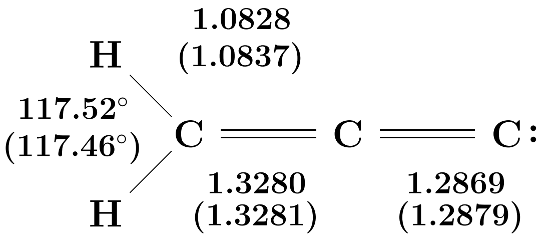


Fig. 2: Equilibrium structure (distances in Å, angles in degrees) of propadienylidene as obtained from an analysis of experimental rotational constants corrected with vibrational corrections obtained from a CCSD(T)/cc-pCVTZ anharmonic force field. Geometrical parameters obtained from a CCSD(T)/cc-pCVQZ optimization are given in parentheses.

3 Magnetic properties

Among the magnetic properties of a molecule, the parameters which characterize the NMR spectrum of a molecule are of particular interest to chemists. The quantum chemical calculation of NMR chemical shifts and also of indirect spin-spin coupling constants is of great importance, as the assignment of experimental NMR spectra is not straightforward. There is no simple relationship between chemical shifts and coupling constants on one hand and the structural parameters of interest on the other hand.

As the calculation of magnetic properties poses a few special problems, their computation is discussed in some detail in this section. Nevertheless, analytic derivative theory (as discussed in the previous sections) is the main prerequisite for the efficient computation of magnetic properties, as magnetazibilities are given as second derivatives of the energy with respect to the magnetic field, NMR chemical shifts as the corresponding mixed derivatives with respect to field and nuclear magnetic moments, and indirect spin-spin coupling constants as second derivative with respect to the corresponding nuclear spins (compare Table 1). In the following, the focus will be on the additional difficulties in the calculation of these properties. Our main focus is on NMR chemical shifts, but a few remarks are also given on the calculation of indirect spin-spin coupling constants.

3.1 Qualitative discussion

Before we discuss the actual computational aspects, it is appropriate to give a qualitative picture of the chemical shielding effect. Consider for this purpose a nucleus K with spin $\mathbf{I}_K$ in an external magnetic field $\mathbf{B}$. The spin is associated with a magnetic moment $\mathbf{m}_K$ according to

$$\mathbf{m}_K = \gamma_K \mathbf{I}_K \tag{48}$$

with γ_K as the gyromagnetic ratio. The magnetic moment $\mathbf{m}_K$ directly interacts with the external field leading to an energy correction of the form

$$\Delta E = -\mathbf{m}_K \cdot \mathbf{B}. \tag{49}$$

If this were the only contribution, NMR spectroscopy would not be able to distinguish between nuclei in different chemical environments.

The phenomenon of chemical shifts can only be understood if the electronic motion is explicitly considered. In particular, one has to take into account that the external magnetic field induces an electronic current[f] and that according to Biot-Savart's law[69] each current generates a magnetic field. As the induced field is proportional to the current and the current proportional to the external field, the induced magnetic field is in first order proportional to the external field. At the position of the nucleus K, the induced field can thus be written as

$$\mathbf{B}_{ind} = -\boldsymbol{\sigma}_K \mathbf{B} \tag{50}$$

with $\boldsymbol{\sigma}_K$ as the chemical shielding tensor. Note that $\boldsymbol{\sigma}_K$ is a tensor, as $\mathbf{B}_{ind}$ is not necessarily parallel or antiparallel to $\mathbf{B}$.

The total magnetic field at the nucleus K is given as the sum of external and internal field

$$\mathbf{B}_{local} = \mathbf{B} + \mathbf{B}_{ind} \tag{51}$$

and the energy correction and the splitting of the energy levels in the presence of an external magnetic field $\mathbf{B}$ is then

$$\Delta E = -\mathbf{m}_K \cdot \mathbf{B}_{local} \tag{52}$$

$$-\mathbf{m}_K(1 - \boldsymbol{\sigma}_K)\mathbf{B}. \tag{53}$$

The latter expression is identical to the shielding term in the effective Hamiltonian H_{NMR} often used in NMR spectroscopy[70]. The shielding term is supplemented in H_{NMR} by a second term which describes the coupling of the spins and thus is responsible for the multiplet structure in NMR spectra[70].

While the effective NMR Hamiltonian is often used to simulate spectra or to deduce the relevant NMR parameters from experimental spectra, the quantum chemical task is different. There, it is the goal to compute the relevant NMR parameters, i.e., the shielding tensors and the spin-spin coupling constants, for a given molecule without any further information.

To complete the introductory discussion, it should be noted that in most cases isotropic shieldings

$$\sigma_K = \frac{1}{3} Tr(\boldsymbol{\sigma}_K) \tag{54}$$

as well as relative shifts

$$\delta = \sigma_{ref} - \sigma_K \tag{55}$$

are reported. The relative shifts δ are given with respect to the shielding σ_{ref} of a reference compound (for example, TMS in case of ^{1}H and ^{13}C). Furthermore, as the chemical shielding is a rather small effect (which, however, can be very precisely measured), the dimensionless shielding constants are usually given in ppm.

---

[f] Note there is no electronic current in the field-free case.

3.2 Shieldings as second derivatives of the energy

Following the basic physical explanation of the chemical shielding effect, it is obvious that the shielding tensor is an electronic property that should be available through quantum chemical calculations. From Eq. (53), it is clear that the shielding tensor is a second-order response property with magnetic field and nuclear magnetic moment as the corresponding perturbations. Accordingly, the shielding tensor can be *computationally* obtained as the following second derivative of the electronic energy

$$\sigma_{ij}^{K} = \left(\frac{d^2 E}{dB_j dm_{Ki}} \right)_{\mathbf{B},\mathbf{m}_K=0} , \tag{56}$$

or in other words, the energy correction given in Eq. (53) can be considered as the corresponding *quadratic* term in a Taylor expansion of the molecular energy with respect to $\mathbf{B}$ and $\mathbf{m}_K$.

$$E(\mathbf{B}, \mathbf{m}_K) = E(0) + \sum_j \sum_i \left(\frac{d^2 E}{dB_j dm_{Ki}} \right)_{\mathbf{B},\mathbf{m}_K=0} B_j \; m_{Ki} + \dots \tag{57}$$

3.3 Molecular Hamiltonian in the presence of a magnetic field

For all property calculations, it is essential to specify first the corresponding perturbed Hamiltonian. While this is a rather straightforward task for most properties, some difficulties arise in case of the magnetic field.

In the presence of an external magnetic field, the momentum operator $\mathbf{p}$ in the electronic Hamiltonian[g]

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \tag{58}$$

needs to be replaced by its mechanical counterpart

$$\mathbf{p} \longrightarrow \boldsymbol{\pi} = \mathbf{p} + \frac{e}{c}\mathbf{A}(\mathbf{r}). \tag{59}$$

In Eq. (59), e denotes the elementary charge (the charge of the electron is $-e$), c the speed of light, and $\mathbf{A}$ the vector potential, which together with the scalar potential $\phi(\mathbf{r})$ represents the fundamental quantity for a theoretical description of electromagnetic field[71]. Note that the Gaussian unit system[72] is used throughout.

The magnetic field is uniquely determined via

$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} \tag{60}$$

from the vector potential $\mathbf{A}$. It is obvious from Eq. (60) that the vector potential suffices to specify the magnetic interactions in the Hamiltonian. Nevertheless, one should note that $\mathbf{B}$ and *not* the potential $\mathbf{A}$ is the observable quantity. We later return to this aspect.

---

[g] For the current discussion it is sufficient to consider a one-electron system, as generalization to many-electron systems is straightforward.

Carrying out the substitution given by Eq. (59), one obtains for the Hamiltonian of an electron in an external magnetic field

$$H = -\frac{(\mathbf{p} - \frac{e}{c}\mathbf{A})^2}{2m} + V(\mathbf{r}). \tag{61}$$

For our purpose, it is sufficient to consider static magnetic fields of the form

$$\mathbf{B} = \text{const} \tag{62}$$

which are adequately described by the vector potential

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}. \tag{63}$$

As the vector potential given in Eq. (63) satisfies the (Coulomb gauge) condition

$$\boldsymbol{\nabla} \cdot \mathbf{A} = 0, \tag{64}$$

we can rewrite the Hamiltonian in Eq. (61) as

$$H = \frac{\mathbf{p}^2}{2m} + \frac{e}{mc}\mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2mc^2}\mathbf{A}^2 + V(\mathbf{r}). \tag{65}$$

Note that $\mathbf{p}$ and not $\boldsymbol{\pi}$ is the canonical conjugate momentum to the position $\mathbf{r}$, so that the operator $\mathbf{p}$ is given by $-i\hbar\boldsymbol{\nabla}$ in the position representation.

Insertion of the explicit form of the vector potential (Eq. (63)) into Eq. (65) then yields for the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{ie\hbar}{2mc}\mathbf{B} \cdot (\mathbf{r} \times \boldsymbol{\nabla}) + \frac{e^2}{8mc^2}[(\mathbf{B} \cdot \mathbf{B})(\mathbf{r} \cdot \mathbf{r}) - (\mathbf{B} \cdot \mathbf{r})(\mathbf{B} \cdot \mathbf{r})] + V(\mathbf{r}) \tag{66}$$

and thus the following expression for the first and second derivative of the Hamiltonian with respect to B_i

$$\frac{\partial h}{\partial B_i} = -\frac{ie\hbar}{2mc}(\mathbf{r} \times \boldsymbol{\nabla})_i \tag{67}$$

$$\frac{\partial^2 h}{\partial B_i \partial B_j} = \frac{e^2}{4mc^2}[(\mathbf{r} \cdot \mathbf{r})\delta_{ij} - r_i r_j]. \tag{68}$$

Considering in addition the vector potential due to the magnetic moments

$$\mathbf{A}' = \frac{\mathbf{m}_K \times (\mathbf{r} - \mathbf{R}_K)}{|\mathbf{r} - \mathbf{R}_K|^3} \tag{69}$$

the corresponding derivative of H with respect to m_K is given by

$$\frac{\partial h}{\partial m_{Kj}} = -\frac{ie\hbar}{mc}\frac{[(\mathbf{r} - \mathbf{R}_K) \times \nabla]_j}{|\mathbf{r} - \mathbf{R}_K|^3} \tag{70}$$

and for the mixed derivative with respect to B_i and m_K the following expression is obtained

$$\frac{\partial^2 h}{\partial B_i \partial m_{Kj}} = \frac{e^2}{2mc^2}\frac{\mathbf{r} \cdot (\mathbf{r} - \mathbf{R}_K)\delta_{ij} - r_j(\mathbf{r} - \mathbf{R}_K)_i}{|\mathbf{r} - \mathbf{R}_K|^3}. \tag{71}$$

From Eqs. (67) and (70), it is clear that the matrix elements of $\partial h/\partial B_i$ and $\partial h/\partial m_N$ are imaginary if the usual real basis functions are employed. This explains why a finite-field calculation of magnetic properties requires the capability of dealing with complex wavefunction parameters. On the other hand, in case of an analytic calculation all matrix elements are evaluated in the *zero-field limit* and thus are either real or purely imaginary. Real arithmetic is then sufficient, as i can be factored out from all imaginary quantities. The only difficulty arises due to the fact that matrices which are symmetric for "real" perturbations

$$\langle\mu|\frac{\partial h}{\partial x}|\nu\rangle = \langle\nu|\frac{\partial h}{\partial x}|\mu\rangle \tag{72}$$

are antisymmetric for "imaginary" perturbations such as the magnetic field

$$\langle\mu|\frac{\partial h}{\partial B_i}|\nu\rangle = (\langle\nu|\frac{\partial h}{\partial B_i}|\mu\rangle)^* = -\langle\nu|\frac{\partial h}{\partial B_i}|\mu\rangle \tag{73}$$

3.4 Gauge-origin dependence in the calculation of magnetic properties

The problem of gauge-invariance (or gauge-origin independence) in the calculation of magnetic properties arises because of the use of the vector potential **A** for the description of the magnetic interactions in the Hamiltonian. While **A** uniquely defines the magnetic field via Eq. (60), there is no unique choice of **A** to a given magnetic field **B**. The reason is the $\boldsymbol{\nabla}$ operator in Eq. (60) which allows to add the gradient of an arbitrary scalar function to **A** without changing the corresponding magnetic field. For a static homogeneous field, for example, the vector potential can be chosen in the general form

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{R}_O) \tag{74}$$

with $\mathbf{R}_O$ as an *arbitrary* parameter, the so-called gauge origin.

The freedom in the choice of **A**, i.e. in fixing the *gauge*, has in principle no consequences, as **B** as observable quantity is uniquely defined. However, one should note that the freedom in choosing the gauge for a given **B** introduces an arbitrary parameter, namely the gauge-origin $\mathbf{R}_O$, into the Hamiltonian. The question is now how this arbitrary parameter $\mathbf{R}_O$ affects the computation of magnetic properties.

The basic physical laws require that values for observable quantities must be independent of the chosen gauge or gauge-origin. This statement is known as the *principle of gauge-invariance* (or in our special case as *gauge-origin independence*). It is an obvious statement, as Hamiltonians differing only in $\mathbf{R}_O$ describe the *same* physical system with the *same* physical properties. The values for the latter therefore cannot depend on $\mathbf{R}_O$ which is exactly what the principle of gauge invariance states. However, it should be noted that gauge invariance is only requested for observable properties and not for non-observable quantities such as, for example, the wavefunction. For the latter gauge invariance cannot be enforced.

It is obvious (and straightforward to demonstrate, see, for example, Ref. 73) that the exact solution to the Schrödinger equation satisfies the requirement of gauge invariance. All properties computed from the exact solution are uniquely defined and, as it should be, independent of the gauge origin $\mathbf{R}_O$. It is also obvious

Table 4. ^{1}H shielding constants (in ppm) for hydrogen fluoride calculated at the HF-SCF level using different basis sets and gauge origins.

	gauge origin		
basis set	center of mass	fluorine	hydrogen
dz+d	29.3	27.6	60.1
tz+d	28.4	27.2	50.8
qz+2d	27.7	27.0	40.4

(though it has to be discussed for each case separately) that gauge invariance is not necessarily ensured for approximate solutions of the Schrödinger equation. This is a major problem for quantum chemistry, as there we deal almost exclusively with such solutions.

Indeed, it is easily shown that none of the routinely applied quantum chemical approaches provides gauge-invariant results for magnetic properties. The origin of this deficiency is easily traced back to the finite-basis set representation used for the molecular orbitals (commonly known as LCAO approximation). To illustrate the problem, Table 4 contains results for the ^{1}H shielding constant in hydrogen fluoride computed at the HF-SCF level using different basis sets and different gauge origins. The results clearly differ for the three gauge origins. Furthermore, it is observed that the largest discrepancies appear for the smaller and more incomplete basis sets. In passing, we note that *exact* HF calculations would provide gauge-origin independent results, as the problem is the basis-set expansion and not the HF approximation.

The main problem with the gauge-dependence of the computational results is that they are no longer uniquely defined. The computed values for magnetic properties depend on a parameter (or parameters) which can be chosen in an arbitrary manner. This also means that results could even become meaningless, when, for example, computed chemical shifts for symmetry-equivalent nuclei are predicted to be different. Clearly, this is an artifact of the calculation.

However, the gauge-dependence problem is more involved, as one would expect from the discussion given so far. Naively, one would assume that unique results can be achieved by simply fixing the gauge origin, for example, to the center of mass of the considered molecule. Of course, such a choice would guarantee unique results, but on the other hand it does not resolve the fundamental problem connected with the gauge problem in the computation of magnetic properties.

A second serious problem in the calculation of magnetic properties is the slow basis set convergence of the results. Fig. 3 displays the convergence for the ^{1}H shielding in case of hydrogen fluoride. It is seen that rather large basis sets are required to obtain reliable results. Convergence to the basis set limit is much slower than in the computation of most other molecular properties. In particular, standard basis sets appear insufficient for the reliable calculation of magnetic properties.

For atoms, the nuclear position represents a natural gauge origin. With this choice, no problem in the finite-basis representation of the magnetic interaction appears, as the usually employed basis functions, i.e., spherical Gaussians centered

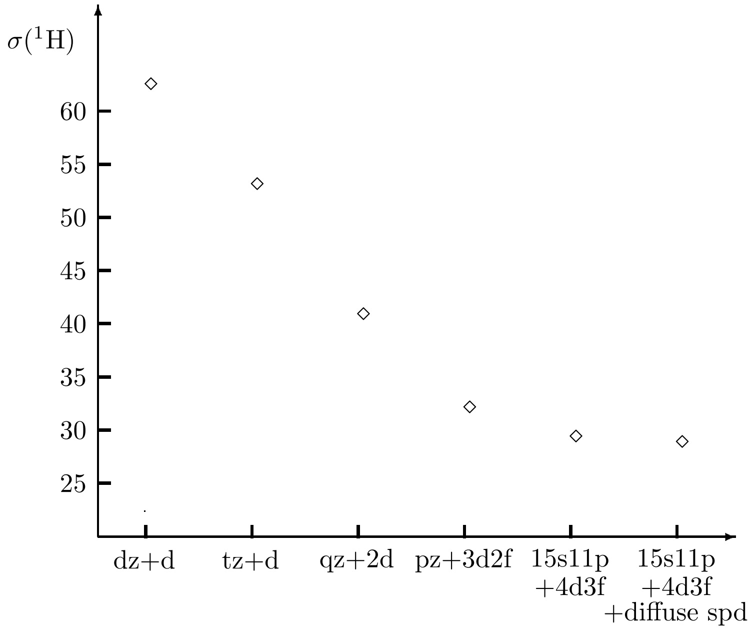


Fig. 3: Basis set convergence in the calculation of the ^{1}H shielding constant of hydrogen fluoride. All calculations have been carried out with the gauge origin at the hydrogen.

at the nuclear position, are eigenfunctions to the angular momentum operator

$$\mathbf{l} = \mathbf{r} \times \mathbf{p}. \tag{75}$$

The same is not the case as soon as the gauge origin is shifted and no longer coincides with the nuclear position. The angular momentum is then defined with respect to the displaced gauge origin

$$\mathbf{l}_O = (\mathbf{r} - \mathbf{R}_O) \times \mathbf{p} \tag{76}$$

and the following holds

$$\mathbf{l}_O|\chi_\mu\rangle = \mathbf{l}|\chi_\mu\rangle + \mathbf{R}_O \times \mathbf{p}|\chi_\mu\rangle \tag{77}$$

when $\mathbf{l}_O$ is applied to a basis function $|\chi_\mu\rangle$. The second term in Eq. (77) involves a simple differentiation of a Gaussian basis function and thus leads to basis functions with by one increased and decreased angular momentum quantum numbers. A proper basis set representation of $\mathbf{l}_O|\chi_\mu\rangle$ thus requires that additional higher angular momentum functions are included in the basis set, i.e. the corresponding p function for a s function, the corresponding d function for a p function, etc. A correct representation of this term would require a complete AO basis which is usually not provided. Shifting the gauge origin away from the nucleus thus deteriorates the description of the magnetic interactions. The deteriorations increases with the size of the displacement.

3.5 Local gauge origin methods

From the discussion above, it is clear why the nucleus is the best gauge origin for atoms. However, a similar *natural* gauge origin does not exist for molecules. It is also obvious from the discussion above that a single gauge origin must be unsatisfactory for molecular calculations. The quality of the description for the various parts of a molecule depends on their distances to the gauge origin. As a single gauge origin can impossibly be optimal for all molecular parts, a rather unbalanced description of the magnetic interactions results.

The only viable way to overcome these problems consists in the use of more than one gauge origin for the external magnetic field. The idea behind this concept of *local* or *distributed gauge origins* is simple, though the technical realization is more involved. To introduce local gauge origins, it is first necessary to partition the molecule (or to be more specific the molecular wavefunction) into *local* fragments. For each fragment, the gauge origin can be then individually chosen in an optimal way. If the local fragments can be assigned to the various atoms in the molecule, the corresponding nuclear position would be, for example, a good choice for the gauge origin.

As within the concept of local gauge origins all molecular parts are described equally well, a balanced description is achieved. A "good" description of the magnetic interactions is ensured, as for each local fragment an optimal choice for the gauge origin is possible.

For a realization of the described concept of local gauge origins, it is necessary to introduce gauge-transformations. A shift of the gauge origin from $\mathbf{R}_O$ to $\mathbf{R}'_O$ is achieved in the theoretical description via a so-called gauge transformation. For a one-electron system, the corresponding equations are

$$\Psi \;\longrightarrow\; \Psi' \;=\; \exp(-\Lambda(\mathbf{r}))\;\Psi \tag{78}$$

$$\hat{H} \;\longrightarrow\; \hat{H}' \;=\; \exp(-\Lambda(\mathbf{r}))\;\hat{H}\;\exp(\Lambda(\mathbf{r})) \tag{79}$$

with the gauge factor defined by

$$\Lambda(\mathbf{r}) \;=\; \frac{ie}{2c\hbar}\,[(\mathbf{R}'_O - \mathbf{R}_O)\times\mathbf{B}]\cdot\mathbf{r}. \tag{80}$$

Expansion of the Hamiltonian H' using the Hausdorff formula

$$\begin{aligned} H' \;&=\; H \;+\; [H,\Lambda] \;+\; \frac{1}{2}[[H,\Lambda],\Lambda]+... && (81)\\ &=\; H - \frac{ie\hbar}{2mc}\mathbf{B}\cdot((\mathbf{R}_O - \mathbf{R}'_O)\times\boldsymbol{\nabla}) + ... && (82)\\ &=\; -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r}) - \frac{ie\hbar}{2mc}\mathbf{B}\cdot((\mathbf{r} - \mathbf{R}'_O)\times\boldsymbol{\nabla}) + ... && (83)\end{aligned}$$

shows that H' is indeed the Hamiltonian with the gauge origin at $\mathbf{R}'_O$ instead of $\mathbf{R}_O$.

To introduce local gauge origins, the concept of gauge transformations needs to be extended, as so far we are only concerned with the change from a given origin to another gauge origin. This extension is easily achieved by introducing more general gauge transformations of the following kind

$$\sum_A \exp(\Lambda_A(\mathbf{r}))\ \hat{P}_A \tag{84}$$

where $\hat{P}_A$ represents a suitable projector on the local fragment A and $\exp(\Lambda_A(\mathbf{r}))$ a gauge transformation to the origin chosen for A. Note that it can be shown that Eq. (84) defines indeed a valid gauge transformation and leaves for the exact solution of the Schrödinger equation all physical observables unchanged. As usual, we have to require for the projector that

$$\sum_A \hat{P}_A \ = \ 1. \tag{85}$$

One should also note that for a many-electron system the corresponding gauge transformation is given by

$$\prod_{\alpha=1}^{N} \exp(\Lambda_A(\mathbf{r}_\alpha))\hat{P}_A^\alpha \tag{86}$$

where α is the electron index and $\hat{P}_A^\alpha$ the corresponding projector.

Following Eq. (84), it is most convenient to define the local fragment at the one-electron level. With the atomic and molecular orbitals as the *one-electron* building blocks for the wavefunction, it appears natural to introduce individual gauge origins for these one-electron functions. The corresponding schemes, i.e., IGLO[74,75], LORG[76], and GIAO[77−80] are nowadays well established and routinely used for NMR chemical shift calculations[h]. In fact, it is justified to state that these schemes first enabled those calculations to be routinely carried out within chemical applications, as the trivial solution to the gauge problem, i.e., the use of very large basis sets, is necessarily restricted to small molecules.

IGLO and LORG are both based on individual gauges for molecular orbitals. However, as standard HF orbitals are usually delocalized, they are not well suited for a local gauge origin approach. It is therefore mandatory to introduce localized occupied orbitals[81] and to define individual gauges for them. This is exactly what is done in the individual gauges for localized orbital (IGLO) approach of Kutzelnigg and Schindler[74,75] and the localized orbital/local origin (LORG) scheme of Bouman and Hansen[76]. Details for both approaches can be found in the original literature.

Considering the need of localized orbitals as disadvantageous, it appears more natural to work with atomic orbitals (which are by construction localized quantities) and to assign to each of them an individual gauge origin. No further manipulations are required in this case. This choice of local gauge origins leads to what is nowadays known as the gauge-including atomic orbital (GIAO) approach[i]. As it seems

---

[h] It should be noted that the IGLO and GIAO approaches are also well suited for the efficient computation of magnetazibilities.

[i] The GIAO method is sometimes also called the London atomic orbital (LAO) approach.

that the GIAO approach is becoming the *standard* for the calculation of magnetic properties, we will discuss it in the following section in some detail.

3.6 The GIAO ansatz

The GIAO ansatz[77−80] consists in choosing local gauge origins for atomic orbitals $|\chi_\mu\rangle$. This means in particular that the corresponding nucleus at which the atomic orbital is centered is chosen as the "natural" gauge origin.

Within the concept of local gauge origins, the GIAO ansatz is based on the following gauge-transformation

$$\sum_\mu \exp(\Lambda_\mu(\mathbf{r}))\ \hat{P}_\mu \tag{87}$$

with the projector on $|\chi_\mu\rangle$ defined by

$$\hat{P}_\mu = \sum_\nu |\chi_\mu\rangle S^{-1}_{\mu\nu} \langle\chi_\nu| \tag{88}$$

and the gauge factor given by

$$\Lambda_\mu(\mathbf{r}) = \frac{ie}{2c\hbar}\ [(\mathbf{R}_\mu - \mathbf{R}_O) \times \mathbf{B}] \cdot \mathbf{r}. \tag{89}$$

with $\mathbf{R}_O$ as the original gauge origin in the Hamiltonian and $\mathbf{R}_\mu$ as the center of the basis function $|\chi_\mu\rangle$. It is obvious that the gauge factor given in Eq. (89) describes a shift of the gauge origin from $\mathbf{R}_O$ to $\mathbf{R}_\mu$. The projector in Eq. (88) is somewhat more involved in order to account for the non-orthogonality of the AOs.

While Eqs. (87) to (89) yield in our opinion a very elegant description of the GIAO approach, a different, though in principle equivalent description is more common.[80] Consider the equations which define the gauge transformations (Eqs. (78) and (79)). These equations can be interpreted such that there is some freedom whether the phase factors (of the gauge transformation) are assigned to the Hamiltonian or to the wavefunction. Eqs. (78) and (79) thus offer two possibilities for the interpretation of the GIAO approach. The first is to apply the local transformation and to work with a modified Hamiltonian but with the same unchanged wavefunction. This means that the latter is described in the usual way with the standard atomic orbitals, etc. The second possibility leaves the Hamiltonian unchanged, but attaches additional phase factors (those from the gauge transformation) to the wavefunction description. In particular, it appears convenient to attach these additional phase factors to the AOs and to describe the GIAO ansatz such that the calculation of magnetic properties are now carried out with the following perturbation-dependent basis functions

$$|\chi_\mu(\mathbf{B})\rangle = \exp(-\frac{ie}{2c\hbar}(\mathbf{B} \times [\mathbf{R}_\mu - \mathbf{R_O}]) \cdot \mathbf{r})|\chi_\mu(0)\rangle \tag{90}$$

instead of the usual field-independent functions $|\chi_\mu(0)\rangle$. The field-dependent basis functions of Eq. (90) have been termed in the literature as *gauge-including atomic* *orbitals*[j] or *London orbitals*.

We will discuss now in some detail why GIAOs provide a satisfactory solution to the gauge-origin problem. Let us take first the *local gauge origin* view, i.e., the description of the GIAO ansatz as an approach where local gauge origins are introduced for AOs. The gauge-origin problem is *solved* here by fixing the gauge in an optimal way. This first provides unique results and second ensures fast basis set convergence, as for each AO the corresponding optimal gauge is used. However, one should avoid the term *gauge invariance* in this context, as the gauge problem is only solved by fixing the gauge in a very special way. However, the results are independent of the original gauge (characterized by the common gauge origin $\mathbf{R}_O$) and in that respect it is appropriate to talk about gauge-origin independent results in the sense that the results for magnetic properties are independent of $\mathbf{R}_O$.

Let us take the second view, i.e., that of perturbation-dependent basis functions. Here, the use of special basis functions ensures proper behavior of the wavefunction in the presence of the magnetic field. Gauge-origin independent results are obtained, as these basis functions are especially tailored to the chosen gauge (the gauge origin $\mathbf{R}_O$ appears in the definition of the GIAOs). Gauge invariance is again not ensured, as invariance is only guaranteed with respect to shifts in the gauge origin $\mathbf{R}_O$, but not with respect to more general gauge transformations. Fast basis set convergence is achieved, because the GIAOs are constructed in such a manner that they provide exact first-order solutions in the presence of the magnetic field provided the corresponding AO is the correct zeroth-order solution[82]. One can argue that the GIAOs already take care of the major effect of the magnetic field perturbation on the wavefunction and that the remaining corrections in MO coefficients, CI coefficients or CC amplitudes are rather small and easily described within the standard techniques.

The fast basis set convergence of GIAO calculations of shielding constants is demonstrated in Fig.4.

We add a discussion on some technical aspects which are best explained in the picture of field-dependent basis functions. As the basis functions now explicitly depend on the magnetic field $\mathbf{B}$, differentiation of the usual unperturbed one- and two-electron integrals necessarily involves additional terms. While a conventional approach just requires the integrals

$$\left(\frac{\partial\langle\chi_\mu|h|\chi_\nu\rangle}{\partial B_i}\right)_{conv} = -\frac{ie\hbar}{2mc}\langle\chi_\mu|(\mathbf{r}\times\boldsymbol{\nabla})_i|\chi_\nu\rangle \tag{91}$$

$$\left(\frac{\partial\langle\chi_\mu|h|\chi_\nu\rangle}{\partial m_{Ki}}\right)_{conv} = -\frac{ie\hbar}{mc}\langle\chi_\mu|\frac{[(\mathbf{r}-\mathbf{R}_K)\times\boldsymbol{\nabla}]_i}{|\mathbf{r}-\mathbf{R}_K|^3}|\chi_\nu\rangle \tag{92}$$

$$\left(\frac{\partial^2\langle\chi_\mu|h|\chi_\nu\rangle}{\partial B_i\partial m_{Kj}}\right)_{conv} = \frac{e^2}{2mc^2}\langle\chi_\mu|\frac{\mathbf{r}\cdot(\mathbf{r}-\mathbf{R}_K)\delta_{ij}-\mathbf{r}_i(\mathbf{r}-\mathbf{R}_K)_j}{|\mathbf{r}-\mathbf{R}_K|^3}|\chi_\nu\rangle \tag{93}$$

---

[j] It should be noted that the GIAOs were originally named in a somewhat misleading manner as gauge-invariant or gauge-independent atomic orbitals. Following a suggestion by Bouman and Hansen[76] the more appropriate name *gauge-including atomic orbitals* has become standard since the beginning of the nineties.

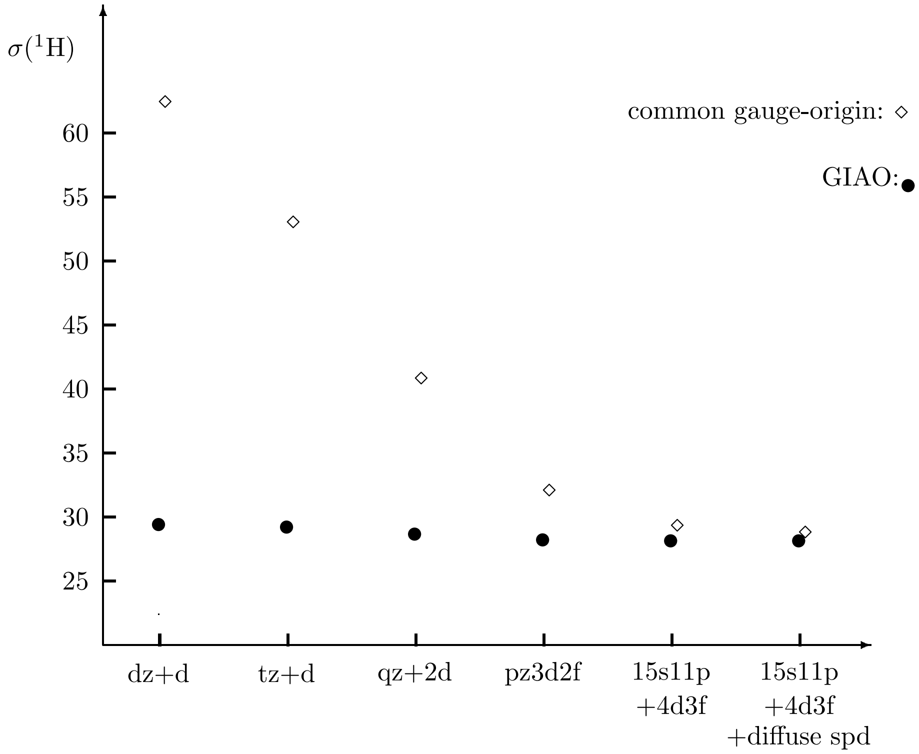


Fig. 4: Comparison of the basis set convergence in common gauge-origin and GIAO calculation of the ^{1}H shielding constant of hydrogen fluoride.

the dependence of the basis functions on B leads to following additional integrals.

$$\left(\frac{\partial\langle\chi_\mu|\chi_\nu\rangle}{\partial B_i}\right)_{GIAO} = \langle\frac{\partial\chi_\mu}{\partial B_i}|\chi_\nu\rangle + \langle\chi_\mu|\frac{\partial\chi_\nu}{\partial B_i}\rangle \tag{94}$$

$$\left(\frac{\partial\langle\chi_\mu|h|\chi_\nu\rangle}{\partial B_i}\right)_{GIAO} = \left(\frac{\partial\langle\chi_\mu|h|\chi_\nu\rangle}{\partial B_i}\right)_{conv} + \langle\frac{\partial\chi_\mu}{\partial B_i}|h|\chi_\nu\rangle + \langle\chi_\mu|h|\frac{\partial\chi_\nu}{\partial B_i}\rangle \tag{95}$$

$$\left(\frac{\partial\langle\chi_\mu|h|\chi_\nu\rangle}{\partial m_{Ki}}\right)_{GIAO} = \left(\frac{\partial\langle\chi_\mu|h|\chi_\nu\rangle}{\partial m_{Ki}}\right)_{conv} \tag{96}$$

$$\begin{aligned}\left(\frac{\partial^2\langle\chi_\mu|h|\chi_\nu\rangle}{\partial B_i\partial m_{Kj}}\right)_{GIAO} &= \left(\frac{\partial^2\langle\chi_\mu|h|\chi_\nu\rangle}{\partial B_i\partial m_{Kj}}\right)_{conv} - \frac{ie\hbar}{mc}\langle\frac{\partial\chi_\mu}{\partial B_i}|\frac{[(\mathbf{r}-\mathbf{R}_K)\times\boldsymbol{\nabla}]_j}{|\mathbf{r}-\mathbf{R}_K|^3}|\chi_\nu\rangle \\ &\quad -\frac{ie\hbar}{mc}\langle\chi_\mu|\frac{[(\mathbf{r}-\mathbf{R}_K)\times\boldsymbol{\nabla}]_j}{|\mathbf{r}-\mathbf{R}_K|^3}|\frac{\partial\chi_\nu}{\partial B_i}\rangle\end{aligned} \tag{97}$$

$$\begin{aligned}\left(\frac{\partial\langle\chi_\mu\chi_\nu|\chi_\sigma\chi_\rho\rangle}{\partial B_i}\right)_{GIAO} &= \langle\frac{\partial\chi_\mu}{\partial B_i}\chi_\nu|\chi_\sigma\chi_\rho\rangle + \langle\chi_\mu\frac{\partial\chi_\nu}{\partial B_i}|\chi_\sigma\chi_\rho\rangle \\ &\quad +\langle\chi_\mu\chi_\nu|\frac{\partial\chi_\sigma}{\partial B_i}\chi_\rho\rangle + \langle\chi_\mu\chi_\nu|chi_\sigma\frac{\partial\chi_\rho}{\partial B_i}\rangle\end{aligned} \tag{98}$$

For a long time, efficient calculation and handling of these integrals (and here in particular of the additional two-electron integrals) was considered a major obstacle in the application of the GIAO approach. However, Pulay pointed out that the additional integrals are closely related to usual geometrical integral derivatives[83] and showed how modern analytic derivative techniques can be used to design an efficient GIAO code at the SCF level[80].

3.7 Availability of methods for the calculation of NMR chemical shifts

Before discussing available methods for the efficient calculation of NMR chemical shifts, let us add a few historical remarks. The suggestion of using gauge-including atomic orbitals goes back to London[77] who has used them in a study of molecular diamagnetism more than 50 years ago. At the end of the fifties, GIAOs were used by Hameka in SCF calculations of shielding constants for a few diatomic molecules[78] and in the seventies by Ditchfield[79]. However due to technical problems in calculating and handling integral derivatives, Ditchfield's work had only limited impact. The breakthrough with respect to applicability was the IGLO development by Kutzelnigg and Schindler[74,75]. By introducing local gauges for localized orbitals, the problem of additional two-electron integrals was avoided in a rather elegant way and calculations of chemical shifts for larger and chemically more interesting molecules became possible. Noteworthy are in particular the numerous applications of the IGLO approach to problems in carbocation chemistry by Schleyer and coworkers[84]. The LORG approach was suggested somewhat later within the random-phase approximation (RPA) context, but has been shown by Kutzelnigg[73] to be closely related to IGLO. The popularity of the GIAO approach in the nineties started with Pulay's seminal work[80]. As the GIAO approach can be considered the most elegant way to deal with the gauge problem, it has been adopted by most groups and implemented in many quantum chemical program packages for the calculation of magnetic properties.

Table 5 lists the currently available schemes for the calculation of NMR chemical shifts. Note that we include only those approaches which take care of the gauge-origin problem via local gauge-origin methods and ignore all other developments, as they cannot be considered well suited for most chemical applications. At the HF-SCF level, three variants are available: GIAO-SCF[79,80], IGLO[74,75], and LORG[76] and all three schemes yield results of similar quality. However, implementations at electron-correlated levels were mainly pursued using GIAOs[85–91,29]. GIAO-MP2 (also known as GIAO-MBPT(2)) provides the largest range of applicability, GIAO-CCSD(T) is a tool for highly accurate prediction of NMR chemical shifts, while the complementary GIAO-MCSCF treatment allows to tackle difficult cases with large static correlation effects. On the other hand, IGLO was generalized to MCSCF wavefunction models (MC-IGLO)[92] and the LORG scheme to second-order LORG (SOLO)[93].

Naturally, there has been also a great interest in calculating NMR chemical shifts using DFT approaches. From a pragmatic point of view, very promising results have so far been obtained[94–102], but it is necessary to add a few remarks. First, it needs to be realized that the Hohenberg-Kohn theorems do not hold in the presence of a magnetic field. They need to be extended (as described by Vignale and Rasolt[103]) to include current-dependent functionals. Most implementations,

Table 5. Available implementations for the calculations of NMR chemical shifts

quantum chemical methods		Ref.
IGLO	Kutzelnigg and Schindler (1982)	75
LORG	Bouman and Hansen (1985)	76
GIAO-SCF	Ditchfield (1974), Wolinski,Pulay, Hinton (1990)	79,80
MC-IGLO	van Wüllen and Kutzelnigg (1993)	92
GIAO-MCSCF	Ruud *et al.* (1994)	87
GIAO-MP2	Gauss (1992)	85,86
GIAO-MP3	Gauss (1994)	88
GIAO-MP4	Gauss, Stanton (1994,1996)	88,91
GIAO-CCSD	Gauss, Stanton (1995)	89,90
GIAO-CCSD(T)	Gauss, Stanton (1996)	91
GIAO-CCSDT-n	Gauss, Stanton (2000)	29
DFT-IGLO	Malkin *et al.* (1993)	94
SOS-DFPT	Malkin *et al.* (1994)	95
GIAO-DFT	Schreckenbach and Ziegler (1995),	96
	Handy *et al.* (1995),	99
	Pulay *et al.* (1996), Cheeseman *et al.* (1996)	97,98
SOLO	Bouman, Hansen (1990)	93

however, ignore that fact and treat magnetic properties by what is called uncoupled DFT. A justification for this choice might be seen in the work of Lee *et al.*[99] who showed that inclusion of the current does not necessarily improve the results[k]. Second, to rectify some problems in the uncoupled DFT approach (which certainly is incomplete from a formal point of view) Malkin *et al.* suggested an *ad hoc* modification of the energy denominator within their sum-over-states density-functional perturbation theory (SOS-DFPT) scheme[95]. Though the results give some justification for this empirical modification, it must be clearly stated that there is no rigorous theoretical justification for Malkin's approach and that a similar manipulation would not have been accepted within the more conventional approaches. Nevertheless, it can be anticipated that DFT treatments of NMR chemical shifts are of great practical importance and will become a routine tool within quantum chemistry.

We will complete our discussion by emphasizing some algorithmic developments in chemical shift calculations aiming at the treatment of larger systems. Implementation of direct methods for GIAO-SCF[105] or IGLO[106] paved the path for the routine treatment of molecular systems with up to 100 atoms. Integral-direct concepts have also been extended to the GIAO-MP2 approach[107]. Together with an efficient treatment of molecular point-group symmetry[108], thus GIAO-MP2 chemical shift calculations became possible on molecules with more than 50 atoms described by more than 600 basis functions (see also section 3.8). However, as the CPU requirements remained unchanged, it appears attractive to couple such integral-direct

---

[k] For a different concept for the treatment of magnetic properties within DFT, see the work by Harris *et al.*[104]

Table 6. Calculated absolute shielding constants (in ppm)

Molecule	Nucleus	σ_e	σ_0	σ(300K)	σ(300K, exp.)
H_2	^{1}H	26.667	26.312	26.298	26.288±0.002
HF	^{1}H	28.84	28.52	28.48	28.54±0.01
	^{19}F	419.6	409.6	409.2	409.6±1.0
CO	^{13}C	4.2	1.9	1.8	0.9±0.9
	^{17}O	-54.3	-60.4	-60.6	-44.8±17.2
N_2	^{15}N	-58.4	-62.5	-62.7	-61.6
F_2	^{19}F	-189.9	-220.8	-225.5	-233.02±1.0

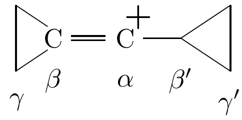
developments with other ideas such as, for example, the local-correlation treatment first suggested by Pulay[109] and recently pursued by Werner and co-workers.[110] Based on a preliminary implementation, test calculations have recently demonstrated that a local GIAO-MP2 (GIAO-LMP2) scheme should hold great promises for the treatment of larger molecules.[111]

Other active areas where methodological developments concerning chemical shift calculations are pursued are the treatment of relativistic effects (important for heavy elements)[112–116], the routine calculation of rovibrational effects (important to improve agreement between theory and experiment)[117–119] and the consideration of solvent effects[120–122]. The latter is of special importance, as the majority of the NMR spectra is measured in solution or the liquid phase.

3.8 Examples for chemical shift calculations

We will give a few examples to demonstrate the range of applications which are possible with the currently available methods for computing chemical shifts. Table 6 reports computed absolute shielding constants needed for establishing absolute NMR scales[117]. In order to provide accurate data, it is here essential to use the GIAO-CCSD(T) methods in combination with large basis sets. The error in the computed absolute shifts of any of the other methods is too large in order to provide reliable data. In addition, consideration of rovibrational and temperature effects is mandatory. To emphasize the importance of such calculations, we note that the current ^{17}O scale is based on calculations[117], as the corresponding experimental scale (based on measured spin-rotation constants) appears to be inaccurate.

For most chemical applications, computation of relative shifts is of central importance. In case of the following vinyl cation



it turned out that GIAO-CCSD(T) calculations were essential to provide an unequivocal assignment[123]. GIAO-HF-SCF and GIAO-MP2 calculations are too inaccurate and only a high-level correlation treatment provides sufficient accuracy. The computed spectra are displayed in Fig. 5:

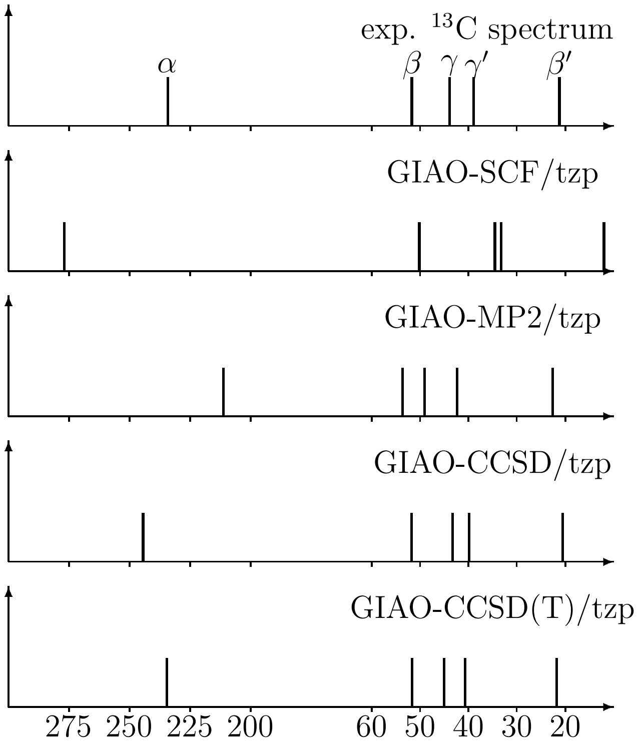


Fig. 5: Calculated and experimental ^{13}C NMR spectra for the 1-cyclopropylcyclopropylidenemethyl cation

Another example is the ^{27}Al NMR spectrum of the Al_4Cp_4 molecule (Fig. 6) measured by Schnöckel and co-workers[124].

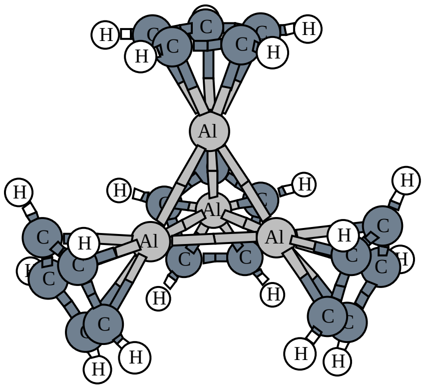
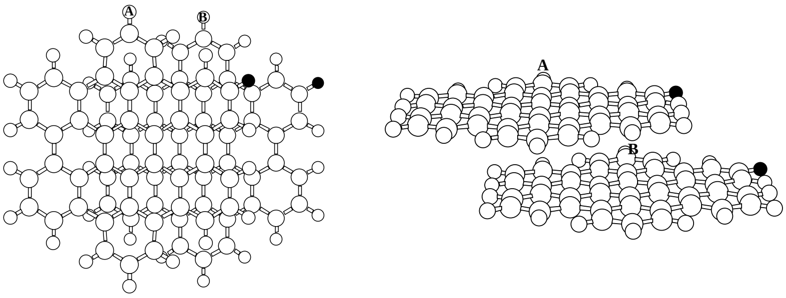


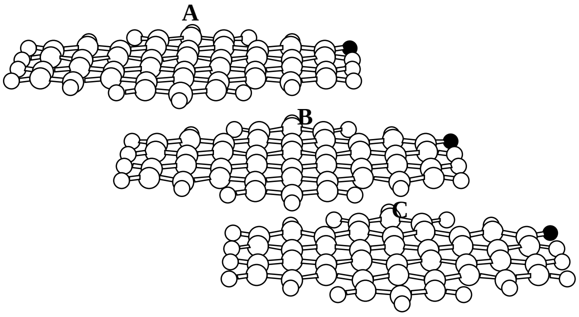
Fig. 6: Structure of Al_4Cp_4

The spectrum was unequivocally assigned to the tetrameric species on the basis of the computed ^{27}Al chemical shifts[124,108], as the experimental value of -111 ppm agrees well with the computed value of -108.5 (GIAO-MP2). Correlation effects amount in this case to about 15 ppm and, thus, are not negligible. The computational cost for the required GIAO-MP2 calculations have been rather demanding. Using a parallel version of the integral-direct program described in Ref. 108, the calculation (44 atoms, 192 electrons, 548 basis functions, molecular symmetry: D_{2d}) required about 6 days on a SGI Power Challenge (4 nodes).

A final example deals with an application of chemical shift calculations in combination with solid-state NMR measurements. The aromatic proton signal for a hexabenzocoronene (HBC) derivative splits in the solid state into three peaks (5.7, 6.9, and 8.3 ppm)[125]. GIAO-SCF calculations on dimeric and trimeric units of HBC (Figure 7) enabled an assignment of the measured ^{1}H NMR chemical shifts to a specific structural model by comparison with computed shifts for various model systems[126].



Computed ^{1}H-NMR shifts: 6.9 / 7.9 / 8.9 ppm



Computed ^{1}H-NMR shifts: 5.9 / 7.4 / 8.7 ppm

Fig. 7: Dimeric and trimeric units of HBC. The experimental chemical shifts for the aromatic protons in the investigated solid HBC derivative are 5.7, 6.9, and 8.3 ppm[125].

For the structure shown in Fig. 7, the best agreement is obtained between calculations and measured values.

3.9 Indirect spin-spin coupling constants

Besides the computation of NMR chemical shifts, theoretical prediction of indirect spin-spin coupling constants J_{KL} is equally important for a full understanding and assignment of experimental NMR spectra. The coupling constants are given as the corresponding second derivatives of the electronic energy with respect to the involved nuclear spins

$$J_{KL} = \frac{1}{3h} \sum_i \frac{d^2 E}{dI_{Ki} dI_{Li}}. \tag{99}$$

It can be shown that there are four contributions to Eq. (99). The first (and for CC and CH coupling constants dominating) term is the Fermi-Contact (FC) contribution described by the following perturbed Hamiltonian

$$\left(\frac{\partial h}{\partial I_{Ki}}\right)_{FC} = -\frac{2\pi e^2 g_K g_e}{3mM_p c^2} \delta(\mathbf{r} - \mathbf{r}_K)\mathbf{s}. \tag{100}$$

The second term describes the spin-dipole (SD) interaction:

$$\left(\frac{\partial h}{\partial I_{Ki}}\right)_{SD} = \frac{e^2 g_K g_e}{4mM_p c^2} \frac{(\mathbf{r}_i - \mathbf{r}_K)^2 \mathbf{s} - 3(\mathbf{s} \cdot (\mathbf{r}_i - \mathbf{r}_K)(\mathbf{r}_i - \mathbf{r}_K)}{|\mathbf{r}_i - \mathbf{r}_K|^5}. \tag{101}$$

Third and fourth terms finally represent the so-called diamagnetic and paramagnetic spin-orbit (DSO and PSO) contributions with

$$\left(\frac{\partial^2 h}{\partial I_{Ki} \partial I_{Lj}}\right)_{DSO} = \frac{g_K g_L e^4}{8mM_p^2 c^4} \frac{(\mathbf{r} - \mathbf{r}_K) \cdot (\mathbf{r} - \mathbf{r}_L)\delta_{ij} - (\mathbf{r} - \mathbf{r}_K)_j (\mathbf{r} - \mathbf{r}_L)_i}{|\mathbf{r} - \mathbf{r}_K|^3 |\mathbf{r} - \mathbf{r}_L|^3} \tag{102}$$

and

$$\left(\frac{\partial h}{\partial I_{Ki}}\right)_{PSO} = -\frac{ie^2 \hbar g_K}{mM_p c^2} \frac{[(\mathbf{r} - \mathbf{R}_K) \times \nabla]_j}{|\mathbf{r} - \mathbf{R}_K|^3}. \tag{103}$$

In Eqs. (100) to (103), $\mathbf{s}$ denotes the operator for the electron spin, m the electron mass, M_p the proton mass, g_K the g factor of the Kth nucleus, and g_e the g factor of the electron.

Though calculation of J_{KL} is not hampered by the gauge problem, its calculation is actually even more problematic. First of all, the FC and SD terms represent so-called triplet operators (note the appearance of the electron spin $\mathbf{s}$ in the expressions given in Eqs. (100) and (101)). The calculation of these contributions to J_{KL} is thus affected by triplet instabilities of the wavefunction and accordingly the HF-SCF approach turns out to be useless in many cases[127]. Second, there are a total of 10 perturbations per nucleus which renders computation of the complete set of spin-spin coupling constants expensive. Third, the basis set convergence in the calculation of the FC term is rather slow[128–130], as the appropriate representation of the delta function operator in the FC contribution in terms of Gaussians is demanding.

As the HF approach fails in most cases, promising results have been so far only obtained at correlated levels. MCSCF calculations[131,132] as well as CCSD calculations[133,134] have been shown to provide reliable theoretical data for these properties. However, both schemes are hampered in the application to larger molecules by high computational requirements.

Therefore, DFT might offer a pragmatic alternative. A first implementation by Malkina *et al.*[135] (within their SOS-DFPT scheme) unfortunately ignores the SD term which in some cases has been proven to be important. A complete implementation within the coupled-perturbed DFT framework that considers all four contributions to J_{KL} has been recently presented by Cremer *et al.*[136] However, further work is still needed before a final conclusion concerning the applicability of DFT in the calculation of spin-spin coupling constants can be given.

4 Frequency-dependent properties

4.1 General theory

While analytic derivative theory is sufficient for the theoretical treatment of time-independent (static) properties, the underlying theory needs to be extended for the calculation of time-dependent (dynamical) properties. In particular, the fact that there is – unlike for the static case – in the time-dependent case no well-defined energy explains why the simple derivative theory discussed so far is not applicable.

Nevertheless, there is large interest in the calculation of dynamical properties. The main examples comprise frequency-dependent polarizabilities and hyperpolarizabilities which are the key quantities in the area of non-linear optics[137,138].

Starting point for the discussion of dynamical properties necessarily is the time-dependent Schrödinger equation[l]

$$H(t)|\Psi\rangle = i\frac{\partial}{\partial t}|\Psi\rangle \tag{104}$$

with the Hamiltonian H consisting of the usual time-independent molecular part H_0 and a time-dependent perturbation $V(t)$:

$$H(t) = H_0 + V(t). \tag{105}$$

For $V(t)$, one generally assumes that it can be written as a sum of periodic perturbations

$$V(t) = \sum_{k=-N}^{N} \exp(-i\omega_k t) \sum_X \epsilon_X(\omega_k) X \tag{106}$$

with ω_k as the frequencies and $\epsilon_X(\omega_k)$ and X denoting the corresponding perturbation strengths and operators. For a periodically oscillating electric field (the most common example), X is the dipole operator μ and $\epsilon_X(\omega_k)$ the corresponding electric field strength.

As $V(t)$ has to be Hermitian, the following relations must hold:

$$X^\dagger = X, \tag{107}$$

---

[l] Atomic units are used here and in the following.

$$\omega_{-k} = -\omega_k, \tag{108}$$

and

$$\epsilon^*_X(\omega_k) = \epsilon_X(\omega_k). \tag{109}$$

Eq. (106) for $V(t)$ can thus be rewritten as

$$V(t) = \epsilon(0)X + 2\sum_{k=1}^{N}\cos(\omega_k t)\sum_X Re(\epsilon_X(\omega_k))X + 2\sin(\omega_k t)\sum_X Im(\epsilon_X(\omega_k))X \tag{110}$$

i.e., in a more common form with the perturbations given in terms of real sine and cosine functions.

The expectation value of an operator X can now be expanded in the form[m]

$$\begin{aligned}\langle X\rangle(t) = \langle X\rangle_0 &+ \sum_{k_1}\exp(-i\omega_{k_1}t)\sum_Y\langle\langle X;Y\rangle\rangle_{\omega_{k_1}}\epsilon_Y(\omega_{k_1})\\ &+\frac{1}{2}\sum_{k_1k_2}\exp(-i(\omega_{k_1}+\omega_{k_2})t)\sum_{Y,Z}\langle\langle X;Y,Z,\rangle\rangle_{\omega_{k_1},\omega_{k_2}}\epsilon_Y(\omega_{k_1})\epsilon_Z(\omega_{k_2}) + ...\end{aligned} \tag{111}$$

with the linear response function $\langle\langle X;Y\rangle\rangle_{\omega_{k_1}}$, the quadratic response function $\langle\langle X;Y,Z\rangle\rangle_{\omega_{k_1}\omega_{k_2}}$), etc. characterizing the time dependence of $\langle X\rangle$. Eq. (111) can be interpreted as an expansion of $\langle X\rangle$ with respect to the Fourier components of the perturbation $V(t)$. The response functions are denoted by $\langle\langle ...\rangle\rangle$. The operator before the semi-colon represents the operator for which the expectation value is computed, while the operators after the semi-colon denote those which are involved in the Fourier components of $V(t)$. The frequencies given as subscript are those connected with the perturbation operators $Y, Z, ...$

For the specific case of $X = \mu_i$, Eq. (111) takes the form

$$\begin{aligned}\langle\mu_i\rangle(t) = \langle\mu_i\rangle_0 &+ \sum_{k_1}\exp(-i\omega_{k_1}t)\sum_j\alpha_{ij}(-\omega_{k_1};\omega_{k_1})\epsilon_j(\omega_{k_1})\\ &+\frac{1}{2}\sum_{k_1,k_2}\exp(-i(\omega_{k_1}+\omega_{k_2})t)\sum_{jk}\beta_{ijk}(-\omega_{k_1}-\omega_{k_2};\omega_{k_1},\omega_{k_2})\epsilon_j(\omega_{k_1})\epsilon_k(\omega_{k_2})\\ &+...\end{aligned} \tag{112}$$

with $\alpha_{ij}(-\omega;\omega)$ as the tensor elements of the frequency-dependent polarizability, $\beta_{ijk}(\omega_1;\omega_2,\omega_3)$ as the tensor elements of the frequency-dependent first hyperpolarizability, etc. Table 7 gives an overview about the various types of polarizabilities and hyperpolarizabilities as well as their relationship to physical effects (for a more detailed discussion see, for example, Ref. 138.) It is important to note in this context that the sum of the frequencies (with explicit consideration of signs!) determines the frequency of the corresponding contribution in the expectation value

---

[m] Note that we assume that the operator X is included in the perturbation $V(t)$.

Table 7. Definition and physical relevance of the various (frequency-dependent) polarizabilities and hyperpolarizabilities

(hyper)polarizability	physical effect
α(0;0)	static polarizability
α(-ω; ω)	frequency-dependent polarizability
β(0;0,0)	static first hyperpolarizability
$\beta(-2\omega;\omega,\omega)$	second harmonic generation (SHG)
$\beta(-\omega;\omega,0)$	dc-Pockels effect (dc-P); electro-optical Pockels Effect (EOPE)
$\beta(0;\omega,\omega)$	optical rectification (OR)
γ(0;0,0,0)	static second hyperpolarizability
$\gamma(3\omega;\omega,\omega,\omega)$	third harmonic generation (THG)
$\gamma(2\omega;\omega,\omega,0)$	dc-second harmonic generation (dc-SHG); electric field induced SHG (EFISH or ESHG)
$\gamma\ (-\omega;\omega,-\omega,\omega)$	intensity-dependent refractive index (IDRI); degenerate four wave mixing (DFWM)
$\gamma\ (-\omega_1;\omega_1,-\omega_2,\omega_2)$	ac-Kerr effect (ac-K); optical Kerr effect (OKE)
$\gamma\ (-\omega;\omega,0,0)$	dc-Kerr effect (dc-K); electro-optical Kerr effect (EOKE)
$\gamma\ (0;\omega,-\omega,0)$	dc-optical rectification (dc-OR); electric field induced optical rectification (EFIOR)

expression. For example, in case of the SHG hyperpolarizability, the resulting contribution to the dipole moment has *twice* the frequency of the originally perturbing field.

It can be shown that the response functions in Eq. (111) and thus the frequency-dependent properties of interest can be determined as derivatives of the so-called time-averaged quasi energy[139]. The latter is given as

$$Q(t) = \langle\tilde{\Psi}|(H - i\frac{\partial}{\partial t})|\tilde{\Psi}\rangle \tag{113}$$

with the phase-isolated wavefunction

$$|\Psi\rangle = \exp(-iF(t))|\tilde{\Psi}\rangle \tag{114}$$

with

$$\frac{dF(t)}{dt} = \langle\tilde{\Psi}|(H - i\frac{\partial}{\partial t})|\tilde{\Psi}\rangle \tag{115}$$

defined in such a way that it coincides in the static case with the usual time-independent wavefunction. Time averaging of $Q(t)$ is performed in such a manner

$$\{Q(t)\}_T = \lim_{T\to\infty}\frac{1}{T}\int_{-T/2}^{T/2} Q(t)dt \tag{116}$$

that T corresponds to multiples of all periods of the considered perturbations.

It can be then demonstrated that the expectation value $\langle X \rangle_0$ corresponds to the first derivative of $\{Q(t)\}$ with respect to the corresponding field strengths[n]

$$\langle X \rangle_0 = \frac{d\{Q\}_T}{d\epsilon_X(0)}, \tag{117}$$

the linear response function to the corresponding second derivative

$$\langle\langle X; Y \rangle\rangle_{\omega_{k_1}} = \frac{d^2\{Q\}_T}{d\epsilon_X(\omega_0) d\epsilon_Y(\omega_{k_1})} \tag{118}$$

with

$$\omega_0 = -\omega_{k_1}, \tag{119}$$

the quadratic response function to the corresponding third derivative

$$\langle\langle X; Y, Z \rangle\rangle_{\omega_{k_1}, \omega_{k_2}} = \frac{d^3\{Q\}_T}{d\epsilon_X(\omega_0) d\epsilon_Y(\omega_{k_1}) d\epsilon_Z(\omega_{k_2})} \tag{120}$$

with

$$\omega_0 = -\omega_{k_1} - \omega_{k_2}, \tag{121}$$

etc. Time-averaging is essential in order to obtain these simple expressions for the response functions. The trick is that time averaging *extracts* the relevant terms from the quasi-energy $Q(t)$ and enforces proper matching of frequencies (as seen in Eqs. (119) and (121)).

The time dependent variation principle can be rewritten in our case as

$$\delta\{Q\}_T = 0. \tag{122}$$

To obtain explicit equations for the wavefunction parameters, it is convenient to expand them in terms of the Fourier components of the perturbations

$$\begin{aligned} c(t) = c^{(0)} &+ \sum_{k_1} \exp(-i\omega_{k_1} t) c^{(1)}(\omega_{k_1}) \\ &+ \sum_{k_1 k_2} \exp(-i(\omega_{k_1} + \omega_{k_2})t) c^{(2)}(\omega_{k_1}, \omega_{k_2}) + ... \end{aligned} \tag{123}$$

and then require fulfillment of the variational condition (Eq. (122)) for each order of the perturbation. This yields in first order

$$\frac{\partial\{Q\}_T}{\partial c^{(0)}} = 0, \tag{124}$$

which is identical to the usual time-independent stationarity condition for c. In higher orders, the following conditions are obtained

$$\frac{d}{d\epsilon_X(\omega_1)} \left(\frac{\partial\{Q\}_T}{\partial c^{(1)}(\omega_2)} \right) = 0 \tag{125}$$

with $\omega_1 = -\omega_2$

$$\frac{d^2}{d\epsilon_X(\omega_1) d\epsilon_Y(\omega_2)} \left(\frac{\partial\{Q\}_T}{\partial c^{(2)}(\omega_3, \omega_4)} \right) = 0 \tag{126}$$

---

[n] Note that all derivatives are taken at the point $\epsilon_X(\omega) = 0, \epsilon_Y(\omega) = 0, ...$

with $\omega_1 + \omega_2 = -\omega_3 - \omega_4$, etc.

For non-variational wavefunction parameters, the same technique as in the static case is used. Accordingly, the derivatives of $Q(t)$ in Eqs. (117) to (126) are replaced by the corresponding derivatives of an energy functional $\tilde{Q}(t)$ (in Ref. 139 called the Lagrangian $L(t)$) with the latter obtained by augmenting $Q(t)$ with the corresponding time-dependent equations ($g(c,t) = 0$) for the wavefunction parameters

$$\tilde{Q}(t) = Q(t) + \lambda g(c,t). \tag{127}$$

Note that in this case, it is sometimes necessary to symmetrize the corresponding expressions for the response functions in order to ensure proper symmetry relations (for a detailed discussion see, for example, section 2.C and 3D of Ref. 139). The symmetrization needs to be carried out with respect to simultaneous complex conjugation and inversion of the sign of the involved frequencies.

With Eqs. (111) to (127), the required theory (usually referred to as *response theory*) for the calculation of frequency-dependent properties is summarized. The given expressions differ from those in the static case mainly by the fact that the energy (the key quantity for static properties) is replaced by the corresponding time-averaged quasi-energy (the key quantity for dynamical properties). However, the same techniques as in the static case, i.e. $(2n + 1)$ and $(2n + 2)$ rules, can be used to deduce computationally efficient expressions for the calculation of dynamical properties.

4.2 Specific examples

As first example, the computation of frequency-dependent polarizabilities at the closed-shell HF-SCF level will be sketched. The corresponding quasi-energy is given in that case by

$$\begin{aligned} Q(t) = & \sum_{\mu\nu} P_{\mu\nu}(t) h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu} \sum_{\sigma\rho} P_{\mu\nu}(t) P_{\sigma\rho}(t) (\langle \mu\sigma|\nu\rho\rangle - \frac{1}{2}\langle \mu\sigma|\rho\nu\rangle) \\ & - i \sum_{i} \sum_{\mu\nu} c^*_{\nu i}(t) S_{\mu\nu} \frac{\partial c_{\mu i}}{\partial t}. \end{aligned} \tag{128}$$

In comparison to the usual HF-SCF energy expression (Eq. (19)), we note that in Eq. (128) MO coefficients (and thus also the density matrix elements) carry an explicit time-dependence and that there is one additional term, namely the one which involves the time derivative of the MO coefficients. As we need to ensure the orthonormality of the MOs, the appropriate starting point is given by the following functional

$$\tilde{Q}(t) = Q(t) - 2 \sum_{i} \varepsilon_{ij} \sum_{\mu\nu} c^*_{\mu i} S_{\mu\nu} c_{\nu j} \tag{129}$$

where we augment the quasi-energy by the orthonormality constraint multiplied with the corresponding, now time-dependent Lagrangian multipliers ε_{ij}.

Following Eq. (123), the MO coefficients $c_{\mu i}(t)$ are expanded in terms of the Fourier components of the electric field perturbations

$$c_{\mu i}(t) = c_{\mu i} + \sum_{k_1} \exp(-i\omega_{k_1} t) c^{(1)}_{\mu i}(\omega_{k_1}) + \sum_{k_1 k_2} \exp(-i(\omega_{k_1} + \omega_{k_2})t) c^{(2)}_{\mu i}(\omega_{k_1}, \omega_{k_2}) + ... \tag{130}$$

$$= c_{\mu i} + \sum_{k_1} \exp(-i\omega_{k_1} t) \sum_X \epsilon_X(\omega_{k_1}) c^X_{\mu i}(\omega_{k_1})$$

$$+ \sum_{k_1 k_2} \exp(-i(\omega_{k_1} + \omega_{k_2})t) \sum_{X,Y} \epsilon_X(\omega_{k_1}) \epsilon_Y(\omega_{k_2}) c^{XY}_{\mu i}(\omega_{k_1}, \omega_{k_2}) + ... \tag{131}$$

Thus, the perturbed coefficients $c^X_{\mu i}(\omega_{k_1}), c^{XY}_{\mu i}(\omega_{k_1}, \omega_{k_2}), ...$ completely characterize the time-dependence of the HF wavefunction. Furthermore, as common in CPHF theory, these coefficients are expanded in terms of the unperturbed MO coefficients

$$c^X_{\mu i}(\omega) = \sum_p c_{\mu p} U^X_{pi}(\omega) \tag{132}$$

with the $U^X_{pi}(\omega)$ as the actual parameters to be determined in the calculation. Similar parametrizations are also used for the higher-order MO coefficients.

Differentiation of $\{\tilde{Q}(t)\}_T$ with respect to electric field components $\epsilon_X(\omega_1)$ and $\epsilon_Y(\omega_2)$ yields then for the frequency-dependent polarizability

$$\alpha_{XY}(\omega_1; \omega_2) = -2 \sum_a \sum_i U^Y_{ai}(-\omega_2) h^X_{ia} - 2 \sum_a \sum_i h^X_{ai} U^Y_{ai}(\omega_2) \tag{133}$$

with

$$\omega_1 = -\omega_2. \tag{134}$$

Corresponding expressions for the hyperpolarizabilities can be found in the literature. They are most conveniently derived using the $(2n + 1)$ rule.

The required coefficients $U^X_{ai}(\omega_{k_1})$ are determined via the so-called time-dependent HF (TDHF) equations which are obtained by differentiating the quasi-energy with respect to MO coefficients $c^{(1)}_{\mu i}$ and the corresponding electric field strengths $\epsilon_X(\omega_1)$. After some rearrangements, the following equations are obtained[o]

$$\sum_{em} (2\langle am|ie\rangle - \langle am|ie\rangle - \omega) U^X_{em}(\omega) + \sum_{em} (2\langle ae|im\rangle - \langle ae|mi\rangle) U^X_{em}(-\omega) = -h^X_{ai}$$

$$\sum_{em} (2\langle am|ie\rangle - \langle am|ie\rangle + \omega) U^X_{em}(-\omega) + \sum_{em} (2\langle ae|im\rangle - \langle ae|mi\rangle) U^X_{em}(\omega) = -h^X_{ai} \tag{135}$$

which can be solved in the usual iterative manner. The TDHF equations resemble very much the usual CPHF equations (compare Eq. (32)). Indeed, the CPHF equations for electric perturbations are obtained in the static limit ($\omega \to 0$), in which $U^X_{ai}(\omega) = U^X_{ai}(-\omega)$. Note that for the time-dependent case, the perturbed

---

[o] Note that for electric perturbations U^X_{ij} is zero.

coefficients for ω and $-\omega$, i.e. $U_{ai}^X(\omega)$ and $U_{ai}^X(-\omega)$ couple and need to determined together.

As a second example, we discuss the computation of frequency-dependent properties within CC theory. The appropriate starting point is here the following quasi-energy functional

$$\tilde{Q}(t) = \langle 0|(1+\Lambda(t))\exp(-T(t))(H - i\frac{\partial}{\partial t})\exp(T(t))|0\rangle. \tag{136}$$

obtained by augmenting the CC quasi-energy with the time-dependent CC equations multiplied by the time-dependent Lagrangian multipliers $\lambda_p(t)$. Orbital relaxation contributions are in Eq. (136) not considered. While for most static properties (geometrical derivatives, magnetic properties, i.e., in general all properties for which perturbation-dependent basis functions are used) inclusion of orbital relaxation is mandatory, the opposite is true for dynamical properties. A closer analysis reveals that a correct pole structure (see the discussion in Ref. 139) is only ensured if orbital relaxation effects are treated via the single excitations (T_1) in an indirect manner and not explicitly included. Explicit consideration of orbital relaxation on the other hand would lead to additional (artificial) second-order poles[139] and thus to an unphysical behavior of the response functions. A further advantage of the so-called *unrelaxed* approach is that the theory as well as corresponding computer implementations are considerably simplified.

For the frequency-dependent polarizability, the following expression is obtained in CC theory

$$\begin{aligned}\alpha_{XY}(-\omega;\omega) = & -\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial Y}\exp(T), T^X(\omega)]0\rangle \\ & -\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial X}\exp(T), T^Y(-\omega)]0\rangle \\ & -\langle 0|(1+\Lambda)[[\exp(-T)H\exp(T), T^Y(-\omega)], T^X(\omega)]|0\rangle \end{aligned} \tag{137}$$

with the perturbed cluster operator $T^X(\omega)^p$ determined as solution of the following equations

$$0 = \langle \Phi_p|\exp(-T)\frac{\partial H}{\partial X}\exp(-T)|0\rangle + \langle \Phi_p|[\exp(-T)(H-\omega)\exp(T), T^X(\omega)]|0\rangle. \tag{138}$$

Corresponding expressions for first and second hyperpolarizabilities have been given in the literature[150,151,154].

4.3 Available implementations

The time-dependent HF scheme for the calculation of frequency-dependent properties has been implemented by Sekino and Bartlett[140] in the eighties employing a general formulation that allows computation of arbitrary polarizabilities and hyperpolarizabilities. This development was later followed by other implementations

---

[p] In line with Eq. (123), $T^X(\omega)$ is defined via the first-order term in the Fourier expansion of $T(t)$.

(see, for example, Refs. 141 and 142); all of them nowadays allow the routine computation of frequency-dependent properties at the HF-SCF level. Concerning the treatment of electron correlation, a first major effort has been made by Rice and Handy[143] to derive and implement frequency-dependent polarizabilities at the MP2 level. As amply discussed in the literature, a correct formulation and implementation of MP2 frequency-dependent polarizabilities (within response theory) has been only achieved later[144,145]. MP2 calculations of first and second hyperpolarizabilities have recently been reported by Kobayashi *et al.*[146]

At the CC level, response theory was first formulated by Monkhorst[147] in 1977. A first implementation for the computation of frequency-dependent polarizabilities was reported in 1994 within the CCSD approximation[148]. An earlier simplified variant based on an equation-of-motion CC ansatz[149] has turned out less satisfying, as it lacked the important property of size extensivity. CCSD calculations for hyperpolarizabilities were first presented by Hättig *et al.*[150,151] in 1997 and 1998. Concerning inclusion of triple excitations, it is important to recognize that the otherwise highly popular CCSD(T) ansatz is not well suited for the calculation of unrelaxed properties. Considering this, Christiansen *et al.* devised a new hierarchy of CC models[152] consisting of CCS, CC2, CCSD, CC3, etc. for the calculation of dynamical properties. CCS only includes single excitations (CCS energies are identical to the corresponding HF-SCF energies, higher-order response-properties, however, differ), CC2 truncates the doubles equations to lowest order, CCSD involves a full treatment of single and double excitations, while CC3 includes for the first time triple excitations with the triples equations truncated to lowest order. To ensure an adequate treatment of orbital relaxation, it is mandatory in this hierarchy of CC models to consider single excitations (T_1) — contrary to usual perturbation arguments — as zeroth order. CC3 implementations for the computation of dynamical polarizabilities and hyperpolarizabilities have recently reported by Christiansen *et al.*[153,154] and for the first time allow near-quantitative predictions for these type of properties (see, for example, Ref. 155).

Finally, it should be mentioned that a lot of effort has been also devoted to compute frequency-dependent properties at the MCSCF level[156−158] and that there is — as for other properties — a great interest in DFT computations of these properties employing time-dependent DFT techniques (see, for example, Ref. 159).

4.4 Example

As an example for the computation of frequency-dependent properties, we show in Fig. 8 the dispersion curve for the refractive index n of N_2. The latter is related to the (frequency-dependent) isotropic polarizability $\overline{\alpha}$ via

$$n \; = 1 + 2\pi \, \overline{\alpha}(\omega) N. \tag{139}$$

Fig. 8 compares results obtained at SCF and various CC levels[q] with those from experimental investigations.[160] It is clearly seen how the results improve (in comparison with experiment) within the CC hierarchy and that CC3 yields by far the best agreement with experiment.

---

[q] All calculations have been carried out for $r(NN) = 2.068$ bohr with the aug-pVQZ basis.

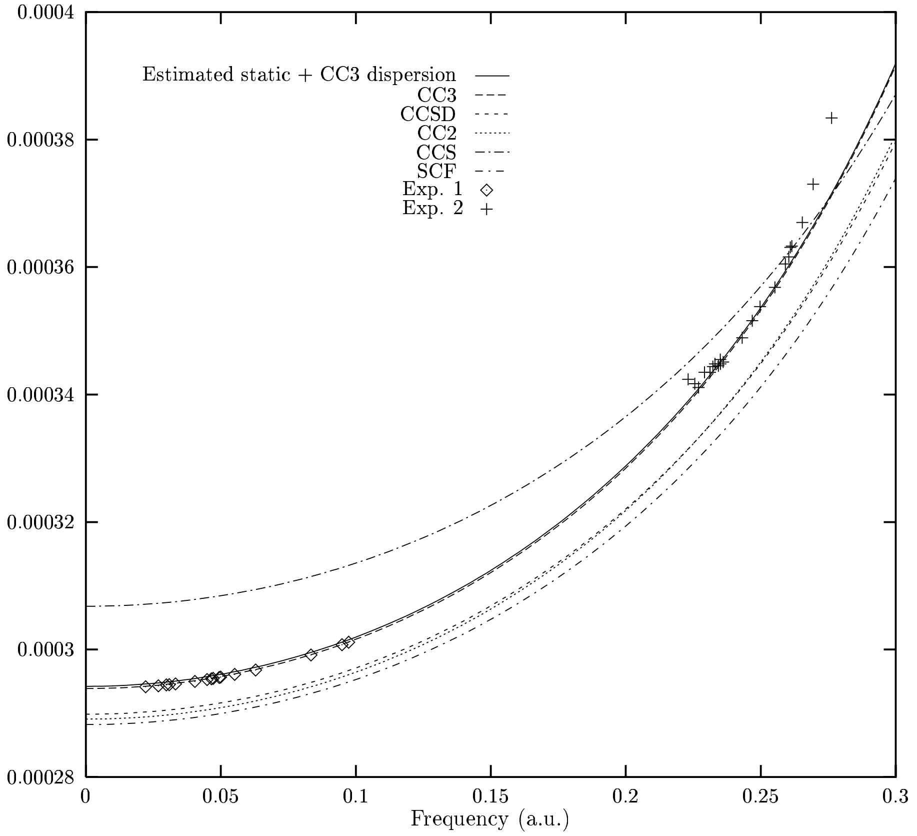


Fig. 8: Refractive index of N_2 as calculated at SCF and various CC levels in comparison with experiment.

5 Summary

The basic concepts for the quantum chemical calculation of molecular properties have been discussed. Focussing on properties specific to a given electronic state, analytic derivative techniques are the essential prerequisite for the accurate and efficient computation of the required energy derivatives. Analytic derivatives techniques have been proven especially important for the computation of magnetic properties. Problems inherent to their calculation such as gauge-origin dependence of the results and slow basis set convergence are best dealt with by using GIAOs, i.e. explicitly magnetic-field dependent basis functions.

The derivative approach to molecular properties can also be extended to dynamical properties. In the framework of response theory, these kind of properties are computed via the corresponding derivatives of the so-called time-averaged quasi energy. As the expressions for dynamical properties coincide in the zero-frequency limit with those for the corresponding static properties, response theory represents a *unifying* concept for molecular properties that covers both the static and dynamic case but also enables computation of excitation energies (via the poles of the response functions) and transition strengths (via the residues of the response functions at the poles).

The importance of the presented concepts can be hardly overestimated, as computation of molecular properties plays a major role in almost all modern applications of quantum chemistry. In this way, it is certainly justified to consider the introduction of analytic derivative techniques (Pulay's paper on HF-SCF gradients in 1969) as an important mile stone in quantum chemistry. There is no doubt that computation of molecular properties as well as method development in this area of quantum chemistry will remain an important topic in the future.

Acknowledgments

The author thanks Dr. Christian Ochsenfeld, Alexander Auer, and Oliver Heun for helpful discussions and a careful reading of the manuscript.

References

1. See, for example, P.W. Atkins, *Molecular Quantum Mechanis*, Oxford University Press, Oxford, 1983, Chapter 13.
2. See, for example, P.W. Atkins, *Molecular Quantum Mechanis*, Oxford University Press, Oxford, 1983, Chapter 5.
3. J. Hellmann, *Einführung in die Quantenchemie*, Deuticke & Co, (1937); R.P. Feynman, *Phys. Rev.* **56**, 340 (1939).
4. See, for example, the discussion by P. Pulay in *Modern Electronic Structure Theory*, D. Yarkony (Ed.), World Scientific, Singapore, 1995, p. 1191.
5. H.B. Schlegel, in *Modern Electronic Structure Theory*, D. Yarkony (Ed.), World Scientific, Singapore, 1995, p. 459.
6. I.M. Mills, in *Modern Spectroscopy: Modern Research*, K.N. Rao, C.W. Matthews, Eds., Academic Press, New York, 1972, p. 115.
7. W.H. Flygare, *Molecular Structure and Dynamics*, Prentice-Hall, Englewood Cliffs, 1978.
8. W. Weltner, Jr., *Magnetic Atoms and Molecules*, Dover, New York, 1989.
9. W. Schneider, W. Thiel, *Chem. Phys. Lett.* **157**, 367 (1989).
10. P. Jørgensen, T. Helgaker, *J. Chem. Phys.* **89**, 1560 (1988); T. Helgaker, P. Jørgensen, *Theor. Chim. Acta* **75**, 111 (1989).
11. A. Dalgarno, A.L. Stewart, *Proc. Roy. Soc.* **A247**, 245 (1958).
12. A. Szabo, N.S. Ostlund, *Modern Quantum Chemistry*, Mc Graw-Hill, New York, 1989, chapter 3.
13. P. Pulay, *Mol. Phys.* **17**, 197 (1969).
14. See, for example, T. Helgaker, P.R. Taylor, in *Modern Electronic Structure Theory*, D. Yarkony (Ed.), World Scientific, Singapore, 1995, p. 725.
15. J. Gerrat, I.M. Mills, *J. Chem. Phys.* **49**, 1719 (1968).
16. J.A. Pople, R. Krishnan, H.B. Schlegel, J.S. Binkley, *Int. J. Quantum. Chem.*

Symp. **13**, 225 (1979).

17. For recent reviews on CC theory, see: R.J. Bartlett, J.F. Stanton, in *Reviews in Computational Chemistry*, Vol. **5**, K.B. Lipkowitz, D.B. Boyd (Eds.), VCH Publisher, New York 1994, p. 65 ff; T.J. Lee, G.E. Scuseria, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, S.R. Langhoff (Ed.), Kluwer Academic Publisher, Dordrecht, 1995, p. 47 ff; R.J. Bartlett, in *Modern Electronic Structure Theory*, D.R. Yarkony (Ed.), World Scientific, Singapore, 1995, p. 1047 ff; J. Gauss, in *Encyclopedia of Computational Chemistry*, P.v.R. Schleyer (Eds.), Wiley, New York, 1998, p. 615 ff.
18. L. Adamowicz, W.D. Laidig, R.J. Bartlett, *Int. J. Quant. Chem. Symp.* **18**, 245 (1984).
19. J.E. Rice, R.D. Amos, *Chem. Phys. Lett.* **122** 585 (1985).
20. R.J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, P. Jørgensen, J. Simons (Eds.), Reidel, Dordrecht, 1986, p. 35.
21. N.C. Handy, H.F. Schaefer, *J. Chem. Phys.* **81**, 5031 (1984).
22. A.C. Scheiner, G.E. Scuseria, J.E. Rice, T.J. Lee, H.F. Schaefer, *J. Chem. Phys.* **87**, 5361 (1987).
23. J. Gauss, J.F. Stanton, R.J. Bartlett, *J. Chem. Phys.* **95**, 2623 (1991).
24. E.A. Salter, G.W. Trucks, R.J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989).
25. G.E. Scuseria, H.F. Schaefer, *Chem. Phys. Lett.* **146**, 23 (1988).
26. G.E. Scuseria, *J. Chem. Phys.* **94**, 442 (1991).
27. T.J. Lee, A.P. Rendell, *J. Chem. Phys.* **94**, 6229 (1991).
28. J.D. Watts, J. Gauss, R.J. Bartlett, *Chem. Phys. Lett.* **200**, 1 (1992).
29. J. Gauss, J.F. Stanton, *Phys. Chem. Chem. Phys.* **2**, 2047 (2000).
30. J. Gauss, J.F. Stanton, in *Recent Advances in Coupled-Cluster Methods*, R.J. Bartlett (Ed.), World Scientific, Singapore, 1997, p. 49.
31. J. Gauss, J.F. Stanton, *Chem. Phys. Lett.* **276**, 70 (1997).
32. S. Bratoz, *Colloq. Int. CNRS* **82**, 287 (1958). See also, M. Allavena, S. Bratoz, *J. Chim. Phys.* **60**, 1199 (1963) and M. Allavena, *Theoret. Chim. Acta* **5**, 21 (1966).
33. For first applications of HF-SCF gradients see, for example, P. Pulay, *Mol. Phys.* **18**, 473 (1970); *Mol. Phys.* **21**, 329 (1971); P. Pulay, W. Meyer, *J. Mol. Spectrosc.* **41**, 59 (1971); *J. Chem. Phys.* **57**, 3337 (1972).
34. N.C. Handy, R.D. Amos, J.F. Gaw, J.E. Rice, E.D. Simandiras, T.J. Lee, R.J. Harrison, W.D. Laidig. G.B. Fitzgerald, R.J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, P. Jørgensen, J. Simons (Eds.), Reidel, Dordrecht, 1986, p. 179.
35. N.C. Handy, R.D. Amos, J.F. Gaw, J.E. Rice, E.D. Simandiras, *Chem. Phys. Lett.* **120**, 151 (1985).
36. R.J. Harrison, G.B. Fitzgerald, W.D. Laidig, R.J. Bartlett, *Chem. Phys. Lett.* **124**, 291 (1986).
37. L. Verluis, T. Ziegler, *J. Chem. Phys.* **88**, 322 (1988).
38. R. Fournier, J. Andzelm, D. Salahub, *J. Chem. Phys.* **90**, 3671 (1989).
39. B. Delley, *J. Chem. Phys.* **94**, 7245 (1991).
40. S. Kato, K. Morokuma, *Chem. Phys. Lett.* **65**, 19 (1979).
41. J.D. Goddard, N.C. Handy, H.F. Schaefer, *J. Chem. Phys.* **71**, 1525 (1979).

42. G.B. Fitzgerald, R. Harrison, W.D. Laidig, R.J. Bartlett, *J. Chem. Phys.* **82**, 4379 (1985).
43. J. Gauss, D. Cremer, *Chem. Phys. Lett.* **138**, 131 (1987).
44. J. Gauss, D. Cremer, *Chem. Phys. Lett.* **153**, 303 (1988).
45. G.W. Trucks, J.D. Watts, E.A. Salter, R.J. Bartlett, *Chem. Phys. Lett.* **153**, 490 (1988).
46. B.R. Brooks, W.D. Laidig, P. Saxe, J.D. Goddard, Y. Yamaguchi, H.F. Schaefer, *J. Chem. Phys.* **72**, 4652 (1980).
47. R. Krishnan, H.B. Schlegel, J.A. Pople, *J. Chem. Phys.* **72**, 4654 (1980).
48. J.E. Rice, T.J. Lee, N.C. Handy, *J. Chem. Phys.* **88**, 7011 (1988).
49. J. Gauss, D. Cremer, *Chem. Phys. Lett.* **150**, 280 (1988).
50. J. Gauss, D. Cremer, *Chem. Phys. Lett.* **163**, 549 (1989).
51. R. Shepard, H. Lischka, P.G. Szalay, T. Kovar, M. Ernzerhof, *J. Chem. Phys.* **96**, 351 (1991).
52. N.C. Handy, D.J. Tozer, C.W. Murray, G.J. Laming, R.D. Amos, *Isr. J. Chem.* **33**, 331 (1993).
53. B.G. Johnson, M.J. Frisch, *J. Chem. Phys.* **100**, 7429 (1994).
54. M.R. Hoffmann, D.J. Fox, J.F. Gaw, Y. Osamura, Y. Yamaguchi, R.S. Grev, G. Fitzgerald, H.F. Schaefer, P.J. Knowles, N.C. Handy, *J. Chem. Phys.* **80**, 2660 (1984).
55. D.J. Fox, Y. Osamura, M.R. Hoffmann, J.F. Gaw, G. Fitzgerald, Y. Yamaguchi, H.F. Schaefer, *Chem. Phys. Lett.* **102**, 17 (1983).
56. H. Koch, H.J.Aa. Jensen, P. Jørgensen, T. Helgaker, G.E. Scuseria, H.F. Schaefer, *J. Chem. Phys.* **92**, 4924 (1990).
57. J.F. Gaw, Y. Yamaguchi, H.F. Schaefer, *J. Chem. Phys.* **81**, 6395 (1984).
58. M.J. Frisch, M. Head-Gordon, J.A. Pople, *Chem. Phys. Lett.* **166**, 275 (1990).
59. M.J. Frisch, M. Head-Gordon, J.A. Pople *Chem. Phys. Lett.* **166**, 281 (1990).
60. F. Haase, R. Ahlrichs, *J. Comp. Chem.* **14**, 907 (1993).
61. B.G. Johnson, M.J. Frisch, *Chem. Phys. Lett.* **216**, 133 (1993).
62. S.P. Brown, I. Schnell, J.D. Brand, K. Müllen, H.W. Spiess, *J. Mol. Struct.*, in press (2000).
63. C. Ochsenfeld, *Phys. Chem. Chem. Phys.* **2**, 2153 (2000).
64. C. Ochsenfeld, *Chem. Phys. Lett.*, in press.
65. J.M. Vrtilek, C.A. Gottlieb, E.W. Gottlieb, T.C. Killian, P. Thaddeus, *Astrophys. J.* **364**, L53 (1990); J. Cernicharo, C.A. Gottlieb, M. Guélin, T.C. Killian, G. Paubert, P. Thaddeus, J.M. Vrtilek, *Astrophys. J.* **138**, L39 (1991).
66. G. Maier, H.-P. Reisenauer, W. Schwab, P. Carsky, B.A. Hess, L.J. Schaad, *J. Amer. Chem. Soc.* **109**, 5183 (1987).
67. C.A. Gottlieb, T.C. Killian, P. Thaddeus, P. Botschwina, J. Flügge, M. Oswald, *J. Chem. Phys.* **98**, 4478 (1993).
68. J. Gauss, J.F. Stanton, *J. Mol. Struct.* **485–486**, 43 (1999); J.F. Stanton, J. Gauss, *Int. Rev. Phys. Chem.* **19**, 61 (2000).
69. L.D. Landau, E.M. Lifschitz, *Lehrbuch der Theoretischen Physik, Bd. II*, Akademie-Verlag, Berlin, 1981, p 120 ff.
70. A. Abragam, *The Principles of Nuclear Magnetic Resonance*, Oxford University Press, Oxford, 1961.

71. L.D. Landau, E.M. Lifschitz, *Lehrbuch der Theoretischen Physik, Bd. II*, Akademie-Verlag, Berlin, 1981, p 120 ff.
72. See, for example, I. Mills, T. Cvitas, K. Homann, N. Kallay, K. Kuchitsu, *Quantities, Units and Symbols in Physical Chemistry*, Blackwell, Oxford, 1993, p. 119 ff.
73. W. Kutzelnigg, *J. Mol. Struct. (Theochem)*, **202**, 11 (1989).
74. W. Kutzelnigg, *Isr. J. Chem.* **19**, 193 (1980).
75. M. Schindler, W. Kutzelnigg, *J. Chem. Phys.* **76**, 1919 (1982).
76. A.E. Hansen, T.D. Bouman, *J. Chem. Phys.* **82**, 5035 (1985).
77. F. London, *J. Phys. Radium* **8**, 397 (1937).
78. H.F. Hameka, *Mol. Phys.* **1**, 203 (1858); H.F. Hameka, *Mol. Phys.* **2**, 64 (1959).
79. R. Ditchfield, *Mol. Phys.* **27**, 789 (1974).
80. K. Wolinski, J.F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **112**, 8251 (1990).
81. See, for example, F. Boys, *Rev. Mod. Phys.* **32**, 296 (1960); J.M. Foster, S.F. Boys, *Rev. Mod. Phys.* **32**, 300 (1960); C. Edminston, K. Ruedenberg, *Rev. Mod. Phys.* **35**, 457 (1963).
82. P. Pulay, J.F. Hinton, K. Wolinski, in *Nuclear Magnetic Shieldings and Molecular Structure*, J.A. Tossell, Ed., Kluwer, Dordrecht, 1993, p. 243.
83. P. Pulay, *Adv. Chem. Phys.* **69** (1987) 241.
84. For a review (in German) , see, P. Buzek, P. von R. Schleyer, S. Sieber, *Chemie in unserer Zeit* **26**, 116 (1992).
85. J. Gauss, *Chem. Phys. Lett.* **191** , 614 (1992).
86. J. Gauss, *J. Chem. Phys.* **99**, 3629 (1993).
87. K. Ruud, T. Helgaker, R. Kobayashi, P. Jørgensen, K.L. Bak, H.J.Aa Jensen, *J. Chem. Phys.* **100**, 8178 (1994).
88. J. Gauss, *Chem. Phys. Lett.* **229**, 198 (1994).
89. J. Gauss, J.F. Stanton, *J. Chem. Phys.* **102**, 251 (1995)
90. J. Gauss, J.F. Stanton, *J. Chem. Phys.* **103**, 3561 (1995).
91. J. Gauss, J.F. Stanton, *J. Chem. Phys.* **104**, 2574 (1996).
92. C. van Wüllen, W. Kutzelnigg, *Chem. Phys. Lett.* **205**, 563 (1993).
93. T.D. Bouman, A.E. Hansen, *Chem. Phys. Lett.* **175**, 292 (1990).
94. V.G. Malkin, O.L. Malkina, D.R. Salahub, *Chem. Phys. Lett.* **204**, 80 (1993).
95. V.G. Malkin, O.L. Malkina, M.E. Casida, D.R. Salahub, *J. Am. Chem. Soc.* **116**, 5898 (1994).
96. G. Schreckenbach, T. Ziegler, *J. Phys. Chem.* **99**, 606 (1995).
97. G. Rauhut, S. Puyear, K. Wolinski, P. Pulay, *J. Phys. Chem.* **100**, 6310 (1996).
98. J.R. Cheeseman, G.W. Trucks, T.A. Keith, M.J. Frisch, *J. Chem. Phys.* **104**, 5497 (1996).
99. A.M. Lee, N.C. Handy, S.M. Colwell, *J. Chem. Phys.* **103**, 10095 (1995).
100. L. Olsson, D. Cremer, *J. Chem. Phys.* **105**, 8995 (1996).
101. L. Olsson, D. Cremer, *J. Phys. Chem.* **100**, 16881 (1996).
102. P.J. Wilson, R.D. Amos, N.C. Handy, *Chem. Phys. Lett.* **312**, 475 (1999).
103. G. Vignale, M. Rasolt, *Phys. Rev. B* **37**, 10685 (1988); G. Vignale, M. Rasolt, D.J.W. Geldart, *Adv. Quant. Chem.* **21**, 235 (1990).

104. C.J. Grayce, R.A. Harris, *Phys. Rev. A* **50**, 3089 (1994); *J. Phys. Chem.* **99**, 2724 (1995); F.R. Salsbury, R.A. Harris, *J. Chem. Phys.* **107**, 7350 (1997); *Chem. Phys. Lett.* **279**, 247 (1997).
105. M. Häser, R. Ahlrichs, H.P. Baron, P. Weis, H. Horn, *Theor. Chim. Acta* **83**, 435 (1992).
106. U. Meier, C. van Wüllen, M. Schindler *J. Comp. Chem.* **13**, 551 (1992).
107. M. Kollwitz, J. Gauss, *Chem. Phys. Lett.* **260**, 639 (1996).
108. M. Kollwitz, M. Häser, J. Gauss, *J. Chem. Phys.* **108**, 8295 (1998).
109. S. Saebø, P. Pulay, *Ann. Rev. Phys. Chem.* **44**, 213 (1993) and references therein.
110. C. Hampel, H.J. Werner, *J. Chem. Phys.* **104**, 6286 (1996); M. Schütz, G. Hetzer, H.-J. Werner, *J. Chem. Phys.* **111**, 5691 (1999); M. Schütz, G. Hetzer, H.-J. Werner, *J. Chem. Phys.*, submitted.
111. J. Gauss, H.-J. Werner, *Phys. Chem. Chem. Phys.* **2**, 2083 (2000).
112. M. Kaupp, O.L. Malkina, V.G. Malkin, P. Pyykkö, *Chem. Eur. J.* **4**, 118 (1998).
113. H. Nakatsuji, H. Takashima, M. Hada, *Chem. Phys. Lett.* **233**, 95 (1995).
114. V.G. Malkin, O.L. Malkina, D.R. Salahub, *Chem. Phys. Lett.* **261**, 335 (1996).
115. J. Vaara, K. Ruud, O. Vahtras, H. Ågren, J. Jokisaari, *J. Chem. Phys.* **109**, 1212 (1998).
116. G. Schreckenbach, T. Ziegler, *Int. J. Quantum Chem.* **60**, 753 (1996).
117. D. Sundholm, J. Gauss, A. Schäfer, *J. Chem. Phys.* **105**, 11051 (1996).
118. A. Auer, J. Gauss, J.F. Stanton, to be published.
119. K. Ruud, P.-O. Åstrand, P.R. Taylor, *J. Chem. Phys.* **112**, 2668 (2000).
120. D. Cremer, L. Olsson, F. Reichel, E. Kraka, *Isr. J. Chem.* **33**, 369 (1993).
121. K.V. Mikkelsen, P. Jørgensen, K. Ruud, T. Helgaker, *J. Chem. Phys.* **106**, 1170 (1997).
122. R. Cammi, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **110**, 7627 (1999).
123. H.-U. Siehl, T. Müller, J. Gauss, P. Buzek, P.von R. Schleyer, *J. Am. Chem. Soc.* **116**, 6384 (1994); J.F. Stanton, J. Gauss, H.-U. Siehl, *Chem. Phys. Lett.* **262**, 183 (1996); J. Gauss, J.F. Stanton, *J. Mol. Struct. (Theochem)* **398–399**, 73 (1997).
124. J. Gauss, U. Schneider, R. Ahlrichs, C. Dohmeier, H. Schnöckel, *J. Am. Chem. Soc.* **115**, 2402 (1993).
125. S.P. Brown, I. Schnell, J.D. Brand, K. Müllen, H.W. Spiess, *J. Am. Chem. Soc.*, **121**, 6712 (1999).
126. C. Ochsenfeld, S.P. Brown, I. Schnell, J. Gauss, H.W. Spiess, *J. Am. Chem. Soc.*, to be submitted (2000).
127. J. Kowalewski, *Prog. NMR Spectr.* **11**, 1 (1977); J. Kowalewski, A. Laaksonen, in *Theoretical Models of Chemical Bonding, Part 3*, Z.B. Maksic (Ed.), Springer, Berlin, 1991, p. 386 ff.
128. J. Geertsen, J. Oddershede, G.E. Scuseria, *J. Chem. Phys.* **87**, 2138 (1987).
129. J. Oddershede, J. Geertsen, G.E. Scuseria, *J. Phys. Chem.* **92**, 3056 (1988); J. Geertsen, J. Oddershede, G.E. Scuseria, *Magn. Reson.* **93**, 455 (1991).
130. T. Helgaker, M. Jaszunski, K. Ruud, A. Gorska, *Theor. Chem. Acc.* **99**, 175

(1998).

131. O. Vahtras, H. Ågren, P. Jørgensen, H.J.Aa. Jensen, S.B. Padkjaedr, T. Helgaker, *J. Chem. Phys.* **96**, 6120 (1992).
132. A. Barszcewicz, M. Jaszunski, K. Trela-Kamienska, T. Helgaker, P. Jørgensen, O. Vahtras, *Theor. Chim. Acta* **87**, 19 (1993); K. Ruud, T. Helgaker, P. Jørgensen, K.L. Bak, *Chem. Phys. Lett.* **226**, 1 (1994); T. Helgaker, M. Jaszunski, K. Ruud, *Mol. Phys.* **91**, 881 (1997).
133. S.A. Perera, H. Sekino, R.J. Bartlett, *J. Chem. Phys.* **101**, 2186 (1994); S.A. Perera, M. Nooijen, R.J. Bartlett, *J. Chem. Phys.* **104**, 3290 (1996).
134. S.A. Perera, R.J. Bartlett, P.v.R. Schleyer, *J. Am. Chem. Soc.* **117**, 8476 (1995); S.A. Perera, R.J. Bartlett, *J. Am. Chem. Soc.* **118**, 7849 (1996).
135. O.L. Malkina, D.R. Salahub, V.G. Malkin, *J. Chem. Phys.* **105**, 8793 (1996).
136. V. Sychrowsky, J. Gräfenstein, D. Cremer, *J. Chem. Phys.*, in press (2000).
137. D. P. Shelton, J. E. Rice, *Chem. Rev.* **94**, 3 (1994).
138. For a review, see D.M. Bishop, P. Norman, in *Handbook of Advanced Electronic and Photonic Materials*, H.S. Nalwa (Ed.), Academic Press, San Diego, in press (2000).
139. O. Christiansen, P. Jørgensen, C. Hättig, *Int. J. Quantum Chem.* **68**, 1 (1998).
140. H. Sekino, R.J. Bartlett, *J. Chem. Phys.* **85**, 976 (1986).
141. S.P. Karna, M. Dupuis, E. Perrin, P.N. Prasad, *J. Chem. Phys.* **92**, 7418 (1990); S.P. Karna, M. Dupuis, *J. Comp. Chem.* **12**, 487 (1991).
142. J.E. Rice, R.D. Amos, S.M. Colwell, N.C. Handy, J. Sanz, *J. Chem. Phys.* **93**, 8828 (1990).
143. J.E. Rice, N.C. Handy, *J. Chem. Phys.* **94**, 4959 (1991).
144. C. Hättig, B. Heß, *Chem. Phys. Lett.* **233**, 359 (1995).
145. F. Aiga, K. Sasagane, R. Itoh, *J. Chem. Phys.* **99**, 3779 (1993).
146. T. Kobayashi, K. Sasagane, F. Aiga, K. Yamaguchi, *J. Chem. Phys.* **110**, 11720 (1999); *J. Chem. Phys.* **111**, 842 (1999).
147. H.J. Monkhorst, *Int. J. Quantum Chem. Symp.* **S11**, 421 (1977).
148. R. Kobayashi, H. Koch, P. Jørgensen, *Chem. Phys. Lett.* **219**, 30 (1994).
149. J.F. Stanton, R.J. Bartlett, *J. Chem. Phys.* **98**. 3029 (1993).
150. C. Hättig, O. Christiansen, H. Koch, P. Jørgensen, *Chem. Phys. Lett.* **269**, 428 (1997).
151. C. Hättig, O. Christiansen, P. Jørgensen, *Chem. Phys. Lett.* **282**, 139 (1998).
152. O. Christiansen, H. Koch, P, Jørgensen, *Chem. Phys. Lett.* **243**, 409 (1995).
153. O. Christiansen, J. Gauss, J.F. Stanton, *Chem. Phys. Lett.* **292**, 437 (1998).
154. J. Gauss, O. Christiansen, J.F. Stanton, *Chem. Phys. Lett.* **296**, 117 (1998).
155. H. Larsen, J. Olsen, C. Hättig, P. Jørgensen, O. Christiansen, J. Gauss, *J. Chem. Phys.* **111**, 1917 (1999).
156. D.L. Yeager, P. Jørgensen, *Chem. Phys. Lett.* **65**, 77 (1979); J. Olsen, P. Jørgensen, *J. Chem. Phys.* **82**, 3235 (1985).
157. H. Hettema, H.J. Aa. Jensen, P. Jørgensen, J. Olsen, *J. Chem. Phys.* **97**, 1174 (1992).
158. D. Jonsson, P. Norman, H. Ågren, *J. Chem. Phys.* **105**, 6401 (1995).
159. S.J.A. Gisbergen, V.P. Osinga, O.V. Gritsenko, R. van Leeuwen, J.G. Snijders, E.J. Baerends, *J. Chem. Phys.* **105**, 3142 (1996); S.J.A. Gisber-

gen, J.G. Snijders, E.J. Baerends, *J. Chem. Phys.* **109**, 10644 (1998).

160. E.R. Peck, B.N. Khanna, *J. Opt. Soc. Am.* **56**, 1059 (1966); P.G. Wilkinson, *J. Opt. Soc. Am.* **50**, 1002 (1960).