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Direct computation of second-order SCF properties of large molecules on workstation computers with an application to large carbon clusters

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Summary. The ab initio SCF computation of second-order properties of large molecules (with 50 atoms or more) on workstation computers is demonstrated for static dipole polarizabilities and nuclear magneting shieldings. The magnetic shieldings are calculated on the basis of gauge including atomic orbitals (GIAO). Algorithmic advances (semi-direct algorithms with efficient integral pre-screening, and use of a quadratically convergent functional for the polarizabilities) are presented together with an illustrative application to the fullerenes C_{60} and C_{70}.

Key words: Direct – CPHF – GIAO – Polarizability – NMR – Magnetic shielding – Carbon – C_{60} – C_{70}

1 Introduction

The calculation of static dipole polarizabilities and nuclear magnetic shieldings at the self-consistent field (SCF) level of theory [1–3] has until recently [4–7] been restricted to relatively small molecules or small basis sets or powerful supercomputers (see, for example, ref. [8–10]). Basis set requirements for accurate polarizabilities, however, cannot be neglected [11, 12], and the gauge invariance problem poses an additional obstacle to calculations of nuclear magnetic shifts [3, 4, 13–15].

This has to be compared to the enormous successes in the calculation of SCF equilibrium geometries: molecular geometries with 40–100 atoms are now routinely optimized [16] with most calculations performed on workstation computers. This advance has been possible with the introduction of "direct" and "semi-direct" methods [17–19] which avoid or reduce the amount of storage and input/output (I/O) of electron repulsion integrals (ERI) over contracted gaussian type basis functions ("atomic orbitals" AO). Recently "direct" and "semi-direct" methods have been extended to Møller–Plesset perturbation theory (MP2) [20–22], and to the calculation of SCF second-derivatives [22].

In this work we extend the "direct" and "semi-direct" techniques to the calculation of static dipole polarizabilities and nuclear magnetic shieldings. The efficiency of the methods is increased by AO-based coupled-perturbed Hartree–

Fock (CPHF) [23] with screening of near-zero ERIs, efficient utilization of point group symmetry, and – in the case of polarizabilities – by a quadratically converging functional for the polarizability tensor. Magnetic shieldings are evaluated by a gauge invariant formalism using "gauge including basis functions" (GIAO) [3, 4].

The two programs "POLLY" (for evaluation of static dipole polarizabilities) and "SHEILA" (magnetic shieldings) are fully compatible with the TURBOMOLE package of programs [22]. It will be demonstrated how SCF second-order properties can be evaluated with the new programs on workstation computers, with adequate basis sets, and for large molecules. As illustrative applications we have chosen the carbon clusters C_{60} and C_{70}.

2 Basic theory

The evaluation of closed-shell SCF second-order properties with respect to two perturbations ξ and η is a standard procedure [2, 3]. Application to large molecules, however, requires additional consideration. To make the present notation [24] transparent we briefly list the basic equations (an AO-based formulation [23] will be used throughout; more detailed presentations can be found in [23, 25]):

Basis set expansion of (doubly occupied) molecular orbitals:

$$|i\rangle = \sum_{\nu} |\nu\rangle C_{\nu i} \tag{1}$$

Orthogonality:

$$C^{+}SC = 1 \tag{2}$$

Closed-shell SCF equations:

$$FC = SC\varepsilon \tag{3}$$

Fock matrix:

$$F = h + G[D] \tag{4}$$

Electron repulsion part of Fock matrix:

$$G_{\nu\mu}[D] = \sum_{\kappa\lambda} \{(\nu^*\mu \mid \kappa^*\lambda) - \tfrac{1}{2}(\nu^*\lambda \mid \kappa^*\mu)\} D_{\lambda\kappa} \tag{5}$$

Density matrix:

$$D = 2CC^{+} \tag{6}$$

The usual orthogonality constraint for first-order molecular orbitals is [25]

$$C^{+}SC^{\xi} = -\tfrac{1}{2}C^{+}S^{\xi}C \tag{7}$$

which leads to non-canonical perturbed orbitals.

The variational constraint for the perturbed molecular orbitals is (CPHF equations):

$$(h^{\xi} + G^{\xi}[D])C + G[D^{\xi}]C - S^{\xi}C\varepsilon + FC^{\xi} - SC^{\xi}\varepsilon = SC\varepsilon^{\xi} \tag{8}$$

where ε_{ij}^{ξ} is non-diagonal due to non-canonicity (Eq. (7)), and:

$$D^{\xi} = 2(C^{\xi}C^{+} + CC^{\xi +}), \qquad h^{\xi} = \frac{\partial}{\partial \xi} h, \quad \text{etc.} \tag{9}$$

(note that h^{ξ} is the derivative of the matrix representation of the one-electron operator, and not the matrix representation of the derivative of the one-electron operator).

Differentiation of the energy Lagrangian [25]:

$$E = \mathrm{tr}\{2C^{+}hC + C^{+}G[D]C - 2(C^{+}SC - 1)\varepsilon\} \tag{10}$$

with respect to the perturbations ξ and η yields:

$$\begin{aligned} E^{\xi\eta} = \mathrm{tr}\{&2C^{+}h^{\xi\eta}C + C^{+}G^{\xi\eta}[D]C - 2C^{+}S^{\xi\eta}C\varepsilon \\ &+ 4C^{\eta +}hC^{\xi} + 4C^{\eta +}G[D]C^{\xi} - 4C^{\eta +}SC^{\xi}\varepsilon \\ &+ 4C^{+}h^{\eta}C^{\xi} + 4C^{+}G^{\eta}[D]C^{\xi} - 4C^{+}S^{\eta}C^{\xi}\varepsilon \\ &+ 4C^{+}h^{\xi}C^{\eta} + 4C^{+}G^{\xi}[D]C^{\eta} - 4C^{+}S^{\xi}C^{\eta}\varepsilon \\ &+ 4C^{+}G[D^{\eta}]C^{\xi}\} \end{aligned} \tag{11}$$

where use has been made of the SCF equations, and of both orthogonality constraints, Eqs. (2, 7), but without using the CPHF condition, Eq. (8).

If the CPHF condition for C^{ξ} is substituted into Eq. (11) one obtains:

$$\begin{aligned} E^{\xi\eta} = \mathrm{tr}\{&2C^{+}h^{\xi\eta}C + C^{+}G^{\xi\eta}[D]C - 2C^{+}S^{\xi\eta}C\varepsilon + 4C^{+}h^{\eta}C^{\xi} \\ &+ 4C^{+}G^{\eta}[D]C^{\xi} - 4C^{+}S^{\eta}C^{\xi}\varepsilon - 2C^{+}S^{\eta}C\varepsilon^{\xi}\}. \end{aligned} \tag{12}$$

For dipole polarizabilities (ξ and η are components of the electric field vector) the basis functions are chosen independent of the perturbation, and Eq. (11) is simplified considerably:

$$\begin{aligned} E^{\xi\eta} = 4\,\mathrm{tr}\{&C^{\eta +}hC^{\xi} + C^{\eta +}G[D]C^{\xi} - C^{\eta +}SC^{\xi}\varepsilon + C^{+}h^{\eta}C^{\xi} \\ &+ C^{+}h^{\xi}C^{\eta} + C^{+}G[D^{\eta}]C^{\xi}\} \end{aligned} \tag{13}$$

where the perturbed MOs (C^{ξ}) are calculated from the simplified orthogonality constraint:

$$C^{+}SC^{\xi} = 0, \tag{14}$$

and from the simplified CPHF equations:

$$h^{\xi}C + G[D^{\xi}]C + FC^{\xi} - SC^{\xi}\varepsilon = SC\varepsilon^{\xi}. \tag{15}$$

If the perturbation is a magnetic field, gauge including basis functions (GIAO) [3] have proven to be most satisfactory [4]. GIAO basis functions, however, have an explicit field dependence, and corresponding terms in Eqs. (7, 8, 11, 12) have to be included.

With an external magnetic field there is yet another complication: since the first-order perturbation is purely imaginary [3], and since this is also true of the first-order perturbed basis functions v^{ξ}, it must be concluded from the linearity of both, CPHF equations and orthogonality constraint, that the first-order perturbed MO coefficients C^{ξ} must also be purely imaginary. All equations, however, are brought into real form if the imaginary unit is factored out and removed [3]. The matrices h^{ξ}, $G^{\xi}[D]$, $G[D^{\xi}]$, D^{ξ}, S^{ξ}, and ε^{ξ} then become skew-symmetric and real. We will, however, not make use of this notation here, although our actual implementation of course avoids imaginary quantities.

3 Quadratically convergent second-order properties

One of the more costly steps in the determination of second-order properties is the solution of the CPHF equations, Eqs. (7, 8). It constitutes the only time-consuming step, if the basis functions do not depend on the perturbation.

Although the CPHF equations are linear in the unknown perturbed orbitals C^ξ one has to resort to iterative algorithms in all but the smallest calculations. The update methods which are commonly used (direct inversion in the iterative subspace (DIIS) [26], and the conjugate gradient method [27]) have been shown to be equivalent for linear systems of equations [28].

Any further improvement of convergence characteristics in the CPHF procedure seems to be possible only by improving the approximate inverse. This approach has successfully been pursued in MO-based CPHF [22] but cannot easily be extended to AO-based CPHF.

It is, however, possible to reduce the number of CPHF iterations simply by relaxing the convergence criterion for C^ξ. The desired second-order properties can still be evaluated at the same or at better accuracy, if the variational formula, Eq. (11), is used instead of Eq. (12). This has been recognized by several authors [25, 29, 30], and to our knowledge has only been tested by Helgaker et al. [30] in an MCSCF application.

Here we present an error analysis for the property to be calculated in terms of the error in the approximate solutions $\tilde{C}^\xi$ of the CPHF equations. With the exact solution C^ξ we can define the error in $\tilde{C}^\xi$ as:

$$\delta C^\xi = \tilde{C}^\xi - C^\xi. \tag{16}$$

δC^η is analogously defined. The approximate solutions $\tilde{C}^\xi$ and $\tilde{C}^\eta$ may be required to obey the orthogonality constraint, Eq. (7), exactly, that is,

$$C^+ S\, \delta C^\xi = 0. \tag{17}$$

One then obtains from Eq. (11) (and exploiting Eq. (8) for the exact C^ξ, C^η):

$$\begin{aligned}\delta E^{\xi\eta} &= E^{\xi\eta}(\tilde{C}^\xi, \tilde{C}^\eta) - E^{\xi\eta}(C^\xi, C^\eta)\\ &= 4\,\mathrm{tr}\{\delta C^{\eta +} h\, \delta C^\xi + \delta C^{\eta +} G[D]\, \delta C^\xi\\ &\quad + C^+ G[\delta D^\eta]\, \delta C^\xi - \delta C^{\eta +} S\, \delta C^\xi \varepsilon\},\end{aligned} \tag{18}$$

that is

$$|\delta E^{\xi\eta}| \sim \|\delta C^\xi\| \cdot \|\delta C^\eta\|. \tag{19}$$

If, on the other hand, Eq. (12) is used for the calculation of $E^{\xi\eta}$, then the error becomes

$$\delta E^{\xi\eta} = 4\,\mathrm{tr}\{C^+ h^\eta\, \delta C^\xi + C^+ G^\eta[D]\, \delta C^\xi - C^+ S^\eta\, \delta C^\xi \varepsilon - \tfrac{1}{2} C^+ S^\eta C\, \delta \varepsilon^\xi\}, \tag{20}$$

where

$$\delta \varepsilon^\xi = C^+ G[\delta D^\xi] C. \tag{21}$$

In this case

$$|\delta E^{\xi\eta}| \sim \|\delta C^\xi\|, \tag{22}$$

and the property error vanishes only linearly with the error in the CPHF solutions.

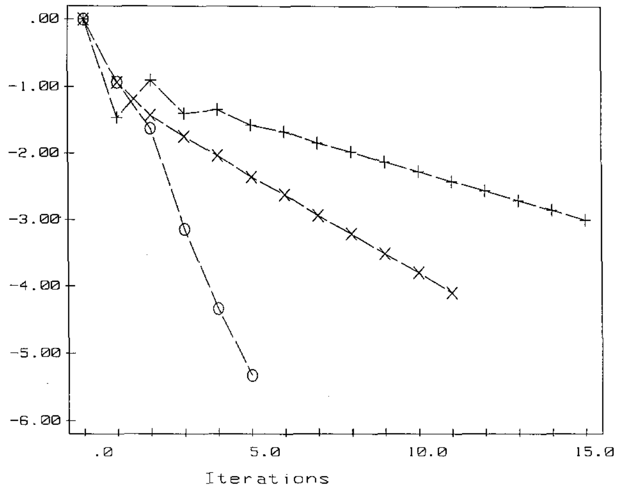

Fig. 1. Log_{10} of the relative error of the calculated polarizability α_{xx} (benzene) with respect to the converged result as a function of iteration index. Three algorithms have been tested. In the first algorithm (+) the perturbed orbitals are iterated after the usual decomposition of the SCF orbital rotation Hessian into $(\varepsilon_a - \varepsilon_i)\delta_{ab}$, and an ERI part; the polarizability is calculated in each iteration from Eq. (12). In the second algorithm (×) the perturbed orbitals are iterated in the same way, but the polarizability is calculated from the variational formula, Eq. (11). The third set of points (○) shows the further improvement of the second algorithm when DIIS is activated

The linear vs. the quadratic convergence of $E^{\xi\eta}$ is demonstrated in Fig. 1 for the calculation of the polarizability tensor component α_{xx} of benzene (the electric field is applied parallel to the molecular plane). The basis set used was a 6-31G + sd + sp [12]. No other means of convergence acceleration was applied. If an iterative subspace convergence acceleration [26] is used in addition to the quadratically convergent procedure, only 5 iterations suffice to obtain six significant digits of $\alpha_{xx} = 77.3418$ a.u.

The drawback of the quadratically convergent functional, Eq. (11), is that both CPHF solutions C^{ξ} and C^{η} have to be calculated. This is not a problem with polarizabilities or geometrical second derivatives, but it proves inconvenient in the calculation of nuclear magnetic shieldings. For this application we implemented the non-variational formula, Eq. (12).

4 Semi-direct algorithm and pre-screening of near-zero integrals

The techniques of ERI evaluation and processing which are used in the direct [17] or semi-direct [19] SCF scheme can be applied to the AO-based solution of CPHF equations with only minor modifications. This is also true for the techniques of integral pre-screening [17, 19].

A batch (NM, KL) of integrals $(\nu\mu \mid \kappa\lambda)$ with $\nu \in N, \mu \in M, \kappa \in K, \lambda \in L$ (the upper case letters designate shell indices) will thus be calculated only if [19]:

$$\max\{4\Delta D^{\Xi}_{KL}, 4\Delta D^{\Xi}_{NM}, \Delta D^{\Xi}_{KM}, \Delta D^{\Xi}_{LM}, \Delta D^{\Xi}_{KN}, \Delta D^{\Xi}_{LN}\} * Q_{NM} Q_{KL} \geqslant \vartheta, \quad (23)$$

where ϑ is a pre-screening threshold like 10^{-10}. Ξ characterizes the set of perturbations $\xi \in \Xi$ which are dealt with at the same time (the three cartesian components of an external electric field for example).

We use

$$Q_{NM} = \max_{\substack{\nu \in N \\ \mu \in M}} (\nu^*\mu \mid \mu^*\nu)^{1/2} \tag{24}$$

and

$$\Delta D_{KL} = \max_{\substack{\kappa \in K \\ \lambda \in L \\ \xi \in \Xi}} |\Delta D^{\xi}_{\kappa\lambda}| \tag{25}$$

in close analogy to [19].

The differential density matrices $\Delta D^{\xi}_{\kappa\lambda}$ correspond to the error-controlled, optimized differential densities of the direct SCF procedure as introduced in Eq. (23) of ref. [19]. We note, however, that for CPHF calculations the minimization of differential (perturbed) densities comes as a by-product of the DIIS procedure if the update procedure is suitably chosen. This is well known, and as a consequence there is no need for an extra step where differential densities are minimized as described in [19].

For calculations of chemical shifts the Coulombic terms $4\Delta D^{\Xi}_{NM}$ and $4\Delta D^{\Xi}_{KL}$ are omitted from Eq. (23). Magnetic shielding calculations for the applications presented later in this paper have been performed with ERI pre-screening in the CPHF step as outlined here.

With magnetic shielding calculations, of course, the CPHF step is not the only time-consuming operation.

It is well known [3, 4] that the use of GIAOs in the calculation of magnetic shieldings leads to "perturbed electron repulsion integrals" like $(\nu^*\mu \mid \kappa^*\lambda^{(\xi)})$ which have as arguments three (unperturbed) basis functions (ν, μ, and κ), and one "perturbed" basis function [3]:

$$\begin{aligned}\lambda^{(\xi)}(\underline{r}) &= -\frac{i}{2c}(\underline{R}_\lambda \times \underline{r})_\xi \lambda(\underline{r}) \\ &= \left(\frac{\partial}{\partial B_\xi} \exp\left(-\frac{i}{2c}(\underline{R}_\lambda \times \underline{r}) \cdot \underline{B}\right)\lambda(\underline{r})\right)_{\underline{B}=\underline{0}}.\end{aligned} \tag{26}$$

$\lambda^{(\xi)}(\underline{r})$ is the derivative of the field dependent GIAO [3] with respect to the external magnetic field $B_\xi \in \Xi = \{B_x, B_y, B_z\}$ taken at $\underline{B} = \underline{0}$. $\underline{R}_\lambda$ is the position of the center of basis function $\lambda(\underline{r})$. The "perturbed integrals" $(\nu^*\mu \mid \kappa^*\lambda^{(\xi)})$ are easily related to geometrical derivative integrals [25], and can be evaluated by a modified gradient integral package.

Talking about pre-screening of "perturbed ERIs", our current implementation of "SHEILA" only uses a simple test on the exponential factors of the "perturbed ERIs" in order to decide whether or not a batch of "perturbed ERIs" has to be evaluated and processed. This can, of course, be improved.

5 Further improvements on integral pre-screening

In this paragraph we present a detailed analysis on how errors due to integral pre-screening affect the calculated second-order properties. This analysis opens the way to further improvements on integral pre-screening techniques. We start with the analysis of the variational formula, Eq. (11). Our considerations will be applicable to AO-based SCF geometrical second derivatives as well. We allow for errors in the perturbed ERIs, here represented by $\tilde{G}^{\xi\eta}$, $\tilde{G}^{\xi}$, $\tilde{G}^{\eta}$:

$$\begin{aligned} \delta G^{\xi\eta} &= \tilde{G}^{\xi\eta} - G^{\xi\eta} \\ \delta G^{\xi} &= \tilde{G}^{\xi} - G^{\xi} \\ \delta G^{\eta} &= \tilde{G}^{\eta} - G^{\eta}. \end{aligned} \tag{27}$$

We also allow for errors in the unperturbed ERIs in the CPHF step:

$$\begin{aligned} \delta G[D^{\xi}] &= \tilde{G}[D^{\xi}] - G[D^{\xi}] \\ \delta G[D^{\eta}] &= \tilde{G}[D^{\eta}] - G[D^{\eta}] \end{aligned} \tag{28}$$

while $G[D] = F - h$ is assumed to be exact.

Since pre-screening of ERIs affects the CPHF step, Eq. (8), we obtain only approximate solutions $\tilde{C}^{\xi}$, $\tilde{C}^{\eta}$, e.g. from:

$$(h^{\xi} + \tilde{G}^{\xi}[D])C + \tilde{G}[\tilde{D}^{\xi}]C - S^{\xi}C\varepsilon + F\tilde{C}^{\xi} - S\tilde{C}^{\xi}\varepsilon = SC\tilde{\varepsilon}^{\xi} \tag{29}$$

(for simplicity we assume this time that the approximate CPHF equations will be solved exactly, so that the errors δC^{ξ}, δC^{η} are solely due to integral pre-screening – or more generally – to integral approximation).

From Eqs. (29, 8) it can be inferred, that:

$$(\delta G^{\xi}[D] + \delta G[\tilde{D}^{\xi}] + G[\delta D^{\xi}])C + F\,\delta C^{\xi} - S\,\delta C^{\xi}\varepsilon = SC\,\delta\varepsilon^{\xi}. \tag{30}$$

From Eqs. (11, 8 and 30), and after some tedious algebra one obtains for the error in the second order property $E^{\xi\eta}$:

$$\begin{aligned} \delta E^{\xi\eta} &= E^{\xi\eta}(\tilde{G}, \tilde{G}^{\xi}, \tilde{G}^{\eta}, \tilde{G}^{\xi\eta}, \tilde{C}^{\xi}, \tilde{C}^{\eta}) - E^{\xi\eta}(G, G^{\xi}, G^{\eta}, G^{\xi\eta}, C^{\xi}, C^{\eta}) \\ &= 4\,\mathrm{tr}\{\tfrac{1}{4}C^{+}\,\delta G^{\xi\eta}[D]C + C^{+}\,\delta G^{\xi}[D]\tilde{C}^{\eta} + C^{+}\,\delta G^{\eta}[D]\tilde{C}^{\xi} \\ &\qquad + C^{+}\,\delta G[\tilde{D}^{\xi}]\tilde{C}^{\eta} - C^{+}\,\delta G^{\xi}[D]\,\delta C^{\eta} - C^{+}\,\delta G[\tilde{D}^{\xi}]\,\delta C^{\eta}\} \\ &\approx 4\,\mathrm{tr}\{\tfrac{1}{4}C^{+}\,\delta G^{\xi\eta}[D]C + C^{+}\,\delta G^{\xi}[D]C^{\eta} + C^{+}\,\delta G^{\eta}[D]C^{\xi} \\ &\quad + C^{+}\,\delta G[D^{\xi}]C^{\eta}\} \end{aligned} \tag{31}$$

where in the last expression higher-order errors have been neglected. This is a surprisingly simple result which has three implications for efficient integral pre-screening:

(1) In the CPHF step (solving for $\tilde{C}^{\xi}$, Eq. (29)) it is tempting to evaluate a batch (NM, KL) of unperturbed ERIs $(\nu\mu \mid \kappa\lambda)$ only if:

$$\begin{aligned} \max\{&4\,\Delta D^{\Xi}_{KL} D^{H}_{NM}, 4\Delta D^{\Xi}_{NM} D^{H}_{KL}, \Delta D^{\Xi}_{KM} D^{H}_{LN}, \Delta D^{\Xi}_{LM} D^{H}_{KN}, \\ &\Delta D^{\Xi}_{LN} D^{H}_{KM}, \Delta D^{\Xi}_{KN}\, D^{H}_{LM}\} * Q_{NM}\, Q_{KL} \geqslant \vartheta \end{aligned} \tag{32}$$

where ϑ is the pre-screening threshold, and:

$$D^{H}_{NM} = \max_{\substack{\nu \in N \\ \mu \in M \\ \eta \in H}} |D^{\eta}_{\nu\mu}| \tag{33}$$

($D^{\eta}_{\nu\mu}$ would be a converged perturbed density which is usually not available). While this simple approach provides the correct answers when one starts with the almost converged solutions of the CPHF equations it may fail to converge properly in realistic applications since there is an intricate interdependence between δD and the integrals which are pre-screened, Eqs. (30, 32) so that higher order errors in Eq. (31) can become dominant in the course of iteration. Yet it is possible to save the two-densities enhanced pre-screening formula, Eq. (32), and in the appendix we show the necessary modifications, especially of Eq. (33), for a numerically stable CPHF procedure which we implemented in our dipole polarizabilities program.

(2) In the calculation and processing of (first order) perturbed ERIs batches $(NM, KL)^{\Xi}$ are evaluated only if:

$$\begin{aligned}&\max\{4D_{KL}D^{H}_{NM}, 4D^{H}_{KL}D_{NM}, D_{KM}D^{H}_{LN}, D^{H}_{KM}D_{LN}, D^{H}_{KN}D_{LM}, D_{KN}D^{H}_{LM}\}\\&\quad * (Q_{NM}R^{\Xi}_{KL} + Q_{KL}R^{\Xi}_{MN}) \geqslant \vartheta. \qquad (34)\end{aligned}$$

Here

$$R^{\Xi}_{KL} = \max_{\substack{\kappa\in K\\ \lambda\in L}} [(\kappa^{*}\lambda^{(\xi)} \mid \lambda^{(\xi)*}\kappa)^{1/2} + (\kappa^{(\xi)*}\lambda \mid \lambda^{*}\kappa^{(\xi)})^{1/2}] \qquad (35)$$

in close analogy to ref. [32]. Wolinski et al. [4] advocated the use of the uncoupled approximation to D^{H} if D^{η} is not known at the time of the evaluation of $(NM, KL)^{\Xi}$. This approach will work well unless the eigenvalues of the SCF stability matrix [31] (also known as the SCF orbital rotation Hessian) become small. In this case results will probably become unsatisfactory due to correlation effects, too. It is to be noted that non-real instabilities may occur earlier than the usual singlet instabilities [31].

(3) The pre-screening of second derivative ERIs (which concerns $G^{\xi\eta}$) has already been described in [32] for the case of SCF second derivatives. It is not relevant in the context of polarizabilities or chemical shifts.

Next we analyze the proliferation of errors due to integral neglect when the non-variational formula, Eq. (12), is used. With the restriction to errors in the (first-order) perturbed integrals some of these considerations have been outlined before by Wolinski et al. [4].

The complete result is:

$$\begin{aligned}\delta E^{\xi\eta} &= E^{\xi\eta}(\tilde{G}^{\xi\eta}, \tilde{G}^{\xi}, \tilde{G}^{\eta}, \tilde{G}, \tilde{C}^{\xi}, \tilde{\varepsilon}^{\xi}) - E^{\xi\eta}(G^{\xi\eta}, G^{\xi}, G^{\eta}, G, C^{\xi}, \varepsilon^{\xi})\\&= 4\,\mathrm{tr}(\tfrac{1}{4}C^{+}\,\delta G^{\xi\eta}[D]C + C^{+}h^{\eta}\,\delta C^{\xi} + C^{+}G^{\eta}[D]\,\delta C^{\xi}\\&\quad + C^{+}\,\delta G^{\eta}[D]\tilde{C}^{\xi} - C^{+}S^{\eta}\,\delta C^{\xi}\varepsilon - \tfrac{1}{2}C^{+}S^{\eta}C\,\delta\varepsilon^{\xi})\\&= 4\,\mathrm{tr}(\tfrac{1}{4}C^{+}\,\delta G^{\xi\eta}C + C^{+}\,\delta G^{\eta}[D]\tilde{C}^{\xi}\\&\quad + C^{+}\,\delta G^{\xi}[D]C^{\eta} + C^{+}\,\delta G[\tilde{D}^{\xi}]C^{\eta}) \qquad (36)\end{aligned}$$

where the last expression is obtained after lengthy algebra from Eq. (30), and from the CPHF condition for C^{η}.

This result is the same as in Eq. (31) as one may have suspected.

Integral pre-screening in the "non-variational algorithm" (which uses Eq. (12)) thus employs the expressions introduced before, Eqs. (32–35).

6 Molecular point group symmetry in second-order properties calculations

Proper use of molecular point group symmetry can speed up calculations of second-order properties considerably. Algorithms for the use of symmetry in AO based CPHF have been described in [33] and [34].

Here we follow general considerations given in [35]. Focusing our attention on the two-electron matrices $G^{\xi}[D]$ and $G[D^{\xi}]$ which are linear in the ERIs (first-order perturbed ERIs and unperturbed ERIs, respectively) we learn from the general symmetrization theorem in [35] that $G^{\xi}[D]$ and $G[D^{\xi}]$ may be calculated from symmetry non-redundant integral batches only, provided the set of perturbations $\xi \in \Xi$ defines a representation of the molecular point group. This representation will also be termed Ξ.

If symmetry redundant integral batches are omitted, and suitable symmetry factors are incorporated into the non-redundant ERIs during their "on-the-flight" evaluation, one obtains (after the usual ERI processing steps) the skeleton matrices $[G^{\xi}[D]]$ and $[G[D^{\xi}]]$ [33–36]. Here the outer square brackets indicate skeleton quantities which still need to be symmetrized [33–36]. The symmetrization step is most easily performed after $[G^{\xi}[D]]$ and $[G[D^{\xi}]]$ have been transformed into a basis of symmetrized atomic basis functions (SAOs) [35].

The symmetrization formula for the SAO skeleton matrix $[G[D^{\xi}]]$ is [35]

$$\langle G[D^{\xi}]\rangle_{k^{\Gamma\gamma},l^{\Gamma'\gamma'}} = \sum_{\xi' \in \Xi} \sum_{\varepsilon=1}^{\dim \Gamma} \sum_{\varepsilon'=1}^{\dim \Gamma'} [G[D^{\xi'}]]_{k^{\Gamma\varepsilon},l^{\Gamma'\varepsilon'}} P^{\Xi \otimes \Gamma \otimes \Gamma'}_{\xi'\varepsilon\varepsilon',\xi\gamma\gamma'} \tag{37}$$

where $|k^{\Gamma\gamma}\rangle$ denotes an SAO which transforms according to a column γ of (matrix) representation Γ. The SAOs $|k^{\Gamma\gamma}\rangle$ and $|l^{\Gamma'\gamma'}\rangle$ are constructed so that Γ, Γ' are irreducible and real [35]. $\langle G[D^{\xi}]\rangle$ is the symmetrized matrix.

$P^{\Xi \otimes \Gamma \otimes \Gamma'}$ is the symmetrizing projector [35] which can also be used to symmetrize $[G^{\xi}[D]]$ in the same way. Since in our application Ξ refers to a homogenous electric or magnetic field ($\dim \Xi = 3$) the matrices $P^{\Xi \otimes \Gamma \otimes \Gamma'}$ do not exceed the dimension $27 * 27$ for non-icosahedral molecular point groups ($75 * 75$ for icosahedral point groups), and are pre-calculated and stored for each pair Γ, Γ', with zero vectors (columns and rows) removed. The symmetrization, Eq. (37), then becomes negligible in terms of computation cost with icosahedral point groups as the only exception (a decomposition of $P^{\Xi \otimes \Gamma \otimes \Gamma'}$ as described in [35] would speed up the symmetrization for icosahedral point groups, but this has not been implemented).

7 Basis set considerations

The prediction of static dipole polarizabilities of larger molecules can be achieved with moderately sized basis sets if one set of polarizability optimized diffuse *s*- and *d*-functions (first or second row elements; hydrogen takes diffuse *s*- and *p*-functions) is added to an energy optimized basis set with at least two basis functions per valence orbital [12]. The errors in the isotropic polarizabilities are of the order of 10–15% [12]. Further basis set extension leads to only marginally improved polarizabilities at the SCF level. The diffuse *s*-functions may be omitted with little penalty in accuracy [12].

Basis set dependencies of magnetic shieldings as obtained by the GIAO formalism [3] have been discussed in [4]. It was observed [4] that elements of the first row (^{13}C, ^{17}O, ^{19}F) are well described by energy optimized TZP basis sets, i.e. basis sets containing three basis functions per valence orbital plus one set of polarization functions at each atom. For second row elements (like ^{33}S) basis set requirements were found to be more stringent: one more set of polarization functions was required, and a partial decontraction of the outermost *p*-primitive in the first p-contraction was necessary [4]; magnetic shieldings as obtained with these basis sets seem to be converged to within a few ppm of the SCF limit [4].

We confirm these results of Spackman [12] and Wolinski et al. [4], and emphasize the suitability of their basis sets for calculations of large molecules, with the exception of basis sets with a large number of very diffuse functions which reduce numerical stability due to a badly conditioned overlap matrix, and which spoil program performance because few integrals containing diffuse functions can be neglected.

8 Application to fullerenes

Since their detection [37] and preparation in macroscopic quantities [38], fullerenes like the soccerball shaped C_{60} and its elongated homologue C_{70} have attracted considerable interest both from experimental and theoretical chemists.

Here we present calculations of SCF second-order properties for these molecules, since their large size and their high symmetry are well suited to test the efficiency of our algorithms.

8.1 Polarizability of C_{60}

The static dipole polarizability of C_{60} has to our knowledge not yet been determined experimentally. Two years ago, in pioneering work, Fowler et al. [8] for the first time calculated the polarizability of C_{60} at the SCF level with a 6-31G* basis set (900 basis functions). Their calculation took 10 days on a CRAY X-MP 48. They obtained a polarizability of $\alpha = 442$ a.u. (1 a.u. $= 1.6488 \times 10^{-41}$ $C^2 m^2 J^{-1}$). The calculation with our semi-direct program POLLY used an 6-31G + sd basis set [12] which also amounts to 900 basis functions (counting 5d-functions per d-shell). The reference geometry of the icosahedral molecule is characterized by the bond lengths 1.446 Å and 1.406 Å, and was obtained by a geometry optimization at the MP2 level of theory with a basis set of DZP quality [39]. Bond lengths from gas-phase electron diffraction [40] are very similar (1.458 Å, 1.401 Å). Ab initio SCF calculations yield more pronounced differences in bond distances [41]. An X-ray structure inferred from a twinned crystal of C_{60} seems to indicate severe distortions from icosahedral symmetry [42].

The calculation of the polarizability was performed on an IBM RISC/6000 320H workstation with 64 MB main storage. It converged within 5 iterations to:

$$C_{60}: \alpha_{xx} = \alpha_{yy} = \alpha_{zz} = 531.9 \text{ a.u.}$$

According to Spackman [12] this value should be accurate to within 10–15% and is probably too low. Comparison to the polarizability calculated in [8] demonstrates the importance of diffuse basis functions.

The wall-clock time elapsed was 1 day and 9 hours. Two-thirds of the time was spent in symmetrization steps due to symmetry group I_h. No ERIs were stored on disc during the CPHF step. Note that the semi-direct programs DSCF [19, 22], POLLY, and SHEILA allow to store integrals according to a user-defined efficiency criterion [19], but this calculation has been done in fully direct mode.

8.2 *Chemical shifts of* C_{60} *and* C_{70}

The ^{13}C-NMR spectrum of C_{60} and C_{70} has been published in [43, 44]. For C_{60} it consists of a single line at 142.68 ppm, and for the nuclei a–e in C_{70} (we use the same notation as in ref. [43]) the shifts are 150.07, 147.52, 146.82, 144.77 and 130.28 ppm, respectively.

Prior to these experimental findings Fowler et al. [8] had calculated the absolute magnetic shielding of carbon in C_{60} to be 98 ppm. They did not use gauge including basis functions (GIAO). Their result thus depends on the choice of origin (center of mass) even though they used an extrapolation technique meant to approach the basis set limit. Their largest calculation, however, employed a 6-31G* basis set: still far from the basis set limit. It does not come as a total surprise then that the absolute carbon shielding they calculated for C_{60} is off by 55 ppm from the experimental value of 43 ppm (which can be determined from the NMR shift and the absolute cabon shielding in benzene [45]).

Later Fowler et al. [9] published shieldings with the gauge origin chosen at the nucleus of interest in C_{60} and obtained (after basis set extrapolation) a much improved absolute shielding of 46 ppm.

Here we report the carbon shielding in C_{60} as calculated by the GIAO-CPHF formalism at the MP2/DZP equilibrium geometry [39]. We used the same DZP basis set also in the CPHF calculation. The obtained absolute carbon shielding was found to be:

$$C_{60} : \sigma = 44.5 \text{ ppm}.$$

This result is in excellent agreement with the result inferred experimentally, though probably somewhat fortuitously.

The calculation took $1\frac{1}{2}$ days on an IBM RISC/6000 550 workstation computer with 64 MB of main memory (200 MB of ERIs were written to disc).

We also calculated the absolute carbon shieldings in C_{70} at the SCF/DZP level of theory. As reference geometry we used the SCF/dzP equilibrium geometry [46] (here we adopt the notation introduced in [41, 46] that dz and DZ refers to $(7s3p)/[4s2p]$ and $(9s5p)/[4s2p]$, respectively). The calculation of the shieldings took $2\frac{1}{2}$ days on an IBM RISC/6000 550 workstation computer: 25 h for the one-electron part plus the first-order perturbed ERIs, and 34 h for the CPHF step, during which 1.2 GB disc storage were allocated for ERIs. C_{70} exhibits D_{5h} symmetry (20 symmetry operations) and one would thus expect at least a factor 6 increase in computation time when going from C_{60} (symmetry group $I_h = 120$ symmetry operations) to C_{70}. It is the CPHF step which takes about equal computation time for both molecules (30 h for C_{60} and 34 h for C_{70}). The reason is the symmetrization step, Eq. (37), which currently is inefficiently implemented for icosahedral point groups: a decomposition of the symmetrizing projector $P^{\Xi \otimes \Gamma \otimes \Gamma'}$ as proposed in [35] (with construction of non-redundant matrix elements equivalent to irreducible tensor elements) would alleviate this problem. Since icosahedral point groups are of limited importance in chemistry (with few, but notable exceptions) we decided not to undertake the extra effort to write a symmetry code optimal for icosahedral point groups.

The calculated carbon shieldings for C_{70} are tabulated in Table 1 and compared to the experimental absolute shieldings calculated from the known carbon shielding in benzene of 57.2 ppm [45], and the measured ^{13}C-NMR shifts in benzene solution [43].

Table 1. Experimental [43] and calculated ^{13}C-NMR shifts (downfield with respect to benzene), and absolute carbon shieldings in C_{60}, C_{70}, and benzene

Mol.	Nucleus	Shift rel. to C_6H_6 (exp)	Shift rel. to C_6H_6 (calc)	Absolute shielding (exp)	Absolute shielding (calc)
C_{60}		14.2	20.8	43.0	44.5
C_{70}	*a*	21.6	24.2	35.6	41.1
	b	18.3	21.1	38.9	44.2
	c	19.0	19.8	38.2	45.5
	d	16.3	17.8	40.9	47.5
	e	1.8	7.9	55.4	57.4
C_6H_6		0	0	57.2 [45]	65.3

The discrepancies between calculated and measured shieldings are larger than for C_{60} but are still in the expected range of error of 7 ppm. The relative sequence of shifts in C_{70} is in very good agreement with experiment except for nuclei *b* and *c* which are only 0.7 ppm apart in the experimental spectrum. Some probable sources of errors are:

(1) Basis set deficiency: for benzene the calculated carbon shielding is 65.3 ppm with the DZP basis set while the basis set limit of the carbon shielding is probably close to [4] or below [47] the experimental value 57.2 ppm. The error in the carbon shielding due to the DZP basis set thus amounts to about 10 ppm in benzene. The error is smaller in most other molecules, and is already much improved if a basis set of TZP quality is employed (especially with regard to relative shifts).

(2) Effects of electron correlation.

(3) The choice of the reference geometry: the SCF equilibrium geometry of C_{70} probably suffers from the same short-comings (too much bond alternation) as the SCF equilibrium geometry of C_{60} [39]. It may be suspected that for the correct equilibrium geometry the ordering of all calculated carbon shieldings is the same as in the experiment.

(4) Solvent effects.

9 Conclusions

The semi-direct calculation of second-order SCF properties (polarizability and magnetic shielding) on workstation computers has been demonstrated for the fullerenes C_{60} and C_{70}. The magnetic shielding calculation for C_{70} (1050 basis functions, D_{5h} symmetry) is unprecedented in size. This calculation ran for $2\frac{1}{2}$ days on a dedicated IBM RISC/6000 550 workstation: this is to be considered a routine application. The accuracy of the calculated carbon shieldings was about 7 ppm (absolute error). The relative sequence of chemical shifts in C_{70} is reproduced within a smaller error margin (Table 1). Application with up to 900 basis functions to less symmetrical molecules can be found in [48].

The GIAO-CPHF method is an invaluable tool for the identification of substances from the NMR spectrum alone: in a first step the structure guess is refined by geometry optimization at the SCF level of theory (or, if possible, at the MP2 level of theory), and in a second step the magnetic shieldings are evaluated and compared to the experimental spectrum. While this approach has been available earlier [4, 5] we extended its applicability to large systems like fullerenes where in the absence of empirical rules the ab initio calculation of chemical shieldings may allow quick confirmation of structure proposals.

Where are the limitations of the method? Chemical shifts can be evaluated at the same price as an SCF plus a gradient calculation. On current workstation computers this allows applications to molecules with ≈ 100 atoms if about 8 or more symmetry operations aid the calculations. At this molecular size 64 MB of main storage have to be available for computational efficiency.

A rigid molecular equilibrium geometry is a necessary prerequisite. Floppy molecules may provide future challenges.

Since the GIAO-CPHF method is based on the SCF method its results become poor when electron correlation becomes important, and it would be desirable to be able to calculate chemical shifts also at the GIAO-MP2 level of theory. Fortunately such an approach has recently been implemented, and GIAO-MP2 calculations for small molecules have become possible [49]. First results from the GIAO-MP2 method [49] indicate strong correlation contributions to ^{17}O chemical shifts in terminal oxygen groups. Other methods for magnetic shielding calculations at the correlated level have also been suggested and implemented – like MCSCF-IGLO [50] – and present a valuable alternative to GIAO-MP2.

The ab initio calculation of static dipole polarizabilities of large molecules on workstation computers is another advance presented in this work. The (semi-)direct CPHF calculation usually takes less time than a (semi-)direct SCF calculation with the same basis set. The calculated static polarizabilities are electronic polarizabilities only: the relaxation of the equilibrium geometry has to be accounted for when less rigid molecular systems are treated [51].

The technical advances in this work may be summarized as follows:

(1) A semi-direct implementation of the CPHF algorithms for static dipole polarizabilities and nuclear magnetic shieldings (based on GIAOs) has been introduced for the first time.

(2) A quadratically converging functional has been used for the polarizabilities to speed up convergence.

(3) A two-densities integral neglect criterion, Eq. (32) (with details given in the appendix), has been introduced for enhanced integral pre-screening in the semi-direct CPHF calculations.

Note added in proof

^{13}C-NMR shieldings (in ppm) for a $(9s5p1d)/[5s3p1d]$ TZP basis set are: 39.4 in C_{60}, 35.5, 38.8, 39.2, 41.7, 59.9 in C_{70}, and 58.4 in benzene, a marked improvement over DZP results.

POLLY now allows the calculation of static hyperpolarizabilities β and, by further numerical differentiation, γ. The 6-31G + sd basis set result for C_{60} is:

$$\gamma_{xxxx} = -\partial^4 E/\partial F_x^4 = 9.0 \cdot 10^4 \text{ a.u.}, \qquad \gamma_{xxyy} = 3.0 \cdot 10^4 \text{ a.u.}$$

Appendix

We outline an algorithm for pre-screening of (unperturbed) ERIs during the iterative solution of the CPHF equations as implemented in our program POLLY for the calculation of static dipole polarizabilities.

The aim is to reach a pre-set accuracy in the components of the polarizability tensor as efficiently as possible. This goal is achieved by the pre-screening formula, Eq. (32) (with $H = \Xi$ in our case), if we choose

$$D^{\Xi(p)}_{KL} = \sum_{q=0}^{p} \max_{\substack{\xi \in \Xi \\ \kappa \in K \\ \lambda \in L}} \left|\Delta D^{\xi(q)}_{\kappa\lambda}\right| \tag{38}$$

where p, q are iteration indices. $\Delta D^{\xi(0)}$ is the perturbed density obtained from solving the uncoupled perturbed Hartree–Fock equations, and $\Delta D^{\xi(q)}$, $q > 0$, is a differential perturbed density obtained from the residuum of the DIIS-optimized perturbed density $D^{\xi(q)}$ of the previous iteration ($D^{\xi(q)} = \sum_{r=0}^{q-1} w_r \, \Delta D^{\xi(r)}$; $w_1 \ldots w_{q-1}$ are determined from $E^{\xi\xi}(D^{\xi(q)}) = \min!$ using the variational formula, Eq. (13)).

The accurate evaluation of the polarizabilities in the iterative subspace will be guaranteed, if the necessary matrix traces tr $\tilde{G}[\Delta D^{\xi(p)}] \, \Delta D^{\eta(q)}$ are consistently carried out in the order $p \geqslant q$ (the error in the iterative subspace polarizabilities will scale with ϑ times a power of the number N of the basis functions (ϑN^2 for statistical cancellation of small errors) provided that the DIIS coefficients remain bound).

Correct over-all convergence of the polarizability is assured (with the possible exception of a badly conditioned SCF stability matrix) since the extension of the iterative subspace by a slightly erroneous update $\Delta\tilde{D}^{\xi(p)}$ (where the error $\delta\Delta D^{\xi(p)}$ is due to $\delta G[D^{\xi(p-1)}]$) affects the polarizability calculated in the extended iterative subspace only in second order of ϑ if $\Delta D^{\xi(p)} \to 0$.

This pre-screening algorithm has proven to be numerically stable: The 6-31G + sd basis [12] used for the calculation of the static dipole polarizability of C_{60} contains diffuse s-functions with orbital exponent $\zeta_s = 0.042$, and d-functions with $\zeta_d = 0.175$; the lowest eigenvalue of the overlap matrix is 5×10^{-7} (the largest eigenvalue is 20). Despite the badly conditioned overlap matrix the polarizability can be calculated in 5 iterations to 4 (numerically) significant digits with the integral neglect threshold set to $\vartheta = 3 \times 10^{-8}$.

This pre-screening algorithm can be extended to mixed second-order properties like magnetic shieldings where only one set of CPHF equations is solved (e.g. with respect to the external magnetic field): D^H in Eq. (33) has to be replaced by $\max(D^H, D^\Xi)$ with D^Ξ as defined in Eq. (38), and with D^H obtained from Eq. (33) using the uncoupled perturbed Hartree–Fock approximation for D^η, $\eta \in H$ (e.g. the perturbations originating from the nuclear magnetic moments).

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