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# Magnetic hyperpolarizabilities in a cubic response formulation

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**Abstract.** We demonstrate the applicability of a recently derived cubic response function formalism for performing fully analytical calculations of hypermagnetizabilities, their anisotropy and their dispersion. The calculations involve the noble gas atoms, He, Ne, and Ar, and the corresponding isoelectronic halogen anions and alkali cations.

## 1. Introduction

Although the theory for magnetically induced non-linear properties of molecules has been known for many years [1] it is not until quite recently that *ab initio* calcalutions of such quantities have been undertaken to any appreciable extent. The two experimental effects of most relevance with respect to magnetic non-linearity are the Faraday effect describing the degree of polarization rotation by a magnetic field, and the Cotton–Mouton effect describing the birefringence of a magnetic material. The key constants for those effects are the Verdet constant and the Cotton–Mouton constant, respectively. Calculations of such constants have previously been hampered by computational difficulties such as slow convergence of basis sets and origin dependency [2–8]. For the Cotton–Mouton effect, which refers to the anisotropy of the hypermagnetizability, $\eta$, a further complication is that its paramagnetic part requires perturbation theory of high order. Except for the computations of Jamieson on hydrogen and helium with the fourth-order coupled Hartree–Fock method [9], calculations of these constants have been accomplished by means of finite field calculations. However, such calculations are quite elaborate for the hypermagnetizability and the precision of values might depend on the particular differentiation scheme. In the present work it is shown that cubic response theory offers an analytical approach to the calculations of hypermagnetizabilities that is generally applicable.

## 2. Method

The hypermagnetizability anisotropy, $\Delta\eta$, that for atoms is directly proportional to the measurable Cotton–Mouton constant, relates to quadratic and cubic response functions in the following way:

$$\Delta\eta(-\omega;\omega,0,0) = \eta_{xx,xx} - \eta_{xx,yy},$$

$$\eta_{ij,kl}(-\omega;\omega,0,0) = -\frac{1}{4}\langle\langle r_i;r_j,L_k,L_l\rangle\rangle_{\omega,0,0} - \langle\langle r_i;r_j,Q_{kl}\rangle\rangle_{\omega,0}. \tag{1}$$

The third-order response function is the paramagnetic contribution, $\eta^p$, and the second-order response function involving the quadrupole operator is the diamagnetic contribution, $\eta^d$. Since $\eta^p_{xx,xx} = 0$ for atoms, only $\langle\langle x;x, L_y, L_y\rangle\rangle_{\omega,0,0}$ needs to be evaluated in the present calculations. The paramagnetic contribution has so far caused difficulties and various approximations have been used. In the language of response functions it is possible to calculate $\eta^p$ through numerical differentiation of a second-order response function (finite-field calculations). Magnetic properties have proven difficult to determine in this fashion and the accuracy of the results may depend on the actual algorithm for the differentiation. We demonstrate here the application of recently developed third-order response theory [10] to calculate hypermagnetizabilities, thereby eliminating the need for numerical differentiation. We use for this purpose the noble gas atoms and their halogen anion and alkali cation isoelectronic counterparts.

At present we have an implementation of the expressions for the third-order response function for reference state wave functions of closed-shell Hartree–Fock type. This approximation is called the random phase approximation (RPA). The response functions are the Fourier coefficients in the Taylor expansion of the time-dependent expectation values of an operator as the reference state is perturbed by a field. Thus the cubic response function will contain all terms to the expectation value that are of third-order in the perturbation. Many molecular properties, both magnetic and electronic, are successfully described within this formalism and deriving the working expressions for the third-order response functions is just another step in this development. Among other properties we will then have the possibility to estimate the hypermagnetizability fully analytically. The cubic response function reads

$$\begin{aligned}\langle\langle A;B,C,D\rangle\rangle_{\omega_1,\omega_2,\omega_3} = {} & N^A_j(\omega_1+\omega_2+\omega_3)T^{[4]}_{jklm}N^B_k(\omega_1)N^C_l(\omega_2)N^D_m(\omega_3)\\ & -N^A_j(\omega_1+\omega_2+\omega_3)[T^{[3]}_{jkl}(\omega_1,\omega_2+\omega_3)N^B_k(\omega_1)N^{CD}_l(\omega_2,\omega_3)\\ & +T^{[3]}_{jkl}(\omega_2,\omega_1+\omega_3)N^C_k(\omega_2)N^{BD}_l(\omega_1,\omega_3)\\ & +T^{[3]}_{jkl}(\omega_3,\omega_1+\omega_2)N^D_k(\omega_3)N^{BC}_l(\omega_1,\omega_2)]\\ & +N^A_j(\omega_1+\omega_2+\omega_3)[B^{[2]}_{jk}N^{CD}_k(\omega_2,\omega_3)+C^{[2]}_{jk}N^{BD}_k(\omega_1,\omega_3)\\ & +D^{[2]}_{jk}N^{BC}_k(\omega_1,\omega_2)] - N^A_j(\omega_1+\omega_2+\omega_3)[B^{[3]}_{j(kl)}N^C_k(\omega_2)\\ & \times N^D_l(\omega_3)+C^{[3]}_{j(kl)}N^B_k(\omega_1)N^D_l(\omega_3)+D^{[3]}_{j(kl)}N^B_k(\omega_1)\\ & \times N^C_l(\omega_2)] + A^{[2]}_{(jk)}[N^B_j(\omega_1)N^{CD}_k(\omega_2,\omega_3)\\ & +N^C_j(\omega_2)N^{BD}_k(\omega_1,\omega_3)+N^D_j(\omega_3)N^{BC}_k(\omega_1,\omega_2)]\\ & -A^{[3]}_{(jkl)}N^B_k(\omega_1)N^C_k(\omega_2)N^D_l(\omega_3),\end{aligned} \tag{2}$$

$$N^X_j(\omega_a) = (E^{[2]}-\omega_a S^{[2]})^{-1}_{jk}X^{[1]}_k \quad X\in\{A,B,C,D\}, \tag{3}$$

$$N_j^{XY}(\omega_a,\omega_b) = (E^{[2]} - (\omega_a + \omega_b)S^{[2]})^{-1}_{jk} XY^{[1]}_k(\omega_a,\omega_b),$$

$$XY^{[1]}_j(\omega_a,\omega_b) = T^{[3]}_{jkl}(\omega_a,\omega_b)N^X_k(\omega_a)N^Y_l(\omega_b) - Y^{[2]}_{jk}N^Y_k(\omega_a) - X^{[2]}_{jk}N^y_k(\omega_b),$$

$$XY \in \{BC,BD,CD\}, \tag{4}$$

where we have introduced

$$T^{[3]}_{jkl}(\omega_1,\omega_2) = (E^{[3]}_{j(kl)} - \omega_1 S^{[3]}_{jkl} - \omega_2 S^{[3]}_{jkl}), \tag{5}$$

$$T^{[4]}_{jklm} = (E^{[4]}_{j(klm)} - \omega_1 S^{[4]}_{jk(lm)} - \omega_2 S^{[4]}_{jl(km)} - \omega_3 S^{[4]}_{jm(kl)}). \tag{6}$$

Indices enclosed in parenthesis are to be permuted symmetrically. The $\boldsymbol{E}^{[i]}$, $\boldsymbol{S}^{[i]}$, and $A^{[i]}$ matrices are hessian, overlap and property matrices of different order. We refer to Ref. [11] for the definitions. Further, we assume that $A$, $B$, $C$ and $D$ refer to one-electron operators corresponding to the perturbing fields. Thus the evaluation of the third-order response function can be separated into two steps; first solving a set of seven linear equations (3) and (4) to obtain the corresponding seven response vectors to be followed by the matrix multiplication (2) for the response function value. The coding of the cubic response formalism includes "direct" strategies in terms of direct one-index transformations, direct atomic orbital constructions of matrices, and direct iterative linear transformations in the solutions of the response equations. None of these are, however, critical to the applications presented here.

## 3. Basis sets

Hyperpolarizability calculations are known to be very sensitive to the choice of basis set, especially considering polarizing and diffuse functions. We have performed a basis set investigation for He and Ne and then employed uncontracted basis sets with exponents from the ANO basis sets by Widmark et al. [12, 13] and Pierloot et al. [14] for the full series of calculations. The basis sets Al–A5 for He are based on the exponents from a (10*s*) set of van Duijneveldt [15] and the basis sets B1–B4 for Ne are based on the basis set by Cernusak et al. [16]. A6 and A5 are the uncontracted ANO basis set. Table 1 lists the employed contractions. All calculations use Cartesian functions.

**Table 1.** Basis set contractions

| He | | Ne | | Atom | |
|---|---|---|---|---|---|
| A1 | ⟨10*s*5*p*⟩ | B1 | (15*s*10*p*)/[10*s*8*p*] | $H^-$ | ⟨8*s*4*p*3*d*⟩ |
| A2 | ⟨10*s*5*p*5*d*⟩ | B2 | (15*s*10*p*8*d*)/[10*s*8*p*6*d*] | $Li^+$ | ⟨14*s*9*p*4*d*3*f*⟩ |
| A3 | ⟨10*s*5*p*5*d*3*f*⟩ | B3 | (15*s*10*p*8*d*4*f*)/[10*s*8*p*6*d*4*f*] | $F^-$ | ⟨14*s*9*p*4*d*3*f*⟩ |
| A4 | ⟨12*s*8*p*7*d*4*f*⟩ | B4 | (15*s*10*p*8*d*4*f*1*g*)/[10*s*8*p*6*d*4*f*1*g*] | $Na^+$ | ⟨17*s*12*p*5*d*4*f*⟩ |
| A5 | ⟨10*s*5*p*4*d*3*f*2*g*⟩ | B5 | ⟨14*s*9*p*4*d*3*f*⟩ | $Cl^-$ | ⟨13*s*10*p*4*d*⟩ |
| A6 | ⟨9*s*4*p*3*d*⟩ | | | Ar | ⟨13*s*10*p*4*d*⟩ |
| [a] | ⟨12*s*8*p*6*d*3*f*⟩ | | | $K^+$ | ⟨17*s*12*p*4*d*⟩ |

[a] From Ref. [5]

## 4. Results

Basis set investigations have been carried through for He and Ne, see Table 2. For He we see that the paramagnetic part is well described using only *s*- and *p*-type functions. This is so because non-redundant orbital excitations for the dipole operator are of the sort $s \rightarrow p,f$ and adding *d*-type functions will therefore not significantly improve the paramagnetic value. Our A6 basis set values underestimates $\eta^p$ by about 7%. It is more difficult to obtain accurate values for the diamagnetic part. The A6 set overestimates $\eta^d_{xx,xx}$ by 11% and underestimates $\eta^d_{xx,yy}$ by 19% causing the $\Delta\eta^d$ values to be poor. Using a basis set with only *s*- and *p*-type functions is clearly not sufficient even for the paramagnetic contribution for Ne due to the occupied *p* orbitals. The basis set B3 is identical to what Refs. [6, 5] used in their numerical differentiation calculations. Our paramagnetic values, however, differ from those reported by Ref. [6] but support those from Ref. [5] with one single exception; we obtain $\eta^p_{xx,yy} = 1.1233$ a.u for $\lambda = 514.5$ nm compared to 1.124 a.u. Our B5 basis set values differ from the B3 values with at the most 24%. Despite this discrepancy, we will use these basis sets to investigate trends for the isoelectronic noble gas-like atoms. The static hypermagnetizability results are presented in Table 3. Theoretical results for $Li^+$ [7] and Ar [5, 2]

**Table 2.** Static values for the hypermagnetizability (a.u.) for He and Ne

| Atom | | $\eta^p_{xx,yy}$ | $\eta^d_{xx,xx}$ | $\eta^d_{xx,yy}$ | $\Delta\eta^d$ |
|---|---|---|---|---|---|
| He | A1 | 0.6869 | − 1.704 | − 2.415 | 0.711 |
| | A2 | 0.6868 | − 1.182 | − 2.794 | 1.612 |
| | A3 | 0.6917 | − 1.203 | − 2.833 | 1.631 |
| | A4 | 0.6931 | − 1.212 | − 2.857 | 1.645 |
| | A5 | 0.6882 | − 1.310 | − 2.760 | 1.450 |
| | A6 | 0.6452 | − 1.361 | − 2.328 | 0.966 |
| | [a] | 0.6930 | − 1.212 | − 2.857 | 1.645 |
| Ne | B1 | 0.521 | − 1.138 | − 2.013 | 0.875 |
| | B2 | 1.050 | − 2.648 | − 4.976 | 2.328 |
| | B3 | 1.050 | − 2.042 | − 5.298 | 3.256 |
| | B4 | 1.050 | − 2.040 | − 5.295 | 3.255 |
| | B5 | 0.928 | − 1.908 | − 4.059 | 2.151 |

[a] From Ref. [5]

**Table 3.** Static values for the hypermagnetizability (a.u.)

| | $\eta^p_{xx,yy}$ | $\eta^d_{xx,xx}$ | $\eta^d_{xx,yy}$ | $\Delta\eta^d$ |
|---|---|---|---|---|
| $H^-$ | $1.946 \times 10^2$ | $-1.974 \times 10^2$ | $-3.554 \times 10^2$ | $1.580 \times 10^2$ |
| He | $6.452 \times 10^{-1}$ | $-1.361 \times 10^0$ | $-2.328 \times 10^0$ | $9.662 \times 10^{-1}$ |
| $Li^+$ | $1.311 \times 10^{-2}$ | $-2.202 \times 10^{-2}$ | $-5.061 \times 10^{-2}$ | $2.859 \times 10^{-2}$ |
| $F^-$ | $2.313 \times 10^1$ | $-3.065 \times 10^1$ | $-7.485 \times 10^1$ | $4.420 \times 10^1$ |
| Ne | $9.275 \times 10^{-1}$ | $-1.908 \times 10^0$ | $-4.059 \times 10^0$ | $2.151 \times 10^0$ |
| $Na^+$ | $1.213 \times 10^{-1}$ | $-2.465 \times 10^{-1}$ | $-6.171 \times 10^{-1}$ | $3.706 \times 10^{-1}$ |
| $Cl^-$ | $1.101 \times 10^2$ | $-1.862 \times 10^2$ | $-4.072 \times 10^2$ | $2.210 \times 10^2$ |
| Ar | $1.225 \times 10^1$ | $-2.409 \times 10^1$ | $-4.620 \times 10^1$ | $2.211 \times 10^1$ |
| $K^+$ | $1.570 \times 10^0$ | $-7.636 \times 10^0$ | $-1.270 \times 10^1$ | $5.061 \times 10^0$ |

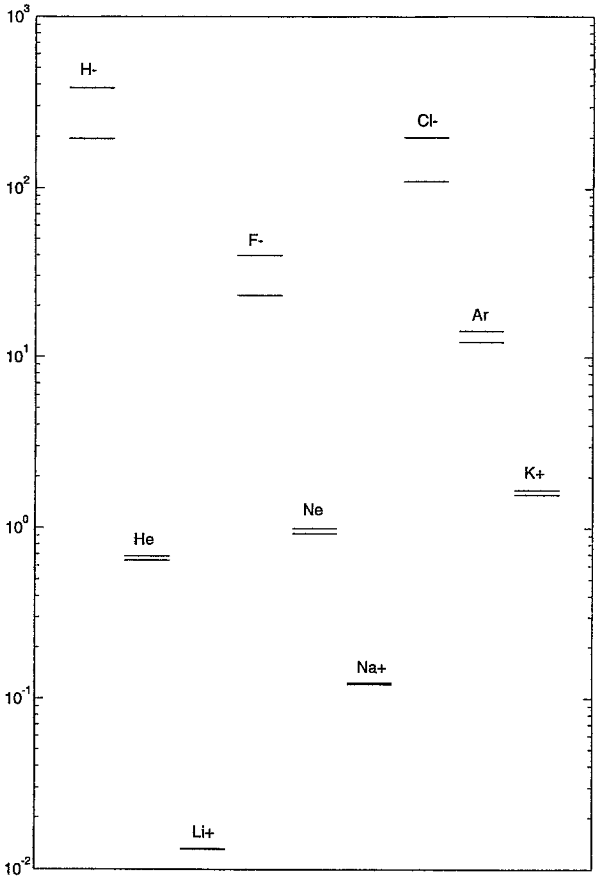

**Fig. 1.** Paramagnetic component, $\eta^{p}_{xx,yy}$, in a.u. Upper and lower bar for $\lambda$ equal to 488 nm and $\infty$, respectively

are available in the literature. The static values for $\Delta\eta^{p}$ and $\Delta\eta^{d}$ for $Li^{+}$ reported by Jamieson [7] are $-0.013115$ a.u. and 0.029193 a.u., respectively. We obtain $-0.01311$ and 0.02859 a.u. taken as further motivation for our choice of basis sets.

Within an isoelectronic series we observe a descending hypermagnetizability with larger nuclear charge. This holds for all components and we show the paramagnetic term, $\eta_{xx,yy}$, in Fig. 1 as an example. The largest difference between the positive and the negative ions is found for the He-like series where the values span over four order of magnitudes. From Fig. 1 we can also see the difference in dispersion; the upper and lower bar for each atom correspond to the different wavelength $\lambda = 488$ nm and $\lambda = \infty$, respectively. The cations and the noble gas atoms display a low dispersion for all components, whereas we see a significant dispersion for the anions due to the smaller excitation energy (c.f. Fig. 2).

## 5. Discussion

With this work we have demonstrated a realization of fully analytical calculations of hypermagnetizabilities. Stable solutions of the response equations have been

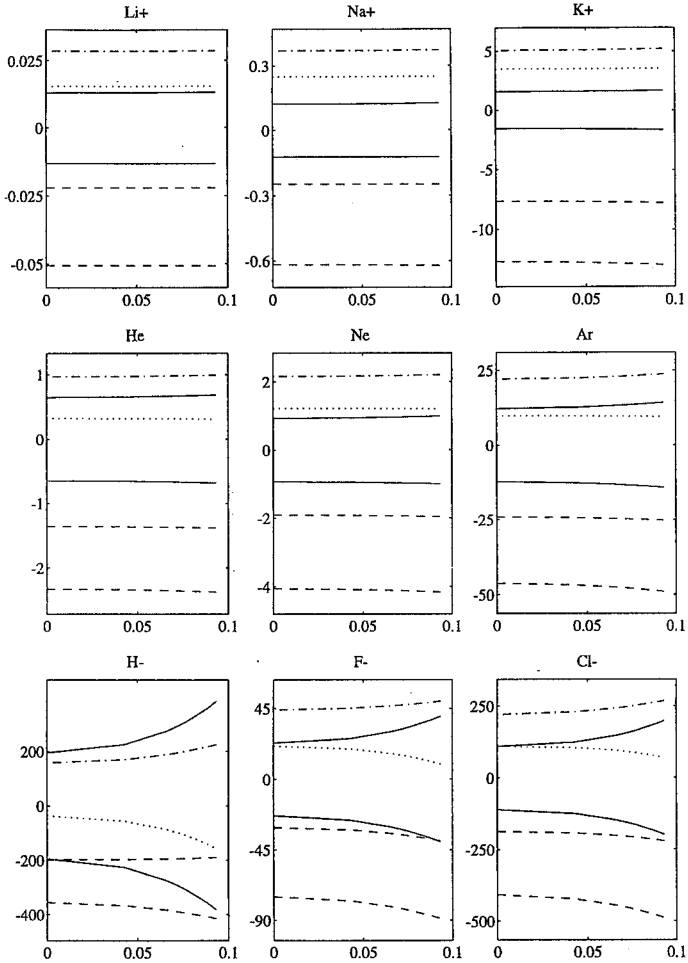

**Fig. 2.** Dispersion for the hypermagnetizability components $\Delta\eta^d$ (dashed-dotted), $\eta^p_{xx,yy}$ (solid, upper), $\Delta\eta$ (dotted), $\Delta\eta^p$ (solid, lower), $\eta^d_{xx,xx}$ (dashed, upper), and $\eta^d_{xx,yy}$ (dashed, lower)

found in each of the applied cases. With the present implementation of cubic response theory, we thus solve one of the complications encountered in calculations of hypermagnetizabilities; others refer to correlation effects, slow basis set convergence and origin dependency. The latter can be overcome for the smallest molecules by retaining large basis set expansions. However, somewhat larger molecules require origin independency, as also has been implemented for lower-order magnetic properties through the so-called field dependent London orbitals [17], molecular orbitals with individual gauges (IGLOS) [18–21], and also through localized orbitals with local origin (LORG) [22]. Implementation of gauge independent orbitals, and of multi-configuration reference states describing correlation, are surely also feasible, although not straightforward, for the cubic response functions.

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**Note added in proof** The disagreement with the result in Ref. [6] is due to a misprint in the same paper as noted in Theor Chim Acta (1995) 90:291