

# The magnetic hyperpolarizability anisotropy of the neon atom

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The anisotropy of the magnetic hyperpolarizability  $\Delta\eta$ , which determines the Cotton–Mouton effect, has been calculated for the Ne atom using the multiconfiguration response method. Our result for  $\Delta\eta$  at wavelength  $\lambda=514.5$  nm,  $2.670\pm 0.145$  (in atomic units of  $\eta$ ), agrees well with previous estimates and falls between the two available experimental values. The calculated dispersion is small, in part due to a cancellation between the paramagnetic and diamagnetic contributions.

## 1. Introduction

Numerous measurements have recently been carried out for atoms and small molecules of the Cotton–Mouton constant, characterizing the magnetic field induced birefringence (see refs. [1–4], and references therein). Ab initio calculations of the magnetic hyperpolarizability tensor  $\eta$ , which determines the Cotton–Mouton constant, have apparently been performed only for systems with two electrons. The calculations for the He atom [5,6] (see also the discussion in ref. [7]) are very accurate and may undoubtedly be used as a calibration standard. Also the H<sub>2</sub> results [6] are presumably accurate, even though the problem of the gauge origin and the existence of vibrational and rotational contributions make the molecular calculations much more difficult. For larger systems only predictions partly based on empirical data have been made [5].

We present here a systematic theoretical study of  $\Delta\eta$  for the neon atom at the ab initio level. We use highly correlated multiconfiguration self-consistent

field (MC SCF) reference functions, a fairly large basis set, and compute both the diamagnetic and the paramagnetic contribution. We have systematically investigated the importance of electron correlation, which enables us to provide a theoretical result with estimated error bars. We have also studied dispersion, hence our result may be compared directly with experiment.

## 2. Theory

The theoretical interpretation of the Cotton–Mouton effect has been described by Buckingham and Pople [8]. In particular, they have shown that for a spherical system the molar Cotton–Mouton constant  ${}_mC$  is proportional to  $\Delta\eta=\eta_{xx,xx}-\eta_{xx,yy}$ , the anisotropy of the magnetic hyperpolarizability. A variety of definitions and units is used in theory and experiment for  ${}_mC$  and  $\Delta\eta$  (see e.g. ref. [9]), moreover the experimental results are often given for  $C_{CM}\sim\lambda {}_mC$ , where  $\lambda$  is the wavelength. Here, we shall

consistently discuss the  $\eta$  tensor given in atomic units. We follow the definitions of Fowler and Buckingham [9] for  $\Delta\eta$ ;  ${}_m C$  can be obtained as

$${}_m C = 2\pi N_A \Delta\eta / 27, \quad (1)$$

where  $N_A$  is Avogadro's constant. For comparison with other works, 1 au of  $\eta$  is  $e^4 a_0^4 / m_e E_h^2$ , it equals  $2.98425 \times 10^{-52} \text{ C}^2 \text{ m}^2 \text{ J}^{-1} \text{ T}^{-2}$  in SI units, or  $2.682108 \times 10^{-44} (4\pi\epsilon_0) \text{ cm}^3 \text{ G}^{-2}$  [6]. Finally, to compare with the experimental  $C_{CM}$  [1,2] given for  $\lambda = 514.4 \text{ nm}$  in  $\text{G}^{-2} \text{ cm}^{-1}$  we have to multiply  $\Delta\eta$  given in au by  $4.400 \times 10^{-20}$ .

For static and uniform electric and magnetic fields  $F$  and  $B$  the tensor  $\eta$  can be related [9] to the change in energy

$$\Delta E = \dots - \frac{1}{4} \eta F F B B \dots \quad (2)$$

(we omit all lower and higher order terms).  
An equivalent expression is

$$\Delta\chi = \dots + \frac{1}{2} \eta F F \dots, \quad (3)$$

where  $\chi$  is the magnetic susceptibility, and  $\Delta\chi$  its change due to the additionally applied electric field. This equation has been successfully used to compute  $\eta$  from a finite-field calculation of  $\chi$  [9].

However,  $\eta$  should in general be treated as a frequency-dependent response property. Similarly to the magnetic susceptibility,  $\eta$  is a sum of a paramagnetic and a diamagnetic contribution. It can be expressed as

$$\eta = -\frac{1}{2} \langle\langle r; r, L, L \rangle\rangle_{\omega,0,0} - \frac{1}{4} \langle\langle r; r, Q \rangle\rangle_{\omega,0}, \quad (4)$$

where  $r$ ,  $Q$  and  $L$  are the dipole moment, the quadrupole moment and the angular momentum operators, and  $\omega$  is the frequency of the electric field.

The double brackets in eq. (4) denote the response functions. We refer to ref. [10] for a detailed analysis of the response to a time-dependent field of the exact state, and of a state described by an MC SCF wavefunction. The formulation of the theory and the resulting equations of the multiconfiguration linear response (MCLR) and quadratic response (MCQR) [10,11] do not depend on the perturbation operators of interest. The computational implementation [11,12] enables the use of large scale MC SCF wavefunctions as unperturbed states with configuration expansions including more than  $10^5$  determinants.

The static value of  $\eta$  which can be determined from the  $\langle\langle r; r, L, L \rangle\rangle_{0,0,0}$  and  $\langle\langle r; r, Q \rangle\rangle_{0,0}$  response functions is equal to the result of a finite field calculation. The frequency-dependent response functions may also be expressed using sum-over-states formulae analogous to those used in the calculations of  $\eta$  for two-electron systems [6]. However, this formulation is not tractable for larger systems; in the used implementation of the multiconfiguration response (MCR) approach the sum-over-states expressions have been rewritten in such way that they may be calculated by solving sets of linear response equations. Finally, we note that the diamagnetic part is equal to  $-\frac{1}{4} B(-\omega; \omega, 0)$ , where  $B$  is the frequency dependent dipole-dipole-quadrupole polarizability.

Jamieson [7] has shown that for atoms advantage can be taken of the spherical symmetry. The angular momentum operator  $L$  commutes with the unperturbed Hamiltonian and the paramagnetic term can be expressed as

$$\Delta\eta^p = -\frac{1}{2} (S_{-4} + 6\omega^2 S_{-6} + 15\omega^4 S_{-8} + \dots), \quad (5)$$

which makes atomic calculations much simpler than molecular calculations.

Bishop and Pipin have recently provided estimates of  $\Delta\eta$  for rare gas atoms [5]. In their analysis the static values of  $\Delta\eta$  are obtained from a mixture of ab initio ( $B$  hyperpolarizabilities) and experimental ( $S_{-4}$  values) results.

We have used a number of different approaches (finite field and linear response, finite field and non-linear response etc.) to test the correctness and the accuracy of the static values of the diamagnetic and paramagnetic components. For  $\omega \neq 0$  the quadratic response program described in ref. [11] was applied to compute  $B(-\omega; \omega, 0)$  and eq. (5) was used to obtain the frequency-dependent paramagnetic term of  $\Delta\eta$  from the computed  $S_{-n}$  values [13]. In a test of our programs, using a rather simple correlated wavefunction we have reproduced almost exactly the best available results for the He atom (correlated frequency-dependent values quoted in table 1 of ref. [7]).

### 3. Results and discussion

The computational procedure follows the pattern

described in detail in the previous calculations of the electric dipole hyperpolarizability of the neon atom [14]. A 10s8p6d4f CGTO basis set was taken from ref. [15] (we use all the Cartesian components for d and f type orbitals, so our SCF results differ slightly from ref. [15]). The calculations were performed for three MC SCF wavefunctions. The first is a restricted active space (RAS) calculation including all single and double excitations from the second (2s, 2p) into the third (3s, 3p, 3d) shell of the Ne atom. The second is a complete active space (CAS) calculation in which all the second and third shell orbitals form the active space, and in the last MC SCF function single and double excitations from the second into the third and fourth (4s, 4p, 4d, 4f) shell are considered. We denote these approximations as SD RAS 3, CAS 3 and SD RAS 4, respectively. Comparing the CAS 3 and SD RAS 3 results, we can estimate the role of multiple excitations, and comparing SD RAS 4 and SD RAS 3 we obtain an estimate of the role of the next shells.

The approximation used for the final value of a property  $Q$  is

$$Q = Q(\text{SD RAS 4}) + Q(\text{CAS 3}) - 1(\text{SD RAS 3}) + \frac{1}{2}(Q(\text{SD RAS 4}) - Q(\text{SD RAS 3})), \quad (6)$$

and the total correction to  $Q(\text{SD RAS 4})$  is treated [14] as an estimate of the uncertainty of the result.

The results of the calculations for  $\Delta\eta$  are shown in table 1. The frequency  $\omega = 0.08856$  au has been chosen, as it corresponds to the wavelength  $\lambda = 514.5$  nm, for which there is a recent experimental result [1]. We have also repeated the SCF and CAS calculations

for  $\omega = 0$ . The value for  $\lambda = 632.8$  nm should be between the  $\omega = 0$  and  $\omega = 0.08856$  au results, therefore we have not done any calculations for this wavelength.

The static results (dia-, para-magnetic and total) are as follows: 3.256, -1.105 and 2.151 au in SCF, and 4.004, -1.317 and 2.687 au for the CAS 3 wavefunction. Comparing with the results in table 1 we find that the dispersion effect is very small at both levels of theory because the contributions from the paramagnetic and diamagnetic terms are of opposite sign and practically cancel. Some of the values obtained for the static properties can be compared with available reference results. For  $-\frac{1}{4}B(0; 0, 0)$  we find 3.4 au from the SCF calculation of Maroulis and Bishop [17], and 4.425 au using the CCSD(T) value of Taylor et al. [18].

The accuracy of the computed paramagnetic contribution can be analyzed using the available experimental data. From the  $S_{-n}$  values given by Kumar and Meath [19] we can calculate the paramagnetic contribution to  $\Delta\eta$ . The experimental value of  $S_{-4}$  yields -1.443 au. Using the experimental values for  $S_{-n}$  we obtain -1.567 au for the wavelength  $\lambda = 514.5$  nm. Our final estimate is close to this result, although in contrast to  $S_{-2}$  and  $S_{-3}$  [14] the suggested uncertainties give results that are slightly outside the experimental ones. We note that in practice the dispersion is described very well for  $\omega < 0.1$  au by the  $\omega^2 S_{-6}$  term.

In summary, none of our results differ significantly from the available reference values. There is a partial cancellation of correlation corrections to the diamagnetic and paramagnetic contributions, and a

Table 1  
Magnetic hyperpolarizability anisotropy for the Ne atom (in au of  $\eta$ )<sup>a)</sup>

	$\Delta\eta$ dia	$\Delta\eta$ para	$\Delta\eta$ total
wavefunction			
SCF	3.330	-1.123	2.207
SD RAS 3	3.980	-1.373	2.607
CAS 3	4.108	-1.422	2.686
SD RAS 4	4.076	-1.413	2.663
estimate	4.152 ± 0.076	-1.482 ± 0.069	2.670 ± 0.145
experiment			1.25 ± 0.07 [1]
experiment ( $\lambda = 632.8$ nm)			4.10 ± 3.00 [16]

<sup>a)</sup> For  $\lambda = 514.5$  nm, unless otherwise stated.

similar cancellation of dispersion effects indicating that the final result for  $\Delta\eta$ ,  $2.670 \pm 0.145$  au, may be more accurate than either of the individual contributions. The calculations also indicate that further experimental investigations are required before a reliable Cotton-Mouton constant is obtained.

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