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MCSCF calculation of response properties of Argon*

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Summary. Analytic equations of the multiconfigurational SCF (MCSCF) response theory are combined with the finite-field (FF) approach to compute static and frequency dependent electric and magnetic properties of the Argon atom. A complete active space (CAS SCF) function including the 3s, 3p, 3d, 4s and 4p orbitals in the active space and a large (17s 13p 7d 5f 3g) basis set are employed. This permits an accurate determination of various linear and non-linear response properties such as e.g. electric dipole polarisability and second hyperpolarisability, Verdet constant, magnetisability and second hyperpolarisability. The results, both for the static values and for the frequency dependence of these properties, compare well with other most recent experimental and theoretical data.

Key words: Argon – MCSCF – Linear response – Quadratic response – Properties

Introduction and theory

Numerous electric, magnetic and optical properties characterising the interaction of an atom or a molecule with weak external fields can be described using perturbation theory. *Ab initio* methods applying analytic and/or numerical perturbation schemes which enable accurate calculations of static and dynamic linear, quadratic, cubic, etc. response properties have been developed. Practical applications indicate that for many atomic and molecular properties the Hartree–Fock approximation is not sufficiently accurate and it is essential to include correlation effects. For a description of the underlying theory, reviews and some examples of recent applications see for example refs. [1–4] and references therein.

A natural extension of the SCF perturbation approach is offered by multiconfigurational SCF (MCSCF) response theory, which we apply in this work. In this formalism, an MCSCF reference function is used to describe the unperturbed system. The basic equations for the linear and quadratic MCSCF response have been given long ago [5–7]; more recently there have been many developments both in the theory and in the computational approach to the problem. The equations

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* Dedicated to Jan Linderberg on the occasion of his 60th birthday

determining the linear, quadratic and cubic (LR, QR and CR) response functions for an MCSCF reference wave function have been derived following the analysis for an exact state [7]. Solution of the LR function in a direct [8, 9] scheme enables calculations with very large ($> 10^6$) configuration spaces. This is a qualitative change, the non-direct codes require matrix inversion and thus limit to ca. 10^3 configurations the Cl expansion. The QR was also implemented for MCSCF states [10] in a direct formulation.

The potential of the LR and QR programs we use is also increasing. The atomic and molecular properties that can presently be calculated include electronic excitation energies, one- and two-photon transition moments, frequency-dependent electric and magnetic polarisabilities and hyperpolarisabilities, long-range interaction coefficients, nuclear shielding constants, spin related properties etc. By coupling analytic response and finite field (FF) methods, higher-order electric and magnetic properties can be evaluated [11].

A few years ago one of us performed a MCSCF LR calculation of the frequency dependent electric dipole polarisabilities of He, Ne and Ar [12]. The use of non-direct codes and the limitations of the hardware at that time did not allow to obtain a completely satisfactory solution to the problem for the Argon atom. With the advent of new theoretical and computational techniques, the implementation of elaborate algorithms and the development of computer ware, accurate studies of first, second- and higher-order properties in atomic systems of the size of Argon became possible. This work presents the results obtained from large-scale multiconfigurational LR and QR calculations for Argon. We computed the following properties:

- static and frequency-dependent electric dipole polarisability;
- static and frequency-dependent second electric dipole hyperpolarisabilities (Kerr effect);
- C_6 and A_6, the coefficients characterising the dispersion contributions to the change of energy and polarisability due to weak intermolecular interactions;
- Verdet constant;
- static and frequency-dependent hypermagnetisability anisotropy (Cotton Mouton constant).

In a related though independent study [13] QR was used to compute two-photon bound–bound transition probabilities in Argon.

Most of the properties here considered were obtained by exploiting suitable moment expansions. LR furnishes directly the Cauchy moments which can be used to compute the dynamic electric dipole polarisabilities in the normal dispersion region through the well known expression (a.u. used throughout, see below)

$$\alpha(-\omega;\omega) = \sum_{n=0}^{\infty} S(-2n-2)(\omega^2)^n. \tag{1}$$

The $S(-2n-2)$ are the dipole Cauchy moments (moments of the dipole oscillator strength distribution). The radius of convergence of this expansion is determined by the first excitation energy, but there are many analytic continuation techniques which permit e.g. evaluation of $\alpha(-i\omega; i\omega)$ for $\omega \to \infty$. $\alpha(-\omega;\omega)$ can be obtained directly, independently and in the whole frequency range by solving the appropriate LR equations [8].

In general analytic calculation of the dynamic second electric dipole hyperpolarisabilities $\gamma(-\omega_0; \omega_1, \omega_2, \omega_3)$ would require a cubic response (CR) approach. For the Kerr hyperpolarisability $\gamma(-\omega; \omega, 0, 0)$ the mixed analytical–numerical formalism [14] can be used. It may be computed using QR + FF, via $\beta(-\omega; \omega, 0)$, or using LR + FF through second numerical derivatives of $\alpha(-\omega; \omega)$. An equivalent of the last approximation can also be obtained from the Cauchy moments, essentially by taking the second derivative of Eq. (1) with respect to the field.

$$\begin{aligned}\gamma(-\omega; \omega, 0, 0) &= 2[\alpha^{(F=f)}(-\omega; \omega) - \alpha^{(F=0)}(-\omega; \omega)]/f^2 \\ &= 2\left\{\sum_{n=0}^{\infty} [S^{(F=f)}(-2n-2) - S^{(F=0)}(-2n-2)](\omega^2)^n\right\}\Big/ f^2,\end{aligned} \tag{2}$$

where f is the strength of the applied field.

This expression can also be used with purely imaginary frequencies to obtain $\gamma(-\mathrm{i}\omega; \mathrm{i}\omega, 0, 0)$, which is of importance in the determination of the dispersion pair polarisabilities for weakly interacting atoms [15–17]. In the long-range interaction of two rare gas atoms (A and B at a distance R), the dispersion contribution to the energy can be obtained from the expansion

$$\Delta E_{\mathrm{disp}}^{\mathrm{AB}} = \sum_{n=6}^{\infty} \frac{C_n}{R^n}. \tag{3}$$

The Casimir-Polder relates C_6 *to* $\alpha(-\omega; \omega)$:

$$C_6 = \frac{3}{\pi} \int_0^{\infty} \alpha^{\mathrm{A}}(-\mathrm{i}\omega; \mathrm{i}\omega)\alpha^{\mathrm{B}}(-\mathrm{i}\omega; \mathrm{i}\omega)\, \mathrm{d}\omega. \tag{4}$$

Similarly the dispersion contribution to the incremental polarisability $\Delta\alpha_{\mathrm{disp}}^{\mathrm{AB}}$ is written as [15]

$$\Delta\alpha_{\mathrm{disp}}^{\mathrm{AB}} = \sum_{n=6}^{\infty} \frac{A_n}{R^n}, \tag{5}$$

$$A_6 = c(1 + P_{\mathrm{AB}}) \int_0^{\infty} \alpha^{\mathrm{A}}(-\mathrm{i}\omega; \mathrm{i}\omega)\gamma^{\mathrm{B}}(-\mathrm{i}\omega; \mathrm{i}\omega, 0, 0)\, \mathrm{d}\omega, \tag{6}$$

where P_{AB} interchanges the two systems and the proportionality constant c varies with the contributions to A_6 of various tensor components of $\alpha^{A}(-\mathrm{i}\omega; \mathrm{i}\omega)$ and $\gamma^{\mathrm{B}}(-\mathrm{i}\omega; \mathrm{i}\omega, 0, 0)$. Analytic continuation techniques and a suitable numerical integration scheme are used to evaluate the integrals in Eqs. (4) and (6) via Eqs. (1) and (2).

For non-zero values of ω, there are two independent components of the $\gamma(-\omega; \omega, 0, 0)$ tensor e.g. $\gamma_{zzzz}(-\omega; \omega, 0, 0)$ and $\gamma_{xxzz}(-\omega; \omega, 0, 0)$. We shall assume here the so-called Kleinman symmetry, that is $\gamma_{xxzz}(-\omega; \omega, 0, 0) = \frac{1}{3}$ $\gamma_{zzzz}(-\omega; \omega, 0, 0)$ for all the frequencies, and discuss only the *zzzz* component. Deviations from Kleinman symmetry have been discussed for the Ar atom by Rice [18] and were found to be very small.

The Verdet constant [19] $V(\omega)$, which in a dilute gas of number density N_0 is related to the dispersion of the optical refractivity [20, 21] and reproduces the dispersion of the Faraday rotation [22, 23] is another property that can be obtained from the Cauchy moments. In the Becquerel form, for atoms [20, 24, 25]

$$V(\omega) = \frac{\pi N_0}{c^2}\, \omega\, \frac{\mathrm{d}\alpha(-\omega; \omega)}{\mathrm{d}\omega} = \frac{2\pi N_0}{c^2} \sum_{n=0}^{\infty} nS(-2n-2)(\omega^2)^n. \tag{7}$$

$V(\omega)$ can also be computed independently by an appropriate combination of the QR functions $\langle\langle r_i; r_j, L_k \rangle\rangle_{\omega,0}$ $(i, j, k \equiv x, y, z)$ involving position (r) and orbital angular moment (L) operators [25–27]. This alternative rigorous approach to the calculation of the Verdet constant is needed for non-spherical systems [25–27]. For atoms it is more computationally demanding than calculations based on Eq. (7).

In spherical systems, the hypermagnetisability anisotropy [28] $\Delta\eta(-\omega; \omega, 0, 0) = \eta_{xx,xx} - \eta_{yy,xx}$ is proportional to the molar Cotton Mouton constant ${}_mC$, which is introduced in the description of the magnetic field induced birefringence [29, 30]. Its dispersion can be given in terms of a sum of paramagnetic and diamagnetic contributions as follows $(i, j, k, l$ run over the x, y, z components; the Einstein summation is implied; Q represents the quadrupole operator):

$$\eta_{ij,kl}(-\omega; \omega, 0, 0) = \eta^{\mathrm{p}}_{ij,kl} + \eta^{\mathrm{d}}_{ij,kl} = -\tfrac{1}{2}\langle\langle r_i; r_j, L_k, L_l \rangle\rangle_{\omega,0,0} - \tfrac{1}{4}\langle\langle r_i; r_j, Q_{kl} \rangle\rangle_{\omega,0}. \tag{8}$$

Fully analytic evaluation of the paramagnetic contribution requires thus the evaluation of the CR function, while the diamagnetic component is described by the QR dipole–dipole–quadrupole electric second hyperpolarisability

$$\Delta\eta^{\mathrm{d}} = -\tfrac{1}{4} B_{xx,xx}(-\omega; \omega, 0) = -\tfrac{1}{4}\langle\langle x; x, \tfrac{1}{2}(3x^2 - r^2) \rangle\rangle_{\omega,0}. \tag{9}$$

On the other hand it has been proved [31, 32] that for atoms the paramagnetic hypermagnetisability anisotropy can be written in terms of a typical Cauchy moment expansion as follows:

$$\Delta\eta^{\mathrm{p}} = -\frac{1}{4}\frac{\mathrm{d}^2\alpha(-\omega; \omega)}{\mathrm{d}\omega^2} = -\frac{1}{4}\sum_{n=0}^{\infty}(2n+1)(2n+2)S(-2n-4)(\omega^2)^n. \tag{10}$$

The static values of the diamagnetic hypermagnetisability anisotropy are obtained by computing the appropriate expectation values with and without an applied finite electric field

$$\eta^{\mathrm{d}}_{xx,xx}(0; 0, 0, 0) = 2(\langle x^2 \rangle^{(F_x = f)} - \langle x^2 \rangle^{(F_x = 0)})/f^2,$$

$$\eta^{\mathrm{d}}_{yy,xx}(0; 0, 0, 0) = 2(\langle y^2 \rangle^{(F_x = f)} - \langle y^2 \rangle^{(F_x = 0)})/f^2. \tag{11}$$

In summary, for most of the properties we have chosen a mixed analytic–numerical computational scheme. The advantage of a purely analytic approach is that one avoids the problems of numerical differentiation (for example, full symmetry can be used). However, for higher-order properties the solution of the analytic equations becomes time-consuming when very large CI expansions and/or basis sets are applied. For some of the properties, we have used both approaches for selected frequencies and verified the accuracy of the calculations.

Atomic units are adopted throughout the paper:

- electric dipole polarisabilities: 1 a.u. $(e^2a_0^2E_{\mathrm{h}}^{-1}) = 1.64878(-41)\ \mathrm{C^2\,m^2\,J^{-1}}$;
- electric dipole second hyperpolarisabilities: 1 a.u. $(e^4a_0^4E_{\mathrm{h}}^{-3}) = 6.23538(-65)\ \mathrm{C^2\,m^4\,J^{-3}}$;
- magnetisabilities: 1 a.u. $(e^2a_0^2m_{\mathrm{e}}^{-1}) = 7.98104(-29)\ \mathrm{J\,T^{-2}}$;
- Verdet constant: 1 a.u. (rad $ea_0h/2\pi$) $= 2.763816(+8)\ \mu\mathrm{min\,G^{-1}\,cm^{-1}}$ (at 1 atm of pressure) $= 8.039624(+4)\ \mathrm{rad\,T^{-1}\,m^{-1}}$.
- hypermagnetisabilities: 1 a.u. $[e^4a_0^4/(m_{\mathrm{e}}E_{\mathrm{h}}^2)] = 2.98425(-52)\ \mathrm{C^2\,m^2\,J^{-1}\,T^{-2}} = 2.682108(-44)(4\pi\varepsilon_0)\ \mathrm{cm^3\,G^{-2}}$.

Results and discussion

The basis set we employed to obtain all the linear response static and dynamic results is summarised in Table 1. A ⟨17s 13p 7d 5f 3g⟩ Cartesian Gaussian uncontracted set (193 basis functions) was built by extending the ⟨17s 13p 6d 2f⟩ set of Ref. [12]. The ⟨16s 10p 5d 2f⟩ uncontracted basis [33], already extended in Ref. [12], was further enlarged by adding one *d* function (exponent 0.21570), three *f* functions (exponents 0.8, 0.0125 and 0.003125) and three *g* functions. Some other basis sets were employed in the course of the investigation, mainly subsets of the basis of Table 1. The computationally intense QR dynamic property calculations were performed using the ⟨17s 13p 6d 3f 1g⟩ uncontracted Cartesian Gaussian subset (137 basis functions) obtained by deleting the most diffuse *d* and *f* and the two inner *g* functions. This basis gave very accurate results for the two-photon bound–bound transition rate between the ground $^1S^e$ and the excited $^1D^e$ states of argon [13]. A slightly larger (⟨19s 15s 7d 3f 1g⟩) set with extra diffuse and extra tight *s* and *p* functions was also employed and we found out that the properties were practically insensitive to the extension of the *s* and *p* manifolds.

Using the basis set of Table 1 we obtained for the SCF ground state energy − 526.810238 a.u., to be compared with the numerical HF limit of − 526.81751 a.u. [34].

The correlated results presented in this work were obtained in the CAS SCF approximation. A complete active space including the 3s, 3p, 3d, 4s and 4p orbitals was selected on the basis of the natural orbital occupation numbers of a second-order Møller-Plesset calculation. The resulting Cl expansion included over 125 000 determinants. The lowest MP2 NO occupation number of an orbital included in the CAS was 0.0056 while the highest occupation number for an orbital excluded from the CAS was 0.0012, thus indicating that a sizeable amount of valence shell correlation for the given basis set is taken into account in our

Table 1. ⟨17s 13p 7d 5f 3g⟩ Cartesian Gaussian uncontracted basis set (193 basis functions)

s	p	d	f	g
118 186.0	660.901	9.45	0.8	0.45
17 688.8	157.219	3.15	0.2	0.22222
4027.3	50.0639	1.05	0.05	0.1
1144.96	18.6119	0.35	0.0125	
376.954	7.43692	0.116667	0.003125	
138.070	3.08857	0.064710		
54.954	1.10267	0.021570		
23.1650	0.414763			
7.37688	0.145449			
2.92369	0.051006			
0.650663	0.017887			
0.232877	0.006273			
0.083348	0.002			
0.029831				
0.010677				
0.003821				
0.001				

approach. The MCSCF wave functions were determined using the SIRIUS program [35]. The integrals were computed with the HERMIT program [36].

The CAS SCF ground state energy was -526.986944 a.u., which is 7.44 mH above the corresponding CAS limit determined using a numerical multiconfigurational HF program [13]. This difference is almost equal to the corresponding SCF value. We have also performed an MP2 calculation, and the correlation energy was -0.530 a.u.. This can be compared with other values close to -0.600 a.u., an estimated MP2 limit of -0.706 a.u. [37] and finally with the -0.7225 a.u. non-relativistic estimate of Ref. [38].

The values of the Cauchy moments $S(-2k-2)$ for even k ranging from 0 to 10 are reported in Table 2. The SCF and correlated (CAS SCF) values are compared with some experimental estimates taken from the literature for the lowest moments [39, 40]. We also report the moments for a finite-field calculation with an electric field of 0.001 a.u. strength. The finite-field values were employed to compute the electric field dependent hyperpolarisabilities $\gamma(-\omega; \omega, 0, 0)$ and $\gamma(-i\omega; i\omega, 0, 0)$ as discussed in the preceding section. This field strength was found adequate to compute accurate and stable values of the electric hyperpolarisabilities and hypermagnetisabilities reported in the tables.

We list in Table 2 only the Cauchy moments that were needed to achieve a satisfactory degree of convergence in the moment expansion for the properties considered here and in the frequency range of interest, although we were able to compute $S(-2k-2)$ for k up to 20. Comparing the reduced 137 function set mentioned above with the basis of Table 1, the $S(-2)$ SCF and CAS SCF values of Table 2 vary by less than 0.07% and $S(-18)$ varies by less than 1.5%. This shows a very high degree of convergence of the moments with respect to the basis set extension.

Table 3 summarises the results obtained for some static electric and magnetic properties, and compares them with other recent theoretical estimates and, when available, experiment. The static values of the electric dipole polarisability $\alpha(0, 0)$ and hyperpolarisability $\gamma(0; 0, 0, 0)$ and the paramagnetic component of the hypermagnetisability $\Delta\eta^{p}(0; 0, 0, 0)$ correspond to the first terms of the respective Cauchy moment expansions. The average values of quadrupole operators were computed to obtain the remaining static properties of Table 3 (see e.g. Eq. (11)). As indicated above, a finite field calculation was needed to compute the electric dipole hyperpolarisabilities and the diamagnetic hypermagnetisabilities.

There is a vast literature on the *ab initio* determination of the electric dipole polarisability, and in the table we report only the most recent references for that property. The SCF value of 10.7606 a.u. is practically on top of the Hartree Fock limit [50]. The CAS SCF number is in very good agreement with that of Rice et al. [42] obtained with CCSD(T) + core correction and with the MP2 estimate of Bishop and Cybulski [47]. The present result improves significantly the previous mutliconfigurational LR estimate of Ref. [12], where a smaller basis set and a complete active space missing the 3d orbital was adopted. This is evidently of fundamental importance for an accurate description of the properties of this atom.

There are several references for both SCF and correlated (essentially MBPT or CCSD(T) plus finite field) static electric dipole second hyperpolarisabilities $\gamma(0; 0, 0, 0)$. We report only a few recent results. Our SCF value is slightly smaller than that of others. Also our CAS SCF estimate is smaller than that of Ref. [42] – a CCSD(T) + core correction calculation – and much smaller than the 1329 a.u. value obtained as best estimate at MP4 level by Cernusak et al. [51]. Techniques based on truncation of infinite-order expansions might suffer from convergence

Table 2. Cauchy moments in a zero electric field and in a finite electric field of 0.001 a.u. The numbers in parentheses are the powers of ten. The basis set of Table 1 was employed. The experimental values refer to a zero field. Atomic units. See text.

	Zero field			Finite field (= 0.001 a.u.)	
k	SCF Moment = $S(-2k-2)$	Correlated Moment = $S(-2k-2)$	Experiment	SCF Moment = $S(-2k-2)$	Correlated Moment = $S(-2k-2)$
0	1.0760601(+ 01)	1.1170776(+ 01)	11.08[a,b]	1.0761075(+ 01)	1.1171337(+ 01)
1	2.5457567(+ 01)	2.8322338(+ 01)	27.91[a], 27.98[b]	2.5462878(+ 01)	2.8329058(+ 01)
2	7.9799025(+ 01)	9.6229594(+ 01)	95.06[a], 94.56[b]	7.9842816(+ 01)	9.6288365(+ 01)
3	3.0069072(+ 02)	3.9286683(+ 02)	391.5[a], 382.1[b]	3.0100605(+ 02)	3.9331561(+ 02)
4	1.2679700(+ 03)	1.7881886(+ 03)	1802.0[a]	1.2700729(+ 03)	1.7913598(+ 03)
5	5.7116137(+ 03)	8.6636736(+ 03)		5.7249565(+ 03)	8.6850017(+ 03)
6	2.6740438(+ 04)	4.3510942(+ 04)		2.6822096(+ 04)	4.3649488(+ 04)
7	1.2809143(+ 05)	2.2316188(+ 05)		1.2857526(+ 05)	2.2403831(+ 05)
8	6.2213413(+ 05)	1.1589846(+ 06)		6.2490794(+ 05)	1.1644117(+ 06)
9	3.0475614(+ 06)	6.0649747(+ 06)		3.0629482(+ 06)	6.0979914(+ 06)
10	1.5008579(+ 07)	3.1886193(+ 07)		1.5091333(+ 07)	3.2084111(+ 07)

[a] Ref. [39]

[b] Ref. [40]

Table 3. Static properties. See text. Atomic units. Basis set of Table 1

	SCF			Correlated				
	This work	Other Refs.	Ref.	This work	Other Refs.	Refs.	Exp.	Ref.
S_0	17.696^{a}	17.814^{b}	[12]	17.693^{a}	17.840^{b}	[12]	18^{c}	
Electric dipole polarisability $\alpha(0;0)$	10.7606^{d}	10.7537	[12]	11.1708^{d}	11.175	[47]	11.074	[44]
		10.757	[41]		11.17 ± 0.05	[42]	11.08	[39]
		10.76	[42]		11.12	[43]		
		10.73	[43]					
Electric dipole second Hyperpolarisability $\gamma(0;0,0,0)$	946.86^{e}	958.9	[41]	1122.58^{e}	1220 ± 30	[42]	1167 ± 6	[46]
		961.3	[18]		1174	[43]		
		966.	[42]					
		974.	[43]					
Magnetic susceptibility $\chi(0;0)$	$-$ 4.3404^{f}	$-$ 4.3391	[41]	$-$ 4.3478^{f}	$-$ 4.3483	[49]	$-$ 4.125	[45]
		$-$ 4.344	[48]		$-$ 4.369	[48]	$-$ 3.939	[20]
Diamagnetic hypermagnetisability $\eta^{d}_{xx,xx}(0;0,0,0)$	$-$ 19.03^{g}	$-$ 18.84	[41]	$-$ 20.80^{g}	$-$ 22.60	[47]		
		$-$ 18.71	[47]					
Diamagnetic hypermagnetisability $\eta^{d}_{yy,xx}(0;0,0,0)$	$-$ 53.52^{h}	$-$ 54.03	[41]	$-$ 59.17^{h}	$-$ 62.42	[47]		
		$-$ 53.58	[47]					
Paramagnetic hypermagnetisability Anisotropy $\Delta\eta^{p}(0;0,0,0)$	$-$ 12.73^{i}	$-$ 12.82	[41]	$-$ 41.16^{i}	$-$ 14.22	[47]		
		$-$ 12.64	[47]					
Hypermagnetisability anistropy $\Delta\eta(0;0,0,0)$	21.76^{j}	22.37	[41]	24.21^{j}	25.59	[47]		
		22.23	[47]					

[a] Mixed length velocity gauge. The exact value is 18, the number of electrons.

[b] Length gauge; [c] Exact

[d] $\alpha(0;0) = S^{(F=0)}(-2)$; [e] $\gamma(0;0,0,0) = 2[S^{(F=f)}(-2) - S^{(F=0)}(-2)]/f^2$; [f] $\chi(0;0) = \langle(x^2+y^2+z^2)\rangle^{(F=0)}/6$; [g] $\eta^{d}_{xx,xx}(0;0,0,0) = 2(\langle x^2\rangle^{(F_x=f)} - \langle x^2\rangle^{(F_x=0)})/f^2$;

[h] $\eta^{d}_{yy,xx}(0;0,0,0) = 2(\langle y^2\rangle^{(F_x=f)} - \langle y^2\rangle^{(F_x=0)})/f^2$; [i] $\Delta\eta^{p}(0;0,0,0) = -S^{(F=0)}(-4)/2$; [j] $\Delta\eta(0;0,0,0) = (\eta^{d}_{xx,xx} - \eta^{d}_{yy,xx}) - \Delta\eta^{p}$

problems, and this might be especially true for high-order properties [43, 51] (for example, in Ref. [43] the MP2 results are "too unstable to include" them). Also, the basis set dependence of high-order properties is not straightforward [42]. However, it is very likely that we miss a part of the dynamic correlation effects, included in other calculations.

The SCF result for the magnetisability of Argon is in close agreement with the others reported in the table. Ruud et al. [49], used the 137 functions subset of the basis of Table 1 to obtain their MCSCF reference result for the magnetisability of Argon. Our magnetisabilities are in satisfactory agreement with the PNO-CEPA results of Reinsch and Meyer [48].

The references for *ab initio* determination of hypermagnetisabilities and hypermagnetisability anisotropies (closely related to the Cotton Mouton constant [28, 52]) are two very recent papers by Bishop and Cybulski [41, 47], who employ a mixed analytical–numerical method at the SCF and MP2 levels of approximation. Their results and ours are in good agreement. A similar study furnished recently accurate results for the hypermagnetisability anisotropy (static value and dispersion) of the Neon atom [11].

From the data of Table 3 for $\Delta\eta^{\mathrm{d}} = \eta^{\mathrm{d}}_{xx,xx} - \eta^{\mathrm{d}}_{yy,xx}$ and Eq. (9) we obtain static limits for the dipole–dipole–quadrupole second hyperpolarisability $B_{xx,xx}(0;0,0)$ of -137.96 a.u. (SCF) and -153.48 a.u. (MCSCF). Cernusak et al. [51] best estimates are -140.9 a.u. (SCF) and -164.3 a.u. (MP4). Other recent SCF values in the literature range from -131 a.u. [53] to -139.9 a.u. [41].

In agreement with what was reported in Ref. [42] the effect of the three *g* functions in the basis on the static electric polarisability and magnetic susceptibilities of Table 3 is negligible. Deleting these functions in the basis modifies the values of the polarisabilities by less than 0.08% and the second hyperpolarisabilities by less than 1.5%. In summary, it appears that we have reached convergence with the basis set for most of the computed static properties. The present CAS SCF results agree well with experiment and with other *ab initio* values. Similar to Neon [47, 54], the CAS SCF results yield smaller values of the correlation corrections than MBPT and CC methods, which include more dynamic correlation effects. The available experimental data indicate that the CAS SCF results slightly underestimate correlation effects, and the other methods tend to overestimate them.

Table 4 and Fig. 1 show the results obtained for the frequency-dependent electric dipole polarisability $\alpha(-\omega;\omega)$, using the Cauchy moment expansion Eq. (1). We have verified for selected values of ω that the results of a direct LR calculation agree to all figures with those of Table 4. The 193 basis function values

Table 4. Electric dipole polarisability $\alpha(-\omega;\omega)$. Atomic units. Basis set of Table 1. The values in the last column were obtained from the experimental Cauchy moments of Ref. [39]

		SCF		Correlated		Exp.
ω (a.u.)	ω (nm)	This work $\alpha(-\omega;\omega)$	Ref. [18] $\alpha(-\omega;\omega)$	This work $\alpha(-\omega;\omega)$	Ref. [18] $\alpha(-\omega;\omega)$	Ref. [39] $\alpha(-\omega;\omega)$
0	∞	10.761	10.73	11.171	11.20	11.08
0.02	2278	10.771	10.74	11.182	11.21	11.09
0.04	1139	10.802	10.77	11.216	11.24	11.12
0.06	759.4	10.853	10.82	11.274	11.30	11.18
0.08	569.5	10.927	10.90	11.356	11.37	11.26
0.10	455.6	11.024	10.99	11.464	11.47	11.37

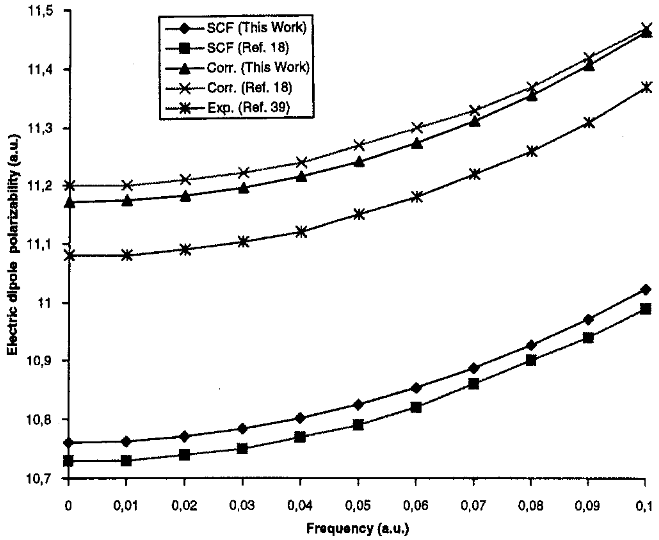

Fig. 1. Electric dipole polarisability $\alpha(-\omega;\omega)$. Atomic units.

reported in the table are on average 0.04% (SCF) and 0.06% (CAS SCF) lower than those obtained with the reduced 137 basis function set. Our correlated results agree well with the recent MP2 estimates by Rice [18] and fairly well with experiment [39].

The electric dipole hyperpolarisability $\gamma(-\omega;\omega,0,0)$ was computed using the Cauchy moment values of Table 2 in Eq. (2) and a finite-field strength of 0.001 a.u. The frequency dependence of the second electric hyperpolarisability for Argon was thus obtained by coupling LR (*not* QR) and FF. A plot of the Kerr effect is given in Fig. 2. The experimental data in Fig. 2 are the Kerr effect values extracted from Ref. [46] using the power series expansion of the second-order hyperpolarisability parallel component [46, 55, 56].

$$\gamma(-\omega_\sigma;\omega_1,\omega_2,\omega_3) \approx \gamma(0;0,0,0)[1 + A\omega_L^2 + B\omega_L^4]. \tag{12}$$

where $\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \omega_3^2$. The fitting of experimental ESHG data in Ref. [46] gives $\gamma(0;0,0,0) = 1165.6108$ a.u., $A = 5.13342$ a.u. and $B = 47.1451$ a.u. Our correlated data for $\gamma(-\omega;\omega,0,0)$ can be best fitted by Eq. (12) with $\gamma(0;0,0,0) = 1122.61$ a.u., $A = 5.96449$ a.u. and $B = 29.3072$ a.u. The most recent computational study of the Kerr effect in Argon is a MP2 calculation by Rice [18], whose data are fitted in Ref. [57] with $\gamma(0;0,0,0) = 1220$ a.u., $A = 5.183$ a.u. and $B = 31.857$ a.u.. The present CAS SCF results and those of Rice [18, 57] go in opposite directions with respect to Shelton's [46] experiment. As with all the other properties discussed here the SCF results are quite distant from experiment and the effect of correlation is significant.

As mentioned in the Theory section, the Cauchy expansion provides also the data needed for the analysis of the dispersion contributions in the weak intermolecular interactions regime. Using Eq. (4), we obtain $C_6 = 62.00$ a.u. at the SCF level and $C_6 = 64.94$ a.u. for the MCSCF calculation. This compares well with other *ab initio* results, such as the 61.833 a.u. value in the SCF approximation of

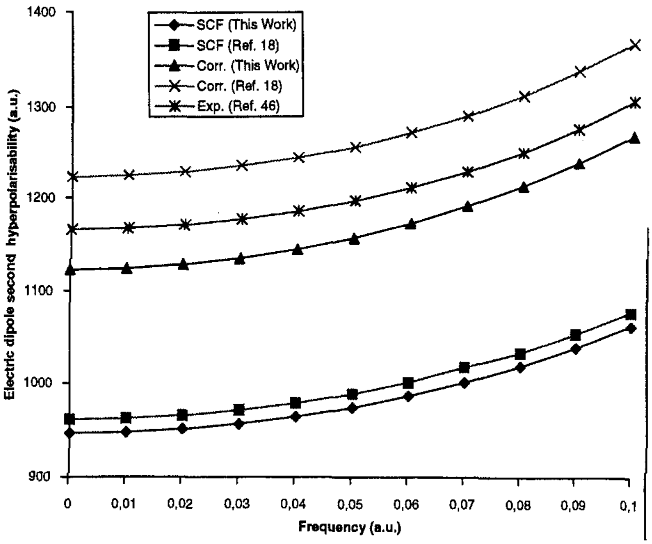

Fig. 2. Electric dipole second hyperpolarisability (Kerr effect), $\gamma(-\omega; \omega, 0, 0)$. Atomic units.

Ref. [58] or the 64.543 a.u. MP2 result of Ref. [59] or with the experimental estimate of 64.30 a.u. found in Ref. [60].

There are apparently no *ab initio* values of A_6 for Ar derived applying explicitly $\gamma(-\mathrm{i}\omega; \mathrm{i}\omega, 0, 0)$ as in Eq. (6). We can however compare our results with the estimates, derived following Hunt et al. [61].

$$A_6 = \frac{7}{9}\frac{C_6\gamma(0;0,0,0)}{\alpha(0,0)}. \tag{13}$$

Our results are 4313 and 4981 a.u. in the SCF and MCSCF approximations, respectively. Both values were obtained applying [7, 6] Padè approximants to the series $\{S^{F=f}(-2k-2) - S^{F=0}(-2k-2)\}$ and appear to be accurate to ± 2%. The corresponding estimates, obtained from SCF and MCSCF values of C_6, $\gamma(0;0,0,0)$ and $\alpha(0;0)$ are 4243 and 5073 a.u., so Eq. (13) provides a very good approximation to A_6. Applying Eq. (13) and using the experimental data we obtain $A_6 = 5270$ a.u. (different data were used in Ref. [61]). Thus both the accurate and approximate values derived from MCSCF Cauchy moment expansion are in much better agreement with experiment than any SCF result.

Table 5 and Fig. 3 show the results obtained for the Verdet constant $V(\omega)$ via Eq. (7). The other determinations of the Verdet constant in Argon are in Refs. [20, 21]. Dalgarno and Kingston [20] used a semiempirical approach to estimate the negative even Cauchy moments to be introduced in Eq. (7). The results of Langhoff's investigations [21], including bounds coming from Stieltjes–Tchebicheff moment theory and reported in Table 5, were obtained from different Cauchy moment distributions. Table 5 and Fig. 3 show also a comparison with the experiment. Correlation improves significantly the Hartree–Fock values, and the CAS SCF results are in very good agreement with experiment and within Langhoff's bounds [21]. The Verdet constant computed at both SCF and CAS SCF level with the smaller (137 basis function) set are at most 0.3% smaller than those of Table 5. We computed for some of the frequencies in Table 5 the Verdet

Table 5. Verdet constant $V(\omega)$. Atomic units $\times 10^{-7}$. Basis set of Table 1.

		This work		Ref. [21]		Exp.	
ω(nm)	ω(a.u.)	SCF $V(\omega)$	Correlated $V(\omega)$	Cauchy val. $V(\omega)$	Mom. th. bounds $V(\omega)$	From. Ref. [39] $V(\omega)$	From. Ref. [62] $V(\omega)$
850	0.05360934	0.13598	0.15151	0.151	0.148 ± 0.083	0.14931	0.147
800	0.05695418	0.15387	0.17148	0.170	0.168 ± 0.094	0.16900	0.167
750	0.06075113	0.17557	0.19571	0.194	0.191 ± 0.107	0.19288	0.190
700	0.06509050	0.20225	0.22552	0.224	0.221 ± 0.124	0.22226	0.218
650	0.07009746	0.23558	0.26279	0.261	0.258 ± 0.145	0.25899	0.255
600	0.07593891	0.27801	0.31026	0.308	0.305 ± 0.173	0.30578	0.305
550	0.08284245	0.33321	0.37210	0.369	0.365 ± 0.21	0.36673	0.365
500	0.09112669	0.40699	0.45486	0.452	0.449 ± 0.26	0.44831	0.445
450	0.10125190	0.50894	0.56944	0.564	0.564 ± 0.33	0.56126	0.557
400	0.11390840	0.65591	0.73509	0.731	0.734 ± 0.43	0.72456	0.716

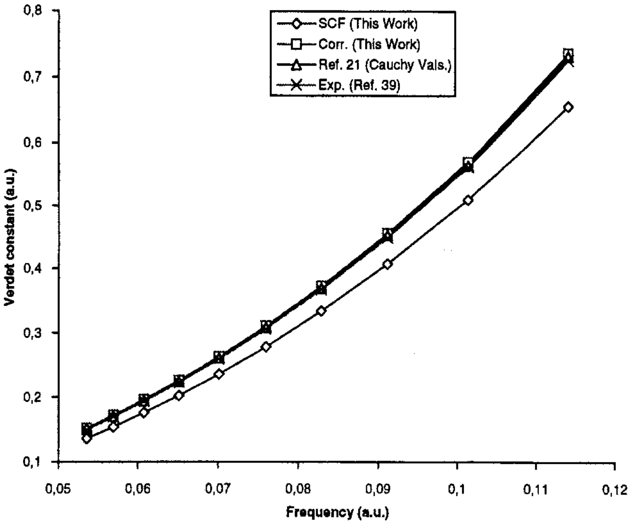

Fig. 3. Verdet constant $V(\omega)$. Atomic units $\times 10^{-7}$.

constant by QR in the 137 functions basis and again the results coincide with those obtained in the same basis via Cauchy moments.

The dispersion of the hypermagnetisability anisotropy $\Delta\eta(-\omega; \omega, 0, 0)$ is displayed in Table 6. Eqs. (9) and (10) were employed to obtain the results of Table 6 for the hypermagnetisability anisotropy of Argon. These equations do not allow to compute separately $\eta_{xx,xx}(-\omega; \omega, 0, 0)$ and $\eta_{yy,xx}(-\omega; \omega, 0, 0)$, but only their difference. Because of the diamagnetic contribution involved the time-consuming QR calculation, the dispersion effects for $\Delta\eta(-\omega; \omega, 0, 0)$ were calculated using the 137 functions basis set. The (absolute value) of the paramagnetic contribution to the hypermagnetisability anisotropy gets larger by a maximum of 0.05 a.u. in the range of frequencies shown when using the larger set, a change of less than 0.4%, for both SCF and CAS SCF. We expect that the basis set dependence of the diamagnetic contribution is similarly small.

A similar study furnished recently accurate results for the hypermagnetisability anisotropy of the Neon atom. As in the case of Neon [11] the overall dispersion in both the SCF and CAS SCF approaches is practically negligible (there was a mistake in the static SCF results in Ref. [11]: the correct values of the paramagnetic and total anisotropies are -1.050 and 2.206 a.u., respectively). The current results are pretty much in agreement with those obtained by Bishop and Cybulski [47] both at Hartree–Fock and correlated (MP2 in Ref. [47]) levels. The comparison with the available experimental number is in this case, contrary to the case of Neon [11], quite favourable.

To summarise, we have shown that very accurate results for various properties of the Argon atom may be obtained applying MCSCF response functions. We have taken advantage of the interrelations between different properties, which are exact for atoms. Therefore, a practical approach based on differentiating the Cauchy expansion with respect to ω and with respect to additional perturbing finite field was used to simplify the calculations. This means that for most of the properties only solutions of linear response equations were required, and a larger basis set and CI expansion were applied than would be possible otherwise.

Table 6. Hypermagnetisability anisotropy $\Delta\eta(\omega; \omega, 0, \phi)$. Atomic units. 137 functions basis set (see text)

		SCF						Correlated							
		This work			Ref. [47]			This work			Ref. [47]			Exp.	
ω (a.u.)	ω (nm)	$\Delta\eta^p$	$\Delta\eta^d$	$\Delta\eta$	$\Delta\eta^p$	$\Delta\eta^d$	$\Delta\eta$	$\Delta\eta^p$	$\Delta\eta^d$	$\Delta\eta$	$\Delta\eta^p$	$\Delta\eta^d$	$\Delta\eta$	$\Delta\eta$	Ref.
0.0	∞	− 12.70	+ 34.21	21.51	− 12.64	+ 34.87	22.23	− 14.13	+ 38.33	24.20	− 14.22	+ 39.82	25.60		
0.04282270	1064	− 13.14	+ 34.66	21.52	− 13.08	+ 35.32	22.24	− 14.67	+ 38.86	24.19	− 14.70	+ 40.32	25.62		
0.06562487	694.3	− 13.77	+ 35.28	21.51	− 13.71	+ 35.95	22.24	− 15.42	+ 39.61	24.19	− 15.37	+ 41.03	25.66		
0.07200277	632.8	− 13.99	+ 35.51	21.52	− 13.94	+ 36.19	22.25	− 15.70	+ 39.88	24.18	− 15.61	+ 41.29	25.68	26.0 ± 1.5	[63]
0.07722602	590.0	− 14.20	+ 35.71	21.51	− 14.14	+ 36.39	22.25	− 15.95	+ 40.12	24.17	− 15.83	+ 41.52	25.69		
0.08855850	514.5	− 14.71	+ 36.20	21.49	− 14.66	+ 36.89	22.23	− 16.57	+ 40.71	24.14	− 16.39	+ 42.09	25.70	28.4 ± 9.1	[29]
0.09321471	488.8	− 14.95	+ 36.43	21.48	− 14.90	+ 37.13	22.23	− 16.86	+ 40.98	24.12	− 16.50	+ 42.35	25.85		

The calculations were performed on a Convex C-3840 with partially vector optimised codes. While the linear response calculations were substantially CPU inexpensive, the quadratic response calculations requested each, for a whole set of frequencies, a few hours of CPU time.

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