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Coupled cluster calculations of Verdet constants

Sonia Coriani [a], Christof Hättig [a], Poul Jørgensen [a], Asger Halkier [a], Antonio Rizzo [b]

[a] *Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark*

[b] *Istituto di Chimica Quantistica ed Energetica Molecolare del Consiglio delle Ricerche, Via Risorgimento 35, 56126 Pisa, Italy*

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Abstract

We present the results of calculations of the Verdet constants for H_2, N_2, C_2H_2 and CH_4, within a recently implemented quadratic response function approach, for the hierarchy of coupled cluster models CCS, CC2 and CCSD. For hydrogen, our FCI results are compared with experiment and with previous calculations of ''benchmark'' quality. The results for nitrogen and acetylene are compared with experiment and former theoretical investigations. For methane, this is the first ab initio study of the Verdet constant. © 1997 Elsevier Science B.V.

1. Introduction and theory

At the end of the last century, Faraday [1,2] showed that the plane of polarization of linearly polarized light is rotated on passage through any substance placed in a magnetic field with non-zero component in the direction of the light beam. This means that in the presence of longitudinal magnetic fields all substances, and not just the chiral ones, show optical activity.

The general name ''Faraday effect'' or ''magnetic optical activity'' is today used for a series of phenomena related to Faraday's first experiments. They consist either of simple rotation of the plane of polarization in regions far from absorption (magnetic circular rotation (MOA), and its dispersion (MORD)) [3,4], or of a rotation–absorption in the absorptive regions (magnetic circular dichroism (MCD)) [4–7].

The theory and experimental details of the Faraday effect in gases are the subject of many reviews [3–5]. In regions far from absorption, the Faraday effect, in its simplest form, may be expressed as

$$\phi = V(\omega)\, Bl, \tag{1}$$

where ϕ is the angle of rotation of the plane of polarization of the linearly polarized light beam, l is the path length, and $\boldsymbol{B} = B\boldsymbol{k}$ is the uniform magnetic field induction. The proportionality constant $V(\omega)$ is known as the ''Verdet constant'' [8]. It is characteristic for a given substance and is a function of concentration, temperature and frequency.

Basically, the optical rotation is due to an anisotropy of the refractive indices for right and left circularly polarized light created by the magnetic field, which makes the right and left handed circular motion around $\boldsymbol{B}$ inequivalent. As shown, for example, in Ref. [9], the phenomenon can be rationalized by means of perturbation theory in terms of the frequency-dependent polarizability in the presence of a static magnetic field. As a consequence, for a molecule in a non-degenerate electronic ground state,

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$V(\omega)$ can be expressed by an appropriate combination of quadratic response functions involving the position ($\boldsymbol{r}$) and orbital angular momentum ($\boldsymbol{L}$) operators

$$V(\omega) = C\omega\epsilon_{\alpha\beta\gamma}\langle\langle r_\alpha; r_\beta, L_\gamma\rangle\rangle_{\omega,0}, \tag{2}$$

where $\langle\langle r_\alpha; r_\beta, L_\gamma\rangle\rangle_{\omega,0}$ is the quadratic response function, ϵ is the Levi-Civita tensor ($\alpha,\beta,\gamma = x,y,z$) and

$$C = \frac{1}{2c}\left(\frac{2\pi N}{4\pi\varepsilon_0}\right)\left(\frac{e}{2m_e}\right), \tag{3}$$

where N is the number density.

For atoms and other spherical systems, the Verdet constant may also be obtained from the Bequerel formula

$$V(\omega) = \frac{\pi e}{m_e c}\left(Na_0^3\right)\frac{\mathrm{d}\alpha}{\mathrm{d}\omega}. \tag{4}$$

By applying this equation to molecules of any symmetry, after replacing α with the mean polarizability $\bar{\alpha}$, an approximation to the molecular Verdet constant, known as the ''normal'' Verdet constant (V_N), is obtained.

From an experimental point of view, the Verdet constants at 76 cm mercury absolute pressure and 0°C for a series of molecules were derived from measurements of induced birefringence at different wavelengths by Ingersoll and Liebenberg in 1956 [10]. The authors claim an accuracy of their data of 1%.

Limiting ourselves to the most recent literature on the subject, ab initio results for the Verdet constant $V(\omega)$ and its ''atomic'' approximation V_N have been obtained for H_2 and D_2 by Bishop and Cybulski [9]. These values can be considered of ''benchmark'' quality, since they were obtained using a James-Coolidge type wavefunction. Ro-vibrational averaging was performed and it was shown that it changes the equilibrium geometry value of $V(\omega)$ by as much as 10%. Note that within the Born-Oppenheimer approximation, there are no purely rotational [11] nor purely vibrational [9] contributions to the Verdet constant, for molecules without a permanent magnetic moment.

Parkinson et al. [12] calculated both $V(\omega)$ and V_N of H_2, N_2, CO and HF, as quadratic response functions and linear response functions, respectively, for a self consistent field (SCF) wavefunction using the dipole length formulation. Electron correlated values of V_N were obtained using the second order polarization propagator approach (SOPPA). These authors also performed zero-point vibrational averaging and showed that, for nitrogen, it affects the results by ca. 2%. Multiconfigurational self consistent field quadratic response (MCSCF-QR) estimates of $V(\omega)$ for N_2 and C_2H_2 have been obtained by Jaszunski et al. [13], at the equilibrium geometries.

In the following, we present results for the Verdet constants of H_2, N_2, C_2H_2 and CH_4, using the recently implemented quadratic response function approach for the hierarchy of coupled cluster models CCS, CC2 and CCSD. A thorough description of the approach is given in Refs. [14,15].

In short, the quadratic response function is obtained, for each model within the coupled cluster hierarchy, as the third derivative of a time-averaged quasi-energy Lagrangian (see Eq. (7) in Ref. [14]) with respect to field strengths. The ''working equation'' reads:

$$\begin{aligned}\langle\langle A;B,C\rangle\rangle_{\omega_B,\omega_C} &= \tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{ABC}\Big\{\tfrac{1}{6}\mathbf{G}\mathbf{T}^A(\omega_A)\mathbf{T}^B(\omega_B)\mathbf{T}^C(\omega_C) \\ &+ \tfrac{1}{2}\overline{\mathbf{T}}^A(\omega_A)\mathbf{B}\mathbf{T}^B(\omega_B)\mathbf{T}^C(\omega_C) \\ &+ \tfrac{1}{2}\mathbf{F}^A\mathbf{T}^B(\omega_B)\mathbf{T}^C(\omega_C) \\ &+ \overline{\mathbf{T}}^A(\omega_A)\mathbf{A}^B\mathbf{T}^C(\omega_C)\Big\},\end{aligned} \tag{5}$$

with $\omega_A = -(\omega_B + \omega_C)$. The operator $\hat{P}^{ABC}$ symmetrizes with respect to the perturbation indices A,B,C and the accompanied frequencies and $\hat{C}^{\pm\omega}$ symmetrizes with respect to an overall sign change of the frequencies and simultaneous complex conjugation. $\mathbf{T}^A,\mathbf{T}^B,\mathbf{T}^C$ and $\overline{\mathbf{T}}^A,\overline{\mathbf{T}}^B,\overline{\mathbf{T}}^C$ are the first-order responses of the cluster amplitudes and the Lagrangian multipliers, respectively. The matrices $\mathbf{G}$, $\mathbf{B}$, $\mathbf{F}^A$ and $\mathbf{A}^A$ are defined as partial derivatives of the coupled cluster quasienergy Lagrangian. For details on the definition of these matrices and the implementation of the contraction of cluster amplitudes and Lagrangian multiplier vectors with these matrices the reader is referred to Refs. [14,16,17].

Due to the pure imaginary nature of the operator representing the magnetic field (iL_γ) and the real nature of the electric dipole operator, the action of the symmetrizer $\hat{C}^{\pm\omega}$ in Eq. (5) reduces to an antisymmetrization with respect to a sign change of ω for the response function $\langle\langle r_\alpha; r_\beta, L_\gamma \rangle\rangle_{\omega,0}$. This is different from the case of electric hyperpolarizabilities considered in Ref. [14], where it reduces to a symmetrization with respect to an overall sign inversion of the frequencies.

When investigating molecular magnetic properties with ab initio methods using finite basis sets, the problem of gauge-origin dependence needs special attention [18]. It is shown in Ref. [19] (see in particular Eq. (25)) that the gauge origin contributions to each response function entering $V(\omega)$ can be expressed in terms of other response functions, which have the same form of as mixed-velocity components as the first hyperpolarizability β, with two equal tensor indices. These contributions are therefore zero for molecules with an inversion centre, where $\beta = 0$ for all components as well as for methane, since in the T_d group all components of β with repeated indices vanish.

2. Computational details

Atomic units have been used throughout this Letter. The conversion factors are [20]:

- 1 au of $\omega = \hbar\omega/E_h = hc/\lambda E_h = 4.556336 \times 10^2/\lambda$ (Å)
- 1 au of V (rad $e\ a_0\ \hbar$) $= 2.763816 \times 10^6 \mu$ min $G^{-1}\ cm^{-1} = 8.039624 \times 10^4$ rad $T^{-1}\ m^{-1}$

STP conditions ($P = 1$ atm, $T = 0\,°C$) and the ideal gas approximation ($V_{mol} = 22.414$ l) are assumed.

For hydrogen, we used the equilibrium distance 1.4 a_0. Note that for this 2 electron system the CCSD model gives the full configuration interaction (FCI) results. The experimental geometries were employed for N_2 [21], C_2H_2 [22] and CH_4 [23]. As for the calculation of hyperpolarizabilities, the choice of the basis is crucial. Several basis sets were investigated, in particular the correlation-consistent basis sets x-aug-cc-pVXZ – where x denotes the augmentation level and X the cardinal number – of Dunning and coworkers [24–26]. These basis sets have been shown to give excellent results for magnetizabilities [27,28] and were designed to perform well for electric properties. Furthermore, for the nitrogen molecule, the III, IV, IVa, IVb basis sets [13], based on Huzinaga's compilation [29], have been used in order to compare directly with the results in Ref. [13]. Basis sets III, IV and IVa were also employed for methane, while for acetylene only basis set II of Ref. [13] – consisting of 108 contracted basis functions – was considered, in addition to Dunning's sets. To obtain the zero-point vibrational average for the N_2 molecule, $V(\omega)$ was computed for 7 different bond distances: $R_0, R_0 \pm 0.2\ a_0, R_0 \pm 0.4\ a_0, R_0 \pm 0.6\ a_0$, and used in conjunction with a CCSD(T) potential energy curve obtained with the aug-cc-pVQZ basis set. The vibrational corrections were determined using VIBROT, which is part of MOLCAS-3 [30].

3. Results and discussion

3.1. Hydrogen

The FCI results for hydrogen are collected in Table 1. The two Dunning basis sets, with cardinal number X equal to Q and 5 were explored systematically, up to triple augmentation and double augmentation, respectively. Addition of diffuse functions is, as expected, mandatory, to approach basis set saturation. For all four frequencies, convergence within

Table 1
FCI Verdet constants of H_2 (au $\times 10^7$)

Basis set	ω (au)			
	0.11391	0.08284	0.06509	0.05360
cc-pVQZ	0.22512	0.11533	0.07025	0.04731
aug-cc-pVQZ	0.45385	0.22868	0.13833	0.09282
d-aug-cc-pVQZ	0.45420	0.22872	0.13832	0.09281
t-aug-cc-pVQZ	0.45406	0.22865	0.13828	0.09278
cc-pV5Z	0.28076	0.14339	0.08723	0.05870
aug-cc-pV5Z	0.45339	0.22835	0.13810	0.09266
d-aug-cc-pV5Z	0.45304	0.22814	0.13797	0.09257
Ref. [9] [a]	0.45556	0.22946	0.13877	0.09312
Ref. [9] [b]	0.50527	0.25361	0.15316	0.10270
exp. [10]	0.501	0.251	0.150	0.103

[a] Equilibrium geometry.
[b] Ro-vibrationally and thermally averaged values.

three decimal digits is achieved with the first augmentation. The second set of diffuse functions changes the results by approximately 0.08%, both at the cc-pVQZ and cc-pV5Z level. At the cc-pVQZ level, the third set of diffuse functions changes the results by ca. 0.03%, and therefore no significant change is expected with further augmentation.

Comparing our results to those of Bishop and Cybulski [9] for a fixed interatomic distance, shows that the first augmentation brings us as close as 99.5% to these ''benchmark'' results. Second and third augmentation do not affect the agreement significantly and no improvement is expected within a ''basis set approach'', unless an augmented basis set of higher quality than cc-pV5Z is used. Direct comparison with experiment is difficult and will not be carried out since, as shown by Bishop, ro-vibrational effects affect the property significantly (around 10%).

3.2. Nitrogen

The CCSD basis set study for nitrogen is shown in Table 2. We report results obtained using the Dunning basis sets, for cc-pVDZ and cc-pVTZ up to the third augmentation level, and for the cc-pVQZ up to the double augmentation level. The basis set convergence shows the same characteristics for all four frequencies. Addition of diffuse functions for a given cardinal number strongly affects the property. At the cc-pVDZ level, the second set of diffuse functions contributes by approximately 13% and the third by $\approx 0.2\%$. At the cc-pVTZ level, going from single to double augmentation, the change is between 3.5 and 3.2%, and with third augmentation it is ca. 0.3%. The difference between the aug and daug results at the cc-pVQZ level is between 0.4–0.5% for all four frequencies, therefore again no significant improvement is expected with further augmentation. The t-aug-cc-pVTZ can be considered a good compromise between accuracy and cost for further analysis.

For the Huzinaga-based sets, convergence at the CCSD level of approximation is less satisfactory. The difference between IVa and IVb results lowers from 2.4% to 1.7%, going from high to low frequencies and their accuracy is in between that obtained with the aug-cc-pVTZ and d-aug-cc-pVTZ sets.

The SCF values obtained with the t-aug-cc-pVTZ basis set (see Table 3) are about 10% lower than the experimental values. The CCSD estimates are slightly

Table 2
CCSD Verdet constants of N_2 with different basis sets (au $\times 10^7$)

Basis set	ω (au)			
	0.11391	0.08284	0.06509	0.05360
cc-pVDZ	−0.03837	−0.02000	−0.01227	−0.00829
aug-cc-pVDZ	0.40413	0.20512	0.12456	0.08371
d-aug-cc-pVDZ	0.46451	0.23562	0.14293	0.09605
t-aug-cc-pVDZ	0.46528	0.23602	0.14318	0.09622
cc-pVTZ	0.07094	0.03686	0.02261	0.01526
aug-cc-pVTZ	0.43453	0.22110	0.13430	0.09031
d-aug-cc-pVTZ	0.44993	0.22856	0.13884	0.09333
t-aug-cc-pVTZ	0.45124	0.22923	0.13925	0.09360
t-aug-cc-pVTZ	0.45705	0.23211	0.14096	0.09475
cc-pVQZ	0.18351	0.09468	0.05789	0.03904
aug-cc-pVQZ	0.44167	0.22456	0.13646	0.09174
d-aug-cc-pVQZ	0.44374	0.22561	0.13699	0.09211
III	0.23682	0.12112	0.07378	0.04967
IV	0.32400	0.16618	0.10136	0.06827
IVa	0.43484	0.22233	0.13505	0.09078
IVb	0.44539	0.22635	0.13741	0.09238
IVb SCF. [13]	0.453	0.230	0.140	0.094
IVb CAS(4 2 2 0 3 1 1 0) [13]	0.507	0.257	0.156	0.105
exp. [10]	0.492	0.251	0.152	0.101

[a] Zero-point averaged values as described in the text.

Table 3
Verdet constants (au$\times 10^7$) of N_2 in the hierarchy CCS, CC2, CCSD (t-aug-cc-pVTZ)

Method	ω (au)			
	0.11391	0.08284	0.06509	0.05360
SCF	0.45334	0.23052	0.13998	0.09412
CCS	0.41156	0.20957	0.12743	0.08570
CC2	0.45691	0.23186	0.14079	0.09461
CCSD	0.45124	0.22923	0.13925	0.09360

below the SCF values, thus not improving the agreement with experiment. For basis set IVb, the correlation contributions introduced by the CCSD approximation are in the opposite direction of the MCSCF results of Ref. [13], which however, are close to the experimental values. Generally speaking, in MCSCF calculations orbital relaxation and static correlation effects are treated explicitly. CCSD on the contrary gives an efficient treatment of the dynamical correlation effects, while orbital relaxation is treated implicitly, through the single excitation manifold. It is nonetheless difficult to understand why the CCSD results are not in better agreement with the experimental results also with respect to the SCF results.

In Table 3, we compare the results obtained for the t-aug-ccpVTZ set for SCF and within the hierarchy of coupled cluster methods CCS, CC2 and CCSD. The CCS and CC2 methods basically ''bracket'' the CCSD estimates. CCS is clearly unsatisfactory, while CC2 performs quite well with respect to CCSD, all deviations between the two models being below 1.2%.

As the change from SCF to CCSD is so small, we do not expect that inclusion of triple excitations could invert the trend described above and bring the results much closer to experiment. However, this aspect requires further investigation.

In order to compare with experiment, one should also consider zero-point vibrational averaging. Parkinson estimated the correction to be around 2% at the RPA level. We performed the zero-point averaging for $v = 0$ and $J = 0$, with the t-aug-cc-pVTZ basis and a CCSD(T) potential curve obtained with the aug-cc-pVQZ basis set. The vibrational corrections were found to be between 1.2–1.3%, for all 4 frequencies and disagreement with experiment is $\approx$ 6–8%.

3.3. Acetylene

The CCSD results for acetylene are collected in Table 4. As for nitrogen both at the cc-pVDZ and cc-pVTZ level, the first and second augmentation are far the most important. Triple augmentation effects are in both cases and for all frequencies negligible. The CCSD results obtained with basis set II are, in spite of the relatively small dimension of the set, in good agreement with the d-aug-cc-pVTZ and t-aug-cc-pVTZ results. This set was chosen in order to compare with the correlated estimates of Jaszunski et al. [13]. The authors performed CASSCF calculations using the same active space as employed for N_2, the two molecular systems being isoelectronic and their results are in excellent agreement with experiment. For the d-aug-cc-pVTZ, the CCSD correlation corrections decrease the SCF values by ca. 18%, but the final results are nevertheless ca. 8% lower than the experimental values – approximately as was the case for the final values for nitrogen.

For the same basis set, the computed values of the Verdet constant in the sequence SCF/CCS/CC2/CCSD (see Table 5), decrease progressively. Correction due to triple excitations is therefore expected to lower the Verdet constant further, bringing us even further away from CASSCF and experiment. However, one should remember that we have not considered rovibrational effects, which may account for some of the discrepancy.

Table 4
CCSD Verdet constants of C_2H_2 for different basis sets (au$\times 10^7$)

Basis set	ω (au)			
	0.11391	0.08284	0.06509	0.05360
cc-pVDZ	0.30579	0.15304	0.09234	0.06188
aug-cc-pVDZ	2.15915	1.04684	0.62377	0.41543
d-aug-cc-pVDZ	2.55322	1.23058	0.73139	0.48646
t-aug-cc-pVDZ	2.55350	1.23086	0.73159	0.48661
II	2.50595	1.20974	0.71946	0.47869
cc-pVTZ	0.89242	0.44600	0.26892	0.18016
aug-cc-pVTZ	2.37612	1.15354	0.68759	0.45800
d-aug-cc-pVTZ	2.50673	1.21195	0.72119	0.47997
t-aug-cc-pVTZ	2.50638	1.21184	0.72114	0.47994
SCF [13]	3.040	1.455	0.862	0.573
CAS(4 2 2 0 3 1 1 0) [13]	2.728	1.313	0.780	0.519
Exp. [10]	2.736	1.329	0.787	0.520

Table 5
Verdet constants ($au \times 10^7$) of C_2H_2 in the hierarchy CCS, CC2, CCSD (d-aug-cc-pVTZ)

Method	ω (au)			
	0.11391	0.08284	0.06509	0.05360
SCF	3.01252	1.44198	0.85470	0.56770
CCS	2.89052	1.38852	0.82422	0.54786
CC2	2.58109	1.24607	0.74107	0.49306
CCSD	2.50673	1.21195	0.72119	0.47997

Table 7
Verdet constants ($au \times 10^7$) of CH_4 in the hierarchy CCS, CC2, CCSD (d-aug-cc-pVTZ)

Method	ω (au)			
	0.11391	0.08284	0.06509	0.05360
SCF	1.09695	0.55194	0.33373	0.22390
CCS	1.08919	0.54870	0.33173	0.22276
CC2	1.26501	0.63354	0.38234	0.25627
CCSD	1.21606	0.60954	0.36799	0.24669

3.4. Methane

The CCSD results for methane are collected in Table 6. To our knowledge, no other results are available in the literature for this system. The computed values of the Verdet constant increase with augmentation. Both at the cc-pVDZ and cc-pVTZ level, the percentage effect of adding diffuse functions is the same for all four frequencies. In particular, at the cc-pVTZ level, the results are once again practically converged with a double augmentation. Once again, the Huzinaga basis sets display a slower convergence pattern. Contrary to N_2, the CCSD values obtained, for example, with the d-aug-cc-pVTZ set are between the SCF estimate (reported in Table 7) and experiment. The CCSD estimates for the d-aug-cc-pVTZ and t-aug-cc-pVTZ sets differ by $\approx 11\%$ from experiment (comparable to the error seen for nitrogen and acetylene at this level of theory), while the SCF d-aug-cc-pVTZ estimates were further off by 18–19% for all four frequencies. The remaining error could maybe be ascribed to ro-vibrational effects and the neglect of triple and higher-order excitations. As for nitrogen, the CCSD results are between the CCS and CC2 ones (see Table 7), CCS being always ca. 16% lower and CC2 overshooting by ca. 3%.

Table 6
CCSD Verdet constants of CH_4 for different basis sets ($au \times 10^7$)

Basis set	ω (au)			
	0.11391	0.08284	0.06509	0.05360
cc-pVDZ	0.30579	0.15304	0.09234	0.06188
aug-cc-pVDZ	1.13124	0.56868	0.34375	0.23059
d-aug-cc-pVDZ	1.22536	0.61358	0.37028	0.24818
t-aug-cc-pVDZ	1.22711	0.61446	0.37081	0.24853
cc-pVTZ	0.60323	0.30411	0.18405	0.12354
aug-cc-pVTZ	1.19813	0.60143	0.36331	0.24536
d-aug-cc-pVTZ	1.21606	0.60954	0.36799	0.24669
t-aug-cc-pVTZ	1.21612	0.60957	0.36800	0.24670
III	0.73562	0.36945	0.22325	0.14973
IV	1.18617	0.59590	0.36007	0.24149
IVa	1.21290	0.60801	0.36708	0.24608
Exp. [10]	1.356	0.685	0.408	0.277

4. Conclusion

We have presented the first coupled cluster quadratic response calculations of Verdet constants for H_2, N_2, C_2H_2 and CH_4, in the hierarchy of CC methods CCS, CC2 and CCSD. The dependence of the constant on electronic correlation, basis set and frequency of the radiation has been considered. The FCI results for the hydrogen molecule are very close to benchmark quality. For nitrogen, dynamical correlation is found not to be important. For acetylene, agreement with experiment and previous MCSCF investigations of the same quality as for N_2, is also poor, even though the correlation corrections to the SCF estimates are significant. For methane, we present the first ab initio estimates of the Verdet constant. The CCSD results for our ''best'' basis set are still away from experiment by approximately 10–12%, but represents an improvement with respect to the corresponding SCF values of ca. 10%. An investigation where the effects of triple excitations are taken into account would certainly be interesting, in order to throw light on the discrepancies between theory and experiment reported here.

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