Cauchy moments and dispersion coefficients using coupled cluster linear response theory

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Expressions for the even Cauchy moments for nonvariational methods have been derived using the time-averaged quasienergy Lagrangian technique. The expressions obtained require the solution of linear equations but do not involve a sum over individual excited-state contributions. An implementation is reported for the coupled cluster models CCS, CC2, and CCSD and calculations have been performed for the Cauchy moments and the Verdet and Cotton–Mouton constants of the Ne atom and for the C_6 dispersion coefficient of the Ne_2 dimer. © *1997 American Institute of Physics.* [S0021-9606(97)01648-6]

I. INTRODUCTION

The oscillator strength sums or Cauchy moments $S(k)$ are important for the description of a variety of molecular properties, for example, dynamic polarizabilities at real and imaginary frequencies,[1] inelastic scattering cross sections,[2] Verdet constants of atoms,[3] dispersion interactions between atoms or molecules[1] and the paramagnetic contribution to the Cotton–Mouton constants of atoms.[4] Despite their usefullness only a limited number of accurate *ab initio* calculations have been reported for these properties, mainly limited to the time-dependent coupled Hartree–Fock (TDCPHF),[5,6] multiconfigurational self-consistent field linear response (MCSCF-LR),[7] second-order polarization propagator approach (SOPPA)[8] and time-dependent second-order Møller–Plesset perturbation theory (TDMP2)[9,10] methods. No calculation has yet been reported using coupled cluster theory, in spite of the success of the coupled cluster method in predicting a wide range of other molecular properties. One reason for this is that Cauchy moments are defined in terms of a sum over excited states of energy weighted oscillator strengths and that is has been difficult to obtain feasible expressions for these sums from the frequency-dependent response functions for coupled cluster as well as for other nonvariational methods. The difficulties encountered in the formulation of response functions for nonvariational methods have recently been overcome through the introduction of time-averaged quasienergy Lagrangians.[11–14] Linear and nonlinear response properties and excitation energies have now been derived and implemented for several nonvariational methods[12,13,15–19] including the hierachy of coupled cluster models CCS, CC2, CCSD, and CC3.[13,15,17–19]

Our aim here is to adopt the technique of time-dependent quasienergy Lagrangians to an efficient calculation of Cauchy moments for nonvariational methods. In Sec. II the expressions for the cauchy moments $S(k)$ for even integer k are derived as derivatives of a time-dependent quasienergy Lagrangian and an implementation is described for the coupled cluster models CCS, CC2, and CCSD. In Sec. III we present the first application to some response properties of the Neon atom.

II. CAUCHY MOMENTS FOR NONVARIATIONAL METHODS AS DERIVATIVES OF A QUASIENERGY LAGRANGIAN

In response theory for exact states the Cauchy moments are usually defined by the sum-over-states formula[20]

$$S_{AB}(k)=\sum_{n\neq 0}^{f} E_{0n}^{k} f_{0n}^{AB}, \tag{1}$$

where E_{0n} are the excitation energies for the transitions from the reference state 0 to the excited states n, and f_{0n}^{AB} are the corresponding oscillator strengths.

$$f_{0n}^{AB}=2E_{0n}\langle 0|A|n\rangle\langle n|B|0\rangle. \tag{2}$$

For large scale calculations the evaluation of the sum-over-states expression is not feasible because the determination of a complete energy spectrum requires the diagonalization of a Hessian or Jacobian of very large dimension. For the variational methods SCF, MCSCF, and (Full) configuration interaction (CI) Eq. (1) has therefore been reformulated as a linear equation problem[6,7] based on a simple identification of the transition matrix elements between the ground state and an excited state for these methods. For nonvariational methods such a simple identification is in general not possible.[21] We therefore follow an alternative route to rewrite Eq. (1) to a form that is feasible also for evaluating the Cauchy moments in coupled cluster theory. The Cauchy moments for even integer k can be calculated as derivatives of the frequency-dependent polarizabilities with respect to the frequency

$$S_{AB}(-2k-2)=\frac{1}{(2k)!}\left(\frac{d}{\omega}\right)^{2k}\boldsymbol{\alpha}_{AB}(-\omega;\omega)\big|_{\omega=0} \quad \text{for } k\geqslant 0, \tag{3}$$

$$S_{AB}(2k)=-\frac{1}{(2k)!}\left(\frac{d}{d\,\frac{1}{\omega}}\right)^{2k}\boldsymbol{\alpha}_{AB}(-\omega;\omega)\big|_{1/\omega=0} \quad \text{for } k=0,1. \tag{4}$$

Note that Cauchy moments $S_{AB}(k)$ for $k>2$ have no physical meaning and are infinite for the exact polarizabilities.

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Equation (3) is derived from the Cauchy moment expansion of the polarizability

$$\boldsymbol{\alpha}_{AB}(-\omega;\omega)=\sum_{n\neq 0}\!\!\!\!\!\!\int \frac{f_{0n}^{AB}}{E_{0n}^2-\omega^2}$$

$$=\sum_{k=0}^{\infty}\omega^{2k}S_{AB}(-2k-2)\quad \text{for } |\omega|<\min(E_{0n}), \tag{5}$$

while Eq. (4) can be obtained from a Taylor expansion of $\alpha_{AB}(-\omega;\omega)$ in the reciprocal frequency $1/\omega$

$$\boldsymbol{\alpha}_{AB}(-\omega;\omega)=\sum_{n\neq 0}\!\!\!\!\!\!\int \frac{1}{\omega^2}\frac{f_{0n}^{AB}}{\left(\frac{1}{\omega}\right)^2 E_{0n}^2-1}$$

$$=\sum_{k=0}^{\infty}\sum_{n\neq 0}\!\!\!\!\!\!\int -\frac{1}{\omega^{2k+2}}E_{0n}^{2k}f_{0n}^{AB}, \tag{6}$$

$$=\sum_{k=0}^{\infty}-\frac{1}{\omega^{2k+2}}S_{AB}(2k)$$

$$\text{for } |1/\omega|<\min(E_{0n}^{-1}), \tag{7}$$

Although the convergence radius of the last expansion is zero for the exact polarizability because the excitation energies E_{0n} are unbounded from above, it can be used to identify expressions for the Cauchy moments $S_{AB}(0)$ and $S_{AB}(2)$. The advantage of the expressions (3) and (4) compared to the sum-over-states formula (1) is that they provide a better starting point for the derivation of feasible expressions for the Cauchy moments as they involve the evaluation of polarizabilities that may straightforward be obtained for both variational and nonvariational methods using a Fourier component variational perturbation theory.[11,14,22]

We consider a molecular or atomic system which in its unperturbed state is defined by the zeroth-order Hamiltonian $H^{(0)}$. The interaction with an oscillating electric field can be described by a time-dependent one-electron perturbation $V(\boldsymbol{\epsilon},t)$

$$V(t,\boldsymbol{\epsilon})=\sum_X H^X\boldsymbol{\epsilon}_X(\omega_X)e^{-i\omega_X t}, \tag{8}$$

$$H(t,\boldsymbol{\epsilon})=H^{(0)}+V(t,\boldsymbol{\epsilon}), \tag{9}$$

where in the dipole approximation H^X is a component of the dipole operator $(\hat{\mu}_x,\hat{\mu}_y,\hat{\mu}_z)$. $\boldsymbol{\epsilon}_X(\omega_X)$ are the accompanied field strenghts for frequency ω_X. We assume that for the method under consideration, a time-dependent quasienergy functional $Q(\lambda,t,\boldsymbol{\epsilon})$ can be constructed which depends on some independent parameters λ. We further assume, that these parameters are determined by a time-dependent set of equations which can be brought to the form

$$e_\mu(\lambda,t,\boldsymbol{\epsilon})-i\frac{d\lambda_\mu}{dt}=0, \tag{10}$$

where $e_\mu(\lambda,t,\boldsymbol{\epsilon})$ does not contain any derivatives with respect to time. Usually the quasienergy functional and the time-dependent equations are implemented by substituting in the normal (unperturbed) energy functional $E(\lambda)$ and equations $e_\mu(\lambda)$ the unperturbed Hamiltonian $H^{(0)}$ by the operator $[H(\boldsymbol{\epsilon},t)-i\,d/dt]$. For the coupled cluster method the quasienergy and the time-dependent equations become, respectively[13,17–19]

$$Q(t_\mu,t,\boldsymbol{\epsilon})=\langle HF|\left(\hat{H}(t,\boldsymbol{\epsilon})-i\frac{d}{dt}\right)\exp(T)|HF\rangle$$

$$=\langle HF|\hat{H}(t,\boldsymbol{\epsilon})\exp(T)|HF\rangle, \tag{11}$$

$$\langle HF|\hat{\tau}_\mu^\dagger\exp(-T)\hat{H}(t,\boldsymbol{\epsilon})\exp(T)|HF\rangle-i\frac{d}{dt}t_\mu(t,\boldsymbol{\epsilon})$$

$$=e_\mu(t_\mu,t,\boldsymbol{\epsilon})-i\frac{d}{dt}t_\mu(t,\boldsymbol{\epsilon})=0, \tag{12}$$

where $T=\Sigma_\mu t_\mu(t,\boldsymbol{\epsilon})\hat{\tau}_\mu$ is the time- and field-dependent cluster operator.

With the above defined prerequisites, a variational time-dependent quasienergy Langrangian can be constructed as

$$L(\lambda,t,\boldsymbol{\epsilon})=Q(\lambda,t,\boldsymbol{\epsilon})+\sum_\mu\overline{\lambda}_\mu\left(e_\mu(\lambda,t,\boldsymbol{\epsilon})-i\frac{d\lambda_\mu}{dt}\right). \tag{13}$$

If the parameters $\lambda_\mu(\boldsymbol{\epsilon},t)$ are expanded in the Fourier components of the external fields

$$\lambda_\mu(\boldsymbol{\epsilon},t)=\lambda_\mu^{(0)}+\lambda_\mu^{(1)}(\boldsymbol{\epsilon},t)+\lambda_\mu^{(2)}(\boldsymbol{\epsilon},t)+\cdots, \tag{14}$$

$$\lambda_\mu^{(1)}(\boldsymbol{\epsilon},t)=\sum_X\lambda_\mu^{(1)}(\omega_X)e^{-i\omega_X t}$$

$$=\sum_X\lambda_\mu^X(\omega_X)\boldsymbol{\epsilon}_X(\omega_X)e^{-i\omega_X t}, \tag{15}$$

and a similar expansion is applied to the Langrangian multipliers $\overline{\lambda}_\mu(\boldsymbol{\epsilon},t)$, the equations for the parameters and for the multipliers and their responses to the external fields can be obtained by requiring that the time-average of the Lagrangian $\{L(\lambda,\boldsymbol{\epsilon},t)\}_T$ is stationary in all Fourier components $\lambda_\mu^{(n)}(\omega_X)$, $\overline{\lambda}_\mu^{(n)}(\omega_X)$ of $\lambda_\mu(\boldsymbol{\epsilon},t)$, and $\overline{\lambda}_\mu(\boldsymbol{\epsilon},t)$.[14,22]

The linear and nonlinear response functions can then be identified as the second and higher derivatives of the real part of the time-averaged quasienergy Lagrangian with respect to the field strengths $\boldsymbol{\epsilon}_X(\omega_X)$.[14,12,22] The frequency-dependent polarizability, the negative of the linear response function, becomes accordingly

$$\boldsymbol{\alpha}_{AB}(\omega_A;\omega_B)=-\left(\frac{d^2\{1/2L(t,\boldsymbol{\epsilon})+1/2L(t,\boldsymbol{\epsilon})^*\}_T}{d\boldsymbol{\epsilon}_A(\omega_A)d\boldsymbol{\epsilon}_B(\omega_B)}\right)_0 \tag{16}$$

$$=-\tfrac{1}{2}\hat{C}^{\pm\omega}\{\boldsymbol{\eta}^A\boldsymbol{\lambda}^B(\omega_B)+\mathbf{F}\boldsymbol{\lambda}^A(\omega_A)\boldsymbol{\lambda}^B(\omega_B)$$

$$+\boldsymbol{\eta}^B\boldsymbol{\lambda}^A(\omega_A)\}, \tag{17}$$

with $\omega_A=-\omega_B$ and the matrix $\mathbf{F}$ and the vectors $\boldsymbol{\eta}^A$ defined as derivatives of the second-order term (in the external perturbation) of the time-averaged Lagrangian

$$\eta_\nu^A = \left(\frac{\partial^2 \{L^{(2)}\}_T}{\partial \epsilon_A(\omega_A) \partial \lambda_\nu^B(\omega_B)} \right)_0, \tag{18}$$

$$F_{\mu\nu} = \left(\frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda_\mu^A(\omega_A) \partial \lambda_\nu^B(\omega_B)} \right)_0. \tag{19}$$

The index 0 indicates that the derivatives are taken at $\epsilon = 0$, i.e., for the unperturbed system and the operator $\hat{C}^{\pm\omega}$ is applied in order to symmetrize with respect to an overall sign change of the frequencies and simultaneous complex conjugation. For the sake of shortness, we use an abbreviated boldface notation with implied Einstein summation meaning that $\boldsymbol{\eta}\boldsymbol{\lambda} = \Sigma_\mu \eta_\mu \lambda_\mu$, $\mathbf{F}\boldsymbol{\lambda}^A\boldsymbol{\lambda}^B = \Sigma_{\mu\nu} F_{\mu\nu} \lambda_\mu^A \lambda_\nu^B$, etc. In the following we restrict our discussion to real multipole operators. The action of $\hat{C}^{\pm\omega}$ reduces then to a symmetrization with respect to $+\omega$ and $-\omega$. The parameters $\boldsymbol{\lambda}^A(\omega_A)$ are determined from the first-order response equation

$$\boldsymbol{\xi}^A + (\mathbf{A} - \omega_A \mathbf{1}) \boldsymbol{\lambda}^A(\omega_A) = 0, \tag{20}$$

where the Jacobian matrix $\mathbf{A}$ and the vector $\boldsymbol{\xi}^A$ are defined by

$$A_{\mu\nu} = \left(\frac{de_\mu}{d\lambda_\nu} \right)_0, \tag{21}$$

$$\xi_\mu^A = \left(\frac{\partial^2 \{L^{(2)}\}_T}{\partial \epsilon_A(\omega_A) \partial \overline{\lambda}_\mu^B(\omega_B)} \right)_0. \tag{22}$$

For the Cauchy moments we need the derivatives of the first-order parameters $\boldsymbol{\lambda}^{(1)}$ with respect to ω and $1/\omega$. They are obtained from Eq. (20) as

$$\left(\frac{d^n \boldsymbol{\lambda}^{(1)}(\omega)}{d\omega^n} \right)_{\omega=0} = -n! \mathbf{A}^{-n-1} \boldsymbol{\xi}^{(1)}, \tag{23}$$

$$\left(\frac{d^n \boldsymbol{\lambda}^{(1)}(\omega)}{d\left(\frac{1}{\omega}\right)^n} \right)_{(1/\omega)=0} = n! \mathbf{A}^{n-1} \boldsymbol{\xi}^{(1)}. \tag{24}$$

To obtain more compact expressions we introduce Cauchy vectors[7] defined as

$$\mathbf{C}^X(n) = -\mathbf{A}^{-n-1} \boldsymbol{\xi}^X. \tag{25}$$

The Cauchy vector for $n \geqslant 0$ are obtained by solution of a recursive set of linear equations

$$\mathbf{C}^X(n) = \mathbf{A}^{-1} \mathbf{C}^X(n-1), \quad \text{for } n \geqslant 0, \tag{26}$$

$$\mathbf{C}^X(-1) = -\boldsymbol{\xi}^X, \tag{27}$$

while Cauchy vectors for $n < -1$ are obtained by successive linear transformations.

$$\mathbf{C}^X(n) = \mathbf{A}\mathbf{C}^X(n+1) \quad \text{for } n < -1. \tag{28}$$

Substitution of Eqs. (23)–(25) into Eq. (17) leads to the following expansions of the frequency-dependent polarizabilities:

$$\boldsymbol{\alpha}_{AB}(-\omega;\omega) = -\sum_{k=0}^{\infty} \omega^{2k} \Big\{ \boldsymbol{\eta}^A \mathbf{C}^B(2k) + \boldsymbol{\eta}^B \mathbf{C}^A(2k) + \sum_{n=0}^{2k} (-1)^n \mathbf{F}\mathbf{C}^A(2k-n)\mathbf{C}^B(n) \Big\} \tag{29}$$

and

$$\boldsymbol{\alpha}_{AB}(-\omega;\omega) = +\sum_{k=0}^{\infty} \omega^{-2k-2} \Big\{ \boldsymbol{\eta}^A \mathbf{C}^B(-2k-2) + \boldsymbol{\eta}^B \mathbf{C}^A(-2k-2) + \sum_{n=0}^{2k} (-1)^n \mathbf{F}\mathbf{C}^A(-2k+n-1) \times \mathbf{C}^B(-n-1) \Big\}, \tag{30}$$

from which the expressions for the Cauchy moments for are identified as

$$S_{AB}(-2k-2) = -\boldsymbol{\eta}^A \mathbf{C}^B(2k) - \boldsymbol{\eta}^B \mathbf{C}^A(2k) - \sum_{n=0}^{2k} (-1)^n \mathbf{F}\mathbf{C}^A(2k-n)\mathbf{C}^B(n) \quad \text{for} \quad k = 0,1 \tag{31}$$

and

$$S_{AB}(2k) = -\boldsymbol{\eta}^A \mathbf{C}^B(-2k-2) - \boldsymbol{\eta}^B \mathbf{C}^A(-2k-2) - \sum_{n=0}^{2k} (-1)^n \mathbf{F}\mathbf{C}^A(-2k+n-1)\mathbf{C}^B(-n-1), \quad \text{for} \quad k = 0,1. \tag{32}$$

Equations (31) and (32) for Cauchy moments $S(k)$ for even integer k require only the solution of a recursive set of linear equations and linear transformations but no complete diagonalization of a Hessian or Jacobian. Equations (31) and (32) are thus computational tractable for large scale calculations. For the variational methods SCF, MCSCF, and (Full) CI Eqs. (31) and (32) are equivalent to the sum-over-states expression (1).[7] For nonvariational correlation methods the calculation of Cauchy moments as derivatives of the linear response function and via the sum-over-states formula (1) will in general give different results. This is not surprising as for nonvariational methods already the definition of the response functions as quasienergy derivatives is inequivalent to a simple sum-over-states definition.

From Eqs. (31)–(32) expressions for a specific method are obtained by inserting in the definition for the intermediates $\boldsymbol{\xi}^X$, $\mathbf{A}$, $\boldsymbol{\eta}^X$, and $\mathbf{F}$ the respective Lagrangian for the method under consideration. In the implementation of the coupled cluster response functions described in Refs. 13, 17, 18, 19, and 23–25 these intermediates were used as a guideline for a decomposition into well defined submodules and the expressions (31)–(32) for the Cauchy moments could therefore be implemented for the coupled cluster models CCS, CC2, and CCSD with only minor modifications to the existing code.

TABLE I. Cauchy moments $S(k)$ for Ne[a] (in a.u.).

k	CCS	CC2	CCSD	DOSD[b]
2	3484[c]	3394[c]	3399[c]	26280
0	10.347[d]	9.714[d]	9.697[d]	10.00[e]
−2	2.462	2.797	2.668	2.669
−4	2.137	3.234	2.857	2.886
−6	3.027	6.058	4.949	5.063
−8	5.320	13.928	10.54	10.86
−10	10.352	35.278	24.73	25.53

[a]The result for the Thomas–Reiche–Kuhn sum rule $S(0)$ with the q-aug-cc-pV5Z basis set on the SCF level is 9.677 a.u.
[b]Reference 2.
[c]With the d-aug-cc-pCV5Z basis set the CCS, CC2 and CCSD results are 18 660, 18 742, and 18 667 a.u., respectively.
[d]With the d-aug-cc-pCV5Z basis set the CCS, CC2, and CCSD results are 10.678, 10.035, and 10.018 a.u., respectively.
[e]Exact value according to the Thomas–Reiche–Kuhn sum rule.

III. APPLICATION TO RESPONSE PROPERTIES OF NEON

The expressions for the Cauchy moments (31) and (32) have been used for the three coupled cluster models CCS, CC2, and CCSD to calculate response properties of the Neon atom. In particular we considered the C_6 dispersion coefficient for the homonuclear Ne_2 dimer, the Verdet constant $V(\omega)$, which is related to the dispersion of the optical refractivity,[26,27] and the Cotton Mouton constant ${}_mC$, which for spherical systems is proportional to the hypermagnetizability anisotropy $\Delta\eta$.[4,28]

To evaluate $\Delta\eta$ one needs in addition to the Cauchy moments the frequency-dependent dipole–dipole–quadrupole hyperpolarizability $B(-\omega;\omega,0)$. For the calculation of B we adopted our recently reported implementation of the coupled cluster quadratic response functions.[19] Because the computation of B requires a basis set with a sufficient number of polarization functions with higher angular momenta we used in all the calculations the quadruple-augmented correlation consistent polarized valence quintuple zeta (q-aug-cc-pV5Z) basis set of Woon and Dunning[29] which consists of a $[28s12p8d7f6g5h/10s9p8d7f6g5h]$ contraction. Test calculations with basis sets of the x-aug-cc-pVXZ and x-aug-cc-pCVXZ series ($x=d,t,q$ and $X=D,T,Q,5$) indicate that the CCSD results obtained with the q-aug-cc-pV5Z basis are converged within 1%, compared to the basis set limit, for all properties reported with the exception of the Cauchy moments $S(0)$ and $S(2)$. To obtain converged results for the latter properties, especially for $S(2)$ would require a large set of thight core polarization functions not included in the present calculation because the effects of core polarization functions on the response properties we are mainly interested in [the Cauchy moments $S(k)$ with $k<0$ and the dipole–dipole–quadrupole hyperpolarizability $B(-\omega;\omega,0)$] are small.

In Table I we have compiled our results for the Cauchy moments obtained with the three coupled cluster models together with the results from the constrained dipole oscillator strength distribution (DOSD) of Kumar and Meath.[2] The empirical DOSD values are expected to be accurate within $\pm 1\%$. For the Cauchy moments $S(k)$ with a negative k we obtained a systematic improvement in the series CCS, CC2, and CCSD, with very accurate results for the latter method. The CCSD results differ from the DOSD values between 0.04% for $S(-2)$ (the static polarizability) and 3% for $S(-10)$. The increase in the errors for the Cauchy moments with decreasing values for k are due to errors in the position of the first pole in the polarizability, i.e., the excitation energy of the first dipole-allowed transition. This can be seen from the limit

$$\lim_{k\to\infty}\frac{S(-k)}{S(-k-2)}=\min(E_{0n}^2). \tag{33}$$

The $S(0)$ moment, the so-called Thomas–Reiche–Kuhn (TRK) sum rule, is for the exact dipole response function equal to the number of electrons. The TRK sum rule is fulfilled by the TDHF, MCSCF, and Full CI methods in the limit of a complete basis set. This is not the case for coupled cluster methods where completeness in the cluster expansion is also required. Deviations form the TRK sum rule $S(0)=N_e$ will thus partly be due to basis set incompleteness and incompleteness in the cluster expansion. The results obtained for Neon in the q-aug-cc-pV5Z basis set show a fast convergence in the series CCS, CC2, CCSD to the corresponding Hartree–Fock result of 9.677 a.u.. The remaining deviation from the electron count is mainly due to missing core polarization functions, which are not present in the q-aug-cc-pV5Z basis set. This is substantiated by the CCSD results obtained with the d-aug-cc-pCV5Z basis set which with 10.018 a.u is very close to the exact number of electrons. The errors caused by the missing core polarization functions are even more exaggerated for $S(2)$: The results obtained with the q-aug-cc-pV5Z basis are too small by almost an order of magnitude and even with the d-aug-cc-pCV5Z basis we get only about 70% of the experimental result.

The frequency-dependent polarizabilities are most directly related to the Cauchy moments by the Cauchy moments expansion Eq. (5). The convergence radius of this expansion is restricted in the complex plane by the excitation energy of the first allowed transition, i.e., the first pole of $\boldsymbol{\alpha}(-\omega;\omega)$ on the real frequency axes. Analytical continuation techniques can be used to extend this expansion beyond $|\omega|=\min(E_{0n})$ in the complex plane and to evaluate $\boldsymbol{\alpha}(-\omega;\omega)$ in particular on the complete imaginary axis $i\omega\to\infty$.

To calculate the C_6 dispersion coefficient which is related to the dipole polarizabilities by the Casimir–Polder relation

$$C_6=\frac{3}{\pi}\int_0^\infty \boldsymbol{\alpha}^A(-i\omega;i\omega)\boldsymbol{\alpha}^B(-i\omega;i\omega)\,d\omega, \tag{34}$$

we used the $[n,n-1]_\beta$ and $[n,n-1]_\alpha$ Padé approximants suggested by Langhoff and Karplus.[30] These approximants provide rigorous lower and upper bounds to the nonexpanded polarizabilities $\boldsymbol{\alpha}(-i\omega;i\omega)$ for $0\leqslant\omega\leqslant\infty$ and can thus be used to obtain lower and upper bounds for C_6. Table II lists the results obtained for C_6 with the $[n,n-1]_\beta$ and

TABLE II. C_6 dispersion coefficients for the homonuclear Ne dimer (in a.u.), calculated from the $[n,n-1]_\alpha$ (lower bound) and $[n,n-1]_\beta$ (upper bound) Padé approximants.

	CCS		CC2		CCSD	
Padé approximant	Lower bound	Upper bound	Lower bound	Upper bound	Lower bound	Upper bound
[1,0]	4.880	9.321	5.457	10.935	5.158	10.177
[2,1]	5.650	6.732	6.332	7.660	5.975	7.188
[3,2]	5.866	6.247	6.588	7.060	6.211	6.636
[4,3]	5.953	6.105	6.682	6.878	6.300	6.473
[5,4]	5.980	6.067	6.731	6.834	6.338	6.432
[6,5]	5.989	6.024	6.737	6.785	6.345	6.386
[7,6]	6.000	6.019	6.750	6.774	6.355	6.378

$[n,n-1]_\alpha$ approximants for different values of n. We obtain a fast convergence of the C_6 coefficients with the order of the Padé approximants. With $n=5$ the results are already converged within $\pm 1\%$ and with $n=7$ the remaining uncertainty of the C_6 coefficients due to the expansion in Cauchy moments is decreased to ± 0.01 a.u.. In Table III we compare our final results with the results of previous theoretical studies and with the recommended semiempirical value from Kumar and Meath.[1] For comparison we have also listed the corresponding results for the static dipole polarizability. As for the Cauchy moments, the results are improved systematically in the series CCS, CC2, and CCSD with a very good accuracy at the CCSD level.

The Verdet constant $V(\omega)$ can for atoms be written in the Becquerel form[26] as

$$V(\omega) = \frac{\pi N_0}{c^2}\,\omega\,\frac{d\boldsymbol{\alpha}(-\omega;\omega)}{d\omega} = \frac{2\pi N_0}{c^2}\sum_{n=1}^{\infty} n\omega^{2n} S(-2n-2). \tag{35}$$

To evaluate Eq. (35) we used the analytic form for $\boldsymbol{\alpha}(-\omega;\omega)$ given by the $[7,6]_\alpha$ Padé approximant. For real frequencies the $[n,n-1]_\alpha$ approximants provide lower bounds to the nonexpanded polarizabilities that are correct to

TABLE III. Static dipole polarizability for Ne and dispersion coefficients for the homonuclear dimer Ne_2 (in a.u.).

	α	C_6
TDHF[b]	2.375	5.514
SDT-MBPT(2)[b]	2.656	6.553
TDMP2[c]	2.720	6.543
DFT[d]	3.02	7.26
CCS[a]	2.462	6.01
CC2[a]	2.797	6.76
CCSD[a]	2.668	6.37
DOSD[e]	2.669 ± 0.027	6.383 ± 0.064

[a]This work.
[b]Reference 34.
[c]Reference 12.
[d]Reference 35.
[e]Reference 1.

TABLE IV. Verdet constant $V(\omega)$ for Ne (in 10^{-9} a.u.).

λ/nm	CCS	CC2	CCSD	DOSD[a]	Exp[b]
363.5	6.41	9.85	8.67	8.76	8.429
400.0	5.25	8.05	7.09	7.16	7.071
436.0	4.40	6.72	5.92	5.98	5.968
450.0	4.12	6.29	5.54	5.60	5.579
500.0	3.32	5.06	4.46	4.51	4.435
546.0	2.77	4.22	3.72	3.76	3.667
550.0	2.73	4.16	3.67	3.70	3.608
578.0	2.47	3.76	3.31	3.35	3.242
589.3	2.37	3.61	3.18	3.22	3.106
600.0	2.29	3.48	3.07	3.10	2.983
650.0	1.94	2.96	2.61	2.63	2.435
700.0	1.67	2.54	2.24	2.27	1.965
750.0	1.46	2.21	1.95	1.97	1.621
800.0	1.28	1.94	1.71	1.73	1.384
850.0	1.13	1.71	1.51	1.53	1.216
900.0	1.01	1.53	1.35	1.36	1.118
987.5	0.84	1.27	1.12	1.13	1.018

[a]Calculated from the effective spectrum in Ref. 1.
[b]Reference 31.

$\mathcal{O}(\omega^{4n-2})$.[30] Table IV and Fig. 1 show the results obtained for $V(\omega)$ with the coupled cluster models CCS, CC2, and CCSD together with the results obtained with the Cauchy moments taken from the work of Kumar and Meath[2] and experimental values from.[31] Again, one obtains a systematic improvement in the series CCS, CC2, and CCSD and the CCSD curve compares excellent with the curve calculated from the DOSD data of Refs. 1 and 2. Both, the CCSD and the DOSD results are in good agreement with the experimental data of Ref. 31 for wavelength between 400 and 600 nm. For wavelengths longer than 600 nm or shorter than 400 nm it is obvious from Fig. 1 that the experiment encounters problems as the experimental data does not fit well to the functional form of $V(\omega)$ in Eq. (35). (For a detailed discussion of the experimental error sources and the problems with the infrared and ultraviolet measurements see Ref. 32).

For atoms, the molar Cotton–Mouton constant ${}_mC$ is proportional to the hypermagnetizability anisotropy $\Delta\eta$

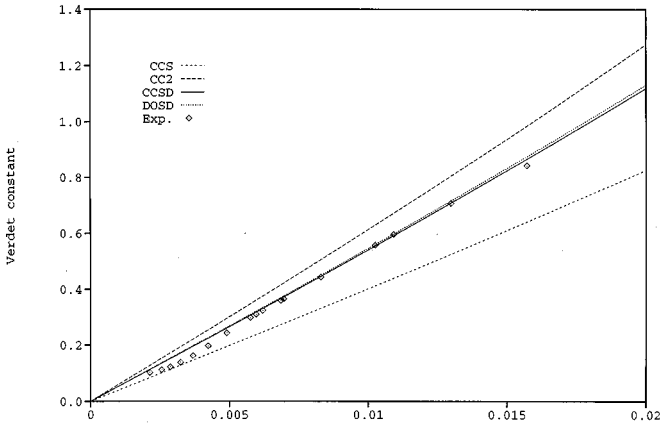


FIG. 1. The Verdet constant for Ne (in 10^{-9} a.u.) plotted against ω^2 (in a.u.).

TABLE V. Magnetic hyperpolarizability anisotropy for Ne (in a.u.).

	$\Delta\eta^{\mathrm{dia}}$	$\Delta\eta^{\mathrm{para}}$	$\Delta\eta$ (total)
Static			
CCS[a]	3.354	−1.068	2.286
CC2[a]	4.888	−1.617	3.271
CCSD[a]	4.298	−1.429	2.869
MCSCF[b]	4.004	−1.317	2.687
PE-MP2[c]	4.484	−1.467	3.017
CCSD(T)[d]	4.425		
DOSD[E]		−1.443	
632.8 nm			
CCS[a]	3.403	−1.117	2.286
CC2[a]	4.984	−1.714	3.280
CCSD[a]	4.376	−1.508	2.868
PE-MP2[c]	4.556	−1.527	3.029
DOSD[e]		−1.524	
exp.[f]			4.10±3.00
514.5 nm			
CCS[a]	3.429	−1.142	2.287
CC2[a]	5.034	−1.766	3.268
CCSD[a]	4.416	−1.550	2.866
MCSCF[b]	4.152±0.076	−1.482±0.069	2.670±0.145
PE-MP2[c]	4.594	−1.560	3.034
DOSD[e]		−1.567	
exp[g]			1.25±0.07

[a]This work.
[b]The cited static values are for a CAS 3 wave function, while the value for 514.5 nm is an estimate based on three different MCSCF wave functions. Ref. 36.
[c]Pseudo-energy MP2, Ref. 37.
[d]Reference 38 and private communication cited in Ref. 36.
[e]Calculated form the effective spectrum in Ref. 1.
[f]W. Huttner, private communication cited in Ref. 36.
[g]Reference 33.

$=\eta_{zz,zz}-\eta_{zz,xx}$.[4] The η tensor can be written as a sum of a paramagnetic and a diamagnetic contribution[4]

$$\eta_{ij,kl}=\eta^{p}_{ij,kl}+\eta^{p}_{ij,kl} =-\tfrac{1}{2}\langle\langle r_i;r_j,L_k,L_l\rangle\rangle_{\omega,0,0}-\tfrac{1}{4}\langle\langle r_i;r_j,Q_{kl}\rangle\rangle_{\omega,0}, \tag{36}$$

where r_i, L_i, and Q_{ij} are components of the dipole, the angular momentum and the second Cartesian moment operator, respectively. The diamagnetic component of $\Delta\eta$ is thus proportional to the frequency-dependent dipole–dipole–quadrupole hyperpolarizability $B(-\omega;\omega,0)$

$$\Delta\eta^{d}=-\tfrac{1}{4}\langle\langle z;z,\tfrac{1}{2}(3z^2-r^2)\rangle\rangle_{\omega,0}=-\tfrac{1}{4}B_{zz,zz}(-\omega;\omega,0). \tag{37}$$

The paramagnetic contribution can for atoms be written as a second derivative of the frequency-dependent polarizability $\boldsymbol{\alpha}(-\omega;\omega)$ with respect to ω and can thus be obtained from a Cauchy moment expansion

$$\Delta\eta^{p}=-\frac{1}{4}\frac{d^2\boldsymbol{\alpha}(-\omega;\omega)}{d\omega^2} =-\frac{1}{4}\sum_{n=0}^{\infty}(2n+1)(2n+2)\omega^{2n}S(-2n-4), \tag{38}$$

$B(-\omega;\omega,0)$ has been calculated analytically using our recent implementation for the coupled cluster quadratic response functions.[19] To evaluate $\Delta\eta^{p}$ we adopted again the $[7,6]_{\alpha}$ Padé approximants obtained from the coupled cluster Cauchy moments. In Table V we compiled the results obtained with the three coupled cluster models and the available experimental and correlated *ab initio* reference values. The results for the coupled cluster response functions are in good agreement, in particular at the CCSD level, with those of previous correlated ab initio calculations, while they disagree by about a factor of two with the experimental result for 514.5 nm of Ref. 33. For 632 nm the error bars of the experimental result are too large to allow for a reliable comparison.

IV. SUMMARY

We have derived expressions for the even Cauchy moments for nonvariational methods which do not involve a sum over states and thus are suitable for large scale correlated *ab initio* calculations. We have implemented these expressions for the three coupled cluster methods CCS, CC2, and CCSD. A first application to the Cauchy moments and the Verdet and Cotton–Mouton constants of the Neon atom and the C_6 dispersion coefficient for the Neon dimer demonstrates that the derived expressions for the Cauchy moments provide an efficient approach for the calculation of Cauchy moments and related response properties. In particular the CCSD result compares favourable with the experiment.

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