Cauchy moments of Ne, Ar, and Kr atoms calculated using the approximate coupled cluster triples model CC3

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Abstract

The Cauchy moments are derived and implemented for the approximate triples model CC3 with the proper N^7 scaling (where N denotes the number of basis functions). The Cauchy moments are calculated for the Ne, Ar, and Kr atoms using the hierarchy of the coupled-cluster models CCS, CC2, CCSD, CC3 and a large correlation-consistent basis sets augmented with diffuse functions. A detailed investigation of the one- and N-electron errors shows that the CC3 results have the accuracy comparable to the experimental results.

I. INTRODUCTION

The calculation of frequency-dependent linear-response properties may be an expensive task, since first-order response equations have to be solved for each considered frequency [1]. The cost may be reduced by introducing the Cauchy expansion in even powers of the frequency for the linear-response function [2]. The expansion coefficients, or Cauchy moments [3], are frequency-independent and need to be calculated only once for a given property. The Cauchy expansion is valid only for the frequencies below the first pole of the linear response function, however, most experiments are also carried out in this frequency region. Moreover, using analytical continuation techniques in the complex plane the Cauchy expansion may be extended beyond this limit [4].

The Cauchy moments are thus very useful in describing molecular properties like dynamic polarizabilities at real and imaginary frequencies [5], inelastic scattering cross sections [6], Verdet constants of atoms [7], dispersion interactions between atoms and molecules [5], and the paramagnetic contribution to the Cotton–Mouton constants of atoms [8]. Cauchy moments have been implemented for the wavefunction models: Hartree-Fock (HF) [9–11], multiconfigurational self-consistent field (MCSCF) [12], and second-order polarization propagator approach (SOPPA) [13, 14]. Using the time-averaged quasi-energy Lagrangian techniques [1] Cauchy moments have also been determined for the coupled cluster (CC) hierarchy of models CCS, CC2, CCSD [4]. We extend in this paper the latter implementation to the approximate triples model CC3. CCS stands for the CC singles model, where all the single excitations from a reference wavefunction are taken into account. In CCSD [15] all the single and double excitations are treated; and in CCSDT all the triples are further added. CC2 model is obtained from CCSD by approximating the doubles equations [16]. Similarly, CC3 is an approximation to CCSDT, where approximations are introduced in the triples equation [17]. The computational cost of the CC2 and CC3 models is reduced compared to CCSD and CCSDT, respectively, and the cost across the hierarchy scales as N^4 (CCS), N^5 (CC2), N^6 (CCSD), N^7 (CC3), where N is the number of basis functions.

The CCS, CC2, CCSD, CC3 hierarchy has been designed specially for the calculation of frequency-dependent properties. In this hierarchy a systematic improvement in the description of the dynamic electron correlation is obtained at each level. For example, comparing CCS, CC2, CCSD, CC3 with FCI singlet and triplet excitation energies showed that the

errors decreased by about a factor 3 at each level in the coupled cluster hierarchy [18]. The CC3 error was as small as 0.016 eV and the accuracy of the CC3 excitation energies was comparable to the one of the CCSDT model [18].

Frequency-dependent polarizabilities and first hyperpolarizabilities have also been calculated to high accuracy using the CC3 model [19–21]. Recently, we have shown that oscillator strengths calculated using the CC3 model are practically gauge invariant [22] and that the accuracy of the CC3 frequency-dependent second hyperpolarizability of the Ne atom is at least the same as the accuracy of the latest experiments [23]. This outstanding accuracy of the CC3 model reflects the importance of the inclusion of triple excitations in the CC wavefunction for accurate description of molecular properties—a fact that has been observed a number of times for static properties calculated using CCSD(T) model [24]. Contrary to the CCSD(T) model, the CC3 model may be used to calculate both static and frequency-dependent properties [17]. The CC3 and CCSD(T) [25] models have comparable accuracy and the same formal computational scaling, N^7, with the CC3 model being iterative and the CCSD(T) model non-iterative.

The results presented in this paper are complementary to the ones of Ref. [4], where the Cauchy moments were calculated for the Ne atom using the CCS, CC2, CCSD hierarchy. A systematic improvement in the quality of the Cauchy moments was found in Ref. [4] when increasing the level of the hierarchy; in particular, the CCSD Cauchy moments were in a very good agreement (0.04%–3%) with the empirical constrained dipole oscillator strength distribution (DOSD) values [6] which are believed to be accurate within $\pm 1\%$. We here investigate the improved accuracy of the Cauchy moments when going from CCSD to CC3.

In the next section we recapitulate the derivation of the Cauchy moment expressions for CC wavefunction models and give the CC3-specific formulas; we also outline an efficient implementation of the CC3 Cauchy moments. Section III contains computational details. In section IV we report the Cauchy moments calculated for the Ne, Ar, and Kr gases using the CCS, CC2, CCSD, CC3 hierarchy and correlation-consistent basis sets augmented with diffuse functions. In particular, we consider the issues of one- and N-electron convergence and compare with the Cauchy moments obtained from the DOSD approach and other experiments.

II. THEORY

The Cauchy moments have been derived in Ref. [4] for CC wavefunctions, using the time-dependent quasi-energy Lagrangian technique [1]. In Sec. II A we recapitulate the important points of that derivation and use it in Sec. II B to derive the CC3-specific formulas.

A. Cauchy moments for coupled cluster wavefunctions

The oscillator strength sums, or Cauchy moments, $S_{AB}(k)$, for an exact state are defined by the sum-over-states formula [3]:

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

where ω_{0n} is the excitation energy for the transition from the reference state $|0\rangle$ to the excited state $|n\rangle$, f_{0n}^{AB} is the oscillator strength:

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

and A and B denote the perturbation operators. The Cauchy moments enter the expansion of the polarizability [2, 4]:

$$\alpha_{AB}(-\omega;\omega) = \sum_{n\neq 0}^{f} \frac{f_{0n}^{AB}}{\omega_{0n}^{2} - \omega^{2}} = \sum_{k=0}^{\infty} \omega^{2k} S_{AB}(-2k-2), \tag{3}$$

where ω denotes the frequency of the external perturbation. The last equality in Eq. (3) is fulfilled for $|\omega| < \min\{\omega_{0n}\}$ [4].

For the non-variational CC wavefunctions, the polarizability is the negative of the linear response function and may therefore be identified as the second derivative of the real part of the time-averaged quasi-energy Lagrangian, L (for the definition of the Lagrangian see, for example, Sec. II B in Ref. [21]), with respect to the field strengths $\epsilon_X(\omega_X)$ [1]:

$$\alpha_{AB}(\omega_A;\omega_B) = -\frac{1}{2} C^{\pm\omega} \left\{ \eta^{A} t^{B}(\omega_B) + \eta^{B} t^{A}(\omega_A) + \mathbf{F} t^{A}(\omega_A)\, t^{B}(\omega_B) \right\}, \tag{4}$$

where $\omega_A = -\omega_B$ and where $C^{\pm\omega}$ is the complex conjugation and frequency sign inversion operator defined by:

$$C^{\pm\omega} g^{AB\cdots}(\omega_A, \omega_B, \cdots) = g^{AB\cdots}(\omega_A, \omega_B, \cdots) + \left(g^{AB\cdots}(-\omega_A, -\omega_B, \cdots) \right)^{*}. \tag{5}$$

The $\mathbf{F}$ matrix and η^A vector in Eq. (4) are defined as the second partial derivatives of the Lagrangian, taken at the zero perturbation strength:

$$\eta^A_{\mu_i} = \left(\frac{\partial^2 L}{\partial \epsilon_A(\omega_A)\, \partial t_{\mu_i}} \right)_0, \tag{6}$$

$$F_{\mu_i \nu_j} = \left(\frac{\partial^2 L}{\partial t_{\mu_i} \partial t_{\nu_j}} \right)_0, \tag{7}$$

where t denotes the unperturbed wavefunction parameters (e.g., the coupled-cluster amplitudes). $t^A(\omega_A)$ in Eq. (4) denote the first-order response of the wavefunction parameters to an external perturbation A oscillating with the frequency ω_A. They are determined from the first-order response equation:

$$t^A(\omega_A) = -(\mathbf{A} - \omega_A \mathbf{I})^{-1} \xi^A, \tag{8}$$

where $\mathbf{I}$ denotes a unit matrix. The Jacobian, $\mathbf{A}$, and the ξ^A vector in Eq. (8) are defined as the second partial derivatives of the Lagrangian:

$$A_{\mu_i \nu_j} = \left(\frac{\partial^2 L}{\partial \bar{t}_{\mu_i} \partial t_{\nu_j}} \right)_0, \tag{9}$$

$$\xi^A_{\mu_i} = \left(\frac{\partial^2 L}{\partial \bar{t}_{\mu_i} \partial \epsilon_A(\omega_A)} \right)_0, \tag{10}$$

where $\bar{t}$ denotes the unperturbed Lagrange multipliers.

Applying the matrix identity

$$(\mathbf{X} - \mathbf{Y})^{-1} = \mathbf{X}^{-1} + \mathbf{X}^{-1}\mathbf{Y}(\mathbf{X} - \mathbf{Y})^{-1} \tag{11}$$

recursively to Eq. (8) we obtain an expansion of the first-order wavefunction parameters:

$$t^A(\omega_A) = \left(-\mathbf{A}^{-1} - \omega_A \mathbf{A}^{-2} - \omega_A^2 \mathbf{A}^{-3} - \omega_A^3 \mathbf{A}^{-4} - \cdots \right) \xi^A, \tag{12}$$

which may be rewritten in terms of Cauchy vectors, $C^A(n)$:

$$t^A(\omega_A) = C^A(0) + \omega_A C^A(1) + \omega_A^2 C^A(2) + \cdots = \sum_{n=0}^{\infty} \omega_A^n C^A(n). \tag{13}$$

Comparing equations (12) and (13) we obtain the recursive procedure for calculating the Cauchy vectors:

$$C^A(-1) \;=\; -\xi^A \tag{14}$$

$$C^A(0) = \mathbf{A}^{-1}C^A(-1) \tag{15}$$

$$C^A(1) = \mathbf{A}^{-1}C^A(0) \tag{16}$$

$$\vdots \tag{17}$$

$$C^A(n) = \mathbf{A}^{-1}C^A(n-1) \quad \text{for } n \geq 0. \tag{18}$$

Inserting Eq. (13) into Eq. (4) we obtain the polarizability expansion:

$$\alpha_{AB}(-\omega;\omega) = -\sum_{k=0}^{\infty}\omega^{2k}\left\{\eta^A C^B(2k) + \eta^B C^A(2k) + \sum_{n=0}^{2k}(-1)^n \mathbf{F}C^A(2k-n)C^B(n)\right\}, \tag{19}$$

where we have introduced explicitly the terms resulting from the $C^{\pm\omega}$ operator. Comparing Eqs. (3) and (19) we identify the Cauchy moments as:

$$S_{AB}(-2k-2) = -\left\{\eta^A C^B(2k) + \eta^B C^A(2k) + \sum_{n=0}^{2k}(-1)^n \mathbf{F}C^A(2k-n)C^B(n)\right\}. \tag{20}$$

Calculation of the Cauchy moments, $S_{AB}(-2k-2)$, thus only requires solving a set of frequency-independent linear equations, Eq. (18), up to order $2k$ and carrying out the linear transformations involving η^A vector and $\mathbf{F}$ matrix, see Eq. (20). Note, that contrary to Eq. (1) no sum over states is involved in this formulation of the Cauchy moments.

B. Cauchy moments for the CC3 model

To calculate the Cauchy moments we first need to solve the equations for the Cauchy vectors, Eq. (18). In the CC3 model this equation may be written as:

$$\begin{pmatrix} C^A_{\mathrm{SD}}(n) \\ C^A_{\mathrm{T}}(n) \end{pmatrix} = \begin{pmatrix} \mathbf{A}_{\mathrm{SD,SD}} & \mathbf{A}_{\mathrm{SD,T}} \\ \mathbf{A}_{\mathrm{T,SD}} & \mathbf{A}_{\mathrm{T,T}} \end{pmatrix}^{-1} \begin{pmatrix} C^A_{\mathrm{SD}}(n-1) \\ C^A_{\mathrm{T}}(n-1) \end{pmatrix}, \tag{21}$$

where the Cauchy vectors and the Jacobian have been partitioned into the contributions originating from the singles-and-doubles (SD) and the triples (T) spaces. The pure triples contribution to the Jacobian is represented by the diagonal matrix consisting of the triple excitation energies, ω_{μ_3}:

$$\mathbf{A}_{\mathrm{T,T}} = \delta_{\mu_3\nu_3}\omega_{\mu_3}, \tag{22}$$

with μ_3 referring to a triples excitation. To keep the CC3 storage demands within acceptable limits, the triples components of the Cauchy vectors cannot be written to the disk or put to the memory and, therefore, no explicit reference to the triples space can be made when

solving Eq. (21). The explicit reference to the triples space may be avoided by projecting all the triples components into the singles-and-doubles space.

To achieve this we write the inverse of the CC3 Jacobian in the form

$$\begin{pmatrix} \mathbf{A}_{\mathrm{SD,SD}} & \mathbf{A}_{\mathrm{SD,T}} \\ \mathbf{A}_{\mathrm{T,SD}} & \mathbf{A}_{\mathrm{T,T}} \end{pmatrix}^{-1} = \begin{pmatrix} \left(\mathbf{A}^{eff}_{\mathrm{SD,SD}}\right)^{-1} & -\left(\mathbf{A}^{eff}_{\mathrm{SD,SD}}\right)^{-1}\mathbf{A}_{\mathrm{SD,T}}\mathbf{A}^{-1}_{\mathrm{T,T}} \\ -\mathbf{A}^{-1}_{\mathrm{T,T}}\mathbf{A}_{\mathrm{T,SD}}\left(\mathbf{A}^{eff}_{\mathrm{SD,SD}}\right)^{-1} & \mathbf{A}^{-1}_{\mathrm{T,T}} + \mathbf{A}^{-1}_{\mathrm{T,T}}\mathbf{A}_{\mathrm{T,SD}}\left(\mathbf{A}^{eff}_{\mathrm{SD,SD}}\right)^{-1}\mathbf{A}_{\mathrm{SD,T}}\mathbf{A}^{-1}_{\mathrm{T,T}} \end{pmatrix}, \tag{23}$$

where

$$\mathbf{A}^{eff}_{\mathrm{SD,SD}} = \mathbf{A}_{\mathrm{SD,SD}} - \sum_{\mu_3} \frac{\mathbf{A}_{\mathrm{SD},\mu_3}\mathbf{A}_{\mu_3,\mathrm{SD}}}{\omega_{\mu_3}} \tag{24}$$

is the effective Jacobian in the singles-and-doubles space. Using Eq. (23) we may express Eq. (21) as a set of two equations:

$$\left(\mathbf{A}^{eff}_{\mathrm{SD,SD}}\right) C^A_{\mathrm{SD}}(n) \;=\; C^{eff}_{SD}(n-1) \tag{25}$$

$$C^A_{\mathrm{T}}(n) \;=\; \mathbf{A}^{-1}_{\mathrm{T,T}}\left(C^A_{\mathrm{T}}(n-1) - \mathbf{A}_{\mathrm{T,SD}}C^A_{\mathrm{SD}}(n)\right) \tag{26}$$

with the effective Cauchy vectors defined as:

$$C^{eff}_{\mathrm{SD}}(n-1) = C^A_{\mathrm{SD}}(n-1) - \sum_{\mu_3} \frac{\mathbf{A}_{\mathrm{SD},\mu_3}C^A_{\mu_3}(n-1)}{\omega_{\mu_3}} \tag{27}$$

Only Eq. (25), which is the counterpart of Eq. (21) in the subspace of $\mathbf{A}_{\mathrm{SD,SD}}$, is solved iteratively. In this equation all the triples components have been projected into the singles-and-doubles space. Once Eq. (25) has been solved the $C^A_{\mathrm{SD}}(n)$ solution vector is stored on disk. The triples component of the solution vector, $C^A_{\mathrm{T}}(n)$, may then be constructed *on the fly* (see Eq. (26)), whenever it is needed. In this way the storage of the triples components is avoided.

The effective singles-and-doubles equation for the Cauchy vectors, Eq. (25), has the same structure as the effective singles-and-doubles equation for the first-order CC3 amplitudes (see Eq. (26) of Ref. [21]), the main difference being that now the right-hand side depends on the solution vector of lower order. Eq. (25) may thus be implemented following the scheme described in [21] with an extra external loop over n (i.e., the Cauchy vectors order).

Let us now consider the calculation of the triples part of the Cauchy vector, $C^A_{\mathrm{T}}(n)$, according to Eq. (26). Expanding $C^A_T(n-1)$ on the right-hand side of Eq. (26) recursively, we obtain:

$$C^A_{\mu_3}(n) \;=\; -\left\{\frac{\xi^A_{\mu_3}}{\omega^{n+1}_{\mu_3}} + \sum_{m=0}^{n} \frac{\sum_{\nu_i;i=1,2} A_{\mu_3,\nu_i}C^A_{\nu_i}(m)}{\omega^{n+1-m}_{\mu_3}}\right\} \tag{28}$$

Eq. (28) leads to the following computational scheme for the triples part of the CC3 Cauchy vectors with $n \geq 0$:

$C_T^A(n) \leftarrow \xi_T^A$

loop $m = 0, n$

$C_T^A(n) \leftarrow C_T^A(n) + \mathbf{A}_{T,SD} C_{SD}^A(m)$

$C_T^A(n) \leftarrow C_T^A(n)/\omega_T$

end loop m

turn sign: $C_T^A(n) \leftarrow -C_T^A$

where ω_T is a vector with ω_{μ_3} elements.

The equation for the triples part of the (frequency-independent) first-order amplitudes, $t_T^A(0)$, has a form:

$$t_T^A(0) = -\mathbf{A}_{\mathrm{T,T}}^{-1} \left(\xi_T^A + \mathbf{A}_{\mathrm{T,SD}} t_{SD}^A(0) \right) \tag{29}$$

and may be viewed as the special case of Eq. (26); indeed, $t_T^A(0)$ is obtained in the first iteration ($m = 0$) of the above computational scheme. The calculation of the $C_{\mu_3}^A(n)$ vectors may thus be implemented as a straightforward generalization of the implementation of Eq. (29) (an extra loop over m and some reorganization are only required). The efficient implementation of Eq. (29) has been described in details in Ref. [21]; the calculations are carried out for two fixed virtual MO indexes leading to the triples vector intermediates of the form $W^{BC}(aijk)$, where B and C are the two fixed virtual indexes, a is the third virtual index, and i, j, k are three occupied indexes—see [21] for details.

Once the equations for the Cauchy vectors have been solved, the Cauchy moments can be calculated according to Eq. (20), which for the CC3 model may be written as:

$$\begin{aligned} S_{AB}(-2k-2) \;=\; & -\eta_{SD}^A C_{SD}^B(2k) - \eta_{SD}^B C_{SD}^A(2k) \\ & - \sum_{n=0}^{2k} (-1)^n \mathbf{F}_{SD,SD} C_{SD}^A(2k-n) C_{SD}^B(n) \\ & - \eta_T^A C_T^B(2k) - \eta_T^B C_T^A(2k) \\ & - \sum_{n=0}^{2k} (-1)^n \mathbf{F}_{SD,T} C_{SD}^A(2k-n) C_T^B(n) \\ & - \sum_{n=0}^{2k} (-1)^n \mathbf{F}_{SD,T} C_{SD}^B(2k-n) C_T^A(n), \end{aligned} \tag{30}$$

where the **F** matrix and the η^X and C^X vectors have been partitioned into the contributions from the singles-and-doubles and the triples spaces.

Since the Cauchy moments formula, Eq. (20), has the same structure as the CC linear response function, Eq. (4), the contractions in Eq. (30) may be implemented by a straightforward generalization of the computational procedures described in Sec. III B of Ref. [21] for the calculation of the CC3 linear response function.

III. COMPUTATIONAL DETAILS

In the next section we present the Cauchy moments, $S(k)$, for the Ne, Ar, and Kr gases calculated using the hierarchy of models CCS, CC2, CCSD, and CC3. We consider the orders k = -2, -4, -6, -8, -10.

All the calculations have been carried out using a local version of the Dalton program package [26]. The implementation of the Cauchy moments for the CCS, CC2, and CCSD models has been described in [4]. The CC3 Cauchy moments have been implemented by us following the outline presented in the previous section.

Dunning's correlation consistent basis sets cc-pVXZ [27] augmented with diffuse functions [28] were used in the calculations. We considered cardinal numbers X=D, T, Q, 5, 6 and single (s), double (d), triple (t), and quadruple (q) augmentations. The orbitals were not allowed to relax in the coupled cluster response calculations.

IV. RESULTS

A. Neon

In Table I we have collected the Cauchy moments, $S(k)$, calculated for the Ne atom using the CCSD model and the n-aug-cc-pVXZ basis-set family. As can be seen from the table, single augmentation is not sufficient for the calculation of the Cauchy moments. On the other hand, going beyond the double augmentation practically does not change the results. In the following we will, therefore, report results obtained using the doubly-augmented basis. The Cauchy moments in general converge smoothly with increasing cardinal number, X, toward the basis-set limit. Only for k = -4, -6, and -8 they first increase from X = D to X = T, and then smoothly decrease. This might reflect the poor quality of the double-zeta basis.

The Cauchy moments of Ne at the CCSD/q-aug-cc-pV5Z level were found in Ref [4] to be converged within 1% compared to the basis-set limit result. We have calculated the Cauchy moments also for the $X = 6$ cardinal number. From the results in Table I it appears that the Cauchy moments at this level are significantly less than one per cent from the basis set limit result.

The Cauchy moments calculated for the Ne atom using the d-aug-cc-pV6Z basis at the different levels of the CC hierarchy are compared in Table II to the DOSD results [6]. Other experimental results are also quoted [29, 30] A systematic improvement toward the DOSD results (which are believed to be accurate within $\pm 1\%$) is observed in the CC hierarchy. The CCS model underestimates, while the CC2 model overestimates the DOSD results. Both the CCSD and CC3 results approach the DOSD values from below. The CCSD Cauchy moments are in a very good agreement with the DOSD results: the discrepancies are between 0.2% ($S(-2)$) and 4.6% ($S(-10)$) and increase monotonically with k. This monotonic increase reflects that the error in the position of the first pole in the polarizability (i.e., the excitation energy to the first dipole-allowed transition) gets increasing weights in the power series expansion of the polarizability [4].

Turning our attention to the CC3 model we observe that the inclusion of triple excitations further improves the quality of the Cauchy moments in the sense that all the CC3 moments are closer to the DOSD results than the CCSD moments. The CC3 and DOSD Cauchy moments are in fact so close that it is worth investigating in more detail the errors associated with the CC3 results.

The excitation energy to the lowest dipole allowed state $2s^2 2p^5 3s^1(P^O)$ was in a benchmark study [18] using the aug-cc-pVDZ basis found to be 19.041 eV (CCSD), 19.240 eV (CC3), 19.206 eV (CCSDT), 19.247 eV (FCI), showing that the CC3 excitation energy is converged, for all practical purposes, in N-electron space. Calculations of the excitation energy using the d-aug-cc-pV5Z and d-aug-cc-pV6Z basis gave 16.773 eV and 16.795 eV (CCSD), 16.811 eV and 16.826 eV (CC3). The CC3 results compare very favorable with the experimental result of 16.848 eV from Ref. [31]. The very small error in the excitation energy at the CC3 level suggests that this error may be neglected in CC3 calculations of the Cauchy moments.

Let us now consider the errors in the CC3 $S(-2)$ Cauchy moment (the static polarizability). From the monotonic convergence of the CCSD doubly augmented basis set calculations

of $S(-2)$ in Table I it appears that that the difference between the 5Z and 6Z results should give a good estimate of the CCSD basis-set error at the 6Z level. CC3/d-aug-pV5Z $S(-2)$ Cauchy moment is 2.670 a.u. Using the CC3/d-aug-pV6Z $S(-2)$ from Table II we may thus estimate the CC3 basis set limit for $S(-2)$ to be 0.005 a.u. below the CC3/d-aug-pV6Z result. The errors resulting from correlation effects beyond CC3 may be estimated from the aug-cc-pVDZ calculations in Ref. [32] where it was found that the FCI static polarizability of Ne was 0.003 a.u. smaller than the corresponding CC3 result. Relativistic effects have been determined in Ref. [33] to increase $S(-2)$ by 0.004 a.u. Adding the basis set, correlation and relativistic contribution gives a decrease in $S(-2)$ of 0.004 a.u. The effects not accounted for in the CC3/d-aug-pV6Z calculation thus to a high degree cancel each other. For the Cauchy moments with the higher values of $|k|$ no relativistic contribution or correlation contribution beyond CC3 have been calculated and it is for that reason difficult to estimate the accuracy of these Cauchy moments. However, the above analysis makes us to believe that the reported Cauchy moments have the accuracy comparable to the experimental results.

B. Argon

The Cauchy moments calculated for the Ar atom at the different levels of the CC hierarchy using d-aug-cc-pV6Z basis are collected in Table III together with the empirical DOSD results [6] and other experimental results [34, 35]. The behavior of the CCS and CC2 models is less systematic than for Ne: these models overestimate the Cauchy moments for the lower values of $|k|$ and then underestimate for higher $|k|$. As in the case of the Ne atom, the CCSD model systematically approaches the DOSD values from below. The CC3 Cauchy moments are first larger than the DOSD values (for k = -2 and -4) and then become smaller than the DOSD values (for the remaining k's). The CC3 model gives generally better agreement with the DOSD values than the CCSD model, the discrepancies being reduced by the factor of 4 ($k = -10$) to 20 ($k = -6$). In most cases the CC2 model is in better agreement with both the CC3 and DOSD values than is the CCSD model. This is due to a fortuitous cancellation of errors at the CC2 level. To make a more detailed analysis of the CC3 uncertainties, the basis-set and correlation error must be established and the relativistic contribution to the Cauchy moments might need to be taken into account.

C. Krypton

The Cauchy moments of Kr (Table IV) have been calculated using the largest currently available correlation-consistent basis augmented with diffuse functions—d-aug-cc-pV5Z basis. As for the Ar atom, the CCS and CC2 results overestimate the DOSD values for smaller $|k|$ and underestimate for larger $|k|$. The CCSD model behaves in the same manner. The CC3 model systematically approaches the DOSD values from below. As observed for Ne and Ar, the discrepancy between the CC3 and DOSD results for Kr is smaller than the discrepancy between CCSD and DOSD. For most of the values of k, the CC2 Cauchy moments are in better agreement with both the CC3 and DOSD values than is the CCSD results. This unexpected good performance of CC2 is again the result of a fortuitous cancellation of errors. For $k = -6$ the situation is extreme—the CC2 result is in better agreement with DOSD than is the CC3 results. Again, any more detailed judgments of the uncertainty of the CC3 Cauchy moments are not possible at this stage.

V. CONCLUSION

The high quality of the CC3 model and the convergence in one-electron space has allowed us to determine the Cauchy moments for Ne which have the accuracy comparable to the experimental results. To arrive at the similar conclusion for the Ar and Kr atoms a more detailed investigation of the convergence in one-electron and N-electron space is required. The relativistic contribution to the Cauchy moments may also need to be taken into account for these two atoms.

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TABLE I: The basis-set convergence of the Cauchy moments $S(k)$ [a.u.] for Ne calculated with the CCSD model and the n-aug-cc-pVXZ basis-set family (all electrons correlated).

	aug	d-aug	t-aug	q-aug
k=-2				
DZ	2.003	2.707	2.715	2.715
TZ	2.433	2.698	2.699	2.699
QZ	2.598	2.680	2.680	2.680
5Z	2.643	2.668	2.668	2.668
6Z	2.650	2.662	2.662	2.662
k=-4				
DZ	1.711	2.916	3.015	3.019
TZ	2.148	2.922	2.943	2.943
QZ	2.485	2.880	2.882	2.882
5Z	2.678	2.858	2.858	2.857
6Z	2.741	2.845	2.845	2.845
k=-6				
DZ	3.009	4.997	5.391	5.404
TZ	3.496	5.072	5.193	5.196
QZ	3.925	4.999	5.018	5.019
5Z	4.328	4.948	4.948	4.948
6Z	4.524	4.915	4.914	4.913
k=-8				
DZ	6.041	10.817	11.890	11.915
TZ	7.110	10.832	11.261	11.272
QZ	7.818	10.637	10.740	10.746
5Z	8.683	10.522	10.535	10.537
6Z	9.235	10.433	10.436	10.437
k=-10				
DZ	12.315	26.571	29.036	29.076
TZ	15.252	25.825	26.975	27.001
QZ	16.944	24.984	25.350	25.372
5Z	19.143	24.636	24.718	24.730
6Z	20.779	24.386	24.426	24.431

TABLE II: The Cauchy moments $S(k)$ for Ne calculated at various levels of the CC hierarchy using the d-aug-cc-pV6Z basis-set (all electrons correlated). All numbers in a.u.

k	CCS	CC2	CCSD	CC3	Experiment	
					DOSD[a]	other[b]
-2	2.461	2.791	2.662	2.665	2.669	2.663[c]
-4	2.137	3.218	2.845	2.859	2.886	2.938
-6	3.030	6.009	4.915	4.946	5.063	5.137
-8	5.328	13.759	10.433	10.485	10.86	10.95
-10	10.359	34.673	24.386	24.442	25.53	25.65

[a]Ref. [6]; [b]Ref. [30]; [c]Ref. [29]

TABLE III: The Cauchy moments $S(k)$ [a.u.] for Ar calculated at various levels of the CC hierarchy using the d-aug-cc-pV6Z basis-set (all electrons correlated).

k	CCS	CC2	CCSD	CC3	Experiment	
					DOSD[a]	other[b]
-2	11.469	11.233	11.084	11.102	11.08	11.08[c]
-4	25.599	28.089	27.360	27.996	27.91	27.92
-6	78.942	94.068	90.761	94.846	95.06	95.26
-8	297.742	378.822	362.949	386.833	391.5	392.0
-10	1260.532	1702.508	1621.707	1760.880	1802	1800

[a]Ref. [6]; [b]Ref. [35]; [c]Ref. [34]

TABLE IV: The Cauchy moments $S(k)$ [a.u.] for Kr calculated at various levels of the CC hierarchy using the d-aug-cc-pV5Z basis-set (all electrons correlated).

k	CCS	CC2	CCSD	CC3	Experiment	
					DOSD[a]	other[b]
-2	17.627	17.119	16.918	16.861	16.79	16.80[c]
-4	52.631	56.665	55.386	56.002	56.32	56.51
-6	216.762	249.399	242.394	248.098	256.7	258.7
-8	1079.250	1302.841	1263.398	1306.458	1404	1419
-10	6002.085	7554.571	7321.634	7639.949	8558	8669

[a]Ref. [6]; [b]Ref. [35]; [c]Ref. [34]