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Dipole Cauchy moments of the atoms H through Ar

An application of the hydrodynamic formulation of time-dependent Kohn–Sham theory using the atomic gradient expansion of the exchange-correlation energy density functional

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Summary. Dipole Cauchy moments of the atoms through Ar are calculated using the hydrodynamic formulation of time-dependent Kohn–Sham theory. The exchange-correlation energy density functional is approximated by the gradient expansion for atoms. Using variational trial functions that contain both linear and nonlinear variational parameters, we are able to reproduce (to three or four significant figures) the static dipole polarizabilities obtained by explicitly solving the relevant differential equations. The resulting dipole Cauchy moments provide a convenient starting point for calculating other properties which result from the linear interaction of atoms with a time varying electric field.

Key words: Time-dependent Kohn–Sham theory — Density functional theory — Cauchy moments

1. Introduction

The dipole Cauchy series is an expansion of the dynamic dipole polarizability as a power series of the applied frequency [1–5]. The Cauchy series is strictly convergent only for frequencies less than the first excitation frequency. However, using the method of Padé approximants this series can be summed within and continued outside its radius of convergence. The "pseudo spectrum" generated from the residues and poles of the Padé approximant can be used to calculate various optical properties of a chemical system which are manifested by the linear interaction between the system and an applied time varying electric field. Therefore, the Cauchy moments store a considerable amount of information about a chemical system.

Employing the hydrodynamic formulation of quantum mechanics for time-dependent Kohn–Sham theory [6–10], we calculate Cauchy moments for atoms through argon. Although the theory is in principle exact, its application is made inexact by the need to approximate the exchange-correlation energy $E_{xc}[\varrho]$ as a functional of the electron density. Thus the calculated results are only as good as the approximation employed. In the present set of calculations we employ a gradient expansion developed by us [11]. This approximation to $E_{xc}[\varrho]$ is superior to most approximations when the number of electrons N is small and it goes asymptotically, for large N, to the Dirac [12] functional.

The various Cauchy moments are obtained from variational solutions of a sequence of functionals based on the hydrodynamic formulation of density functional theory [8–10]. The chosen trial functions are sufficiently flexible and convergence is rapid enough to allow us to accurately reproduce the results obtained from the solutions of the differential equations. To ascertain the accuracy of our results, we compare our calculated static dipole polarizabilities to the accurate multiconfiguration perturbation theory calculations of Meyer and co-workers [13, 14].

2. Method of solution

The dynamic dipole polarizability, for frequencies less than the first excitation frequency, can be written as a Cauchy series,

$$\alpha(\omega) = \sum_{i=0}^{\infty} a_i \omega^{2i}, \tag{1}$$

where ω is the frequency of incident radiation and the a_i are the Cauchy moments. Employing the hydrodynamic formulation of time-dependent Kohn–Sham theory [8–10], we may obtain the individual Cauchy moments from

$$a_i = -2 \sum_{k=1}^{N} \langle \psi_{i,k} | h^{(1)} | \chi_k^{(0)} \rangle, \tag{2}$$

where N represents the number of electrons in the system, $h^{(1)}$ is the dipole moment operator and the $\chi_k^{(0)}$ are the solutions to the set of unperturbed Kohn–Sham equations [15]

$$h^{(0)} \chi_k^{(0)} = \varepsilon_k^{(0)} \chi_k^{(0)}. \tag{3}$$

Here $h^{(0)}$ is the Kohn–Sham Hamiltonian with eigenvalues $\varepsilon_k^{(0)}$. The first-order functions $\psi_{i,k}$ are defined by the following sequence of functionals

$$L_0[\{\psi_{0,k}\}] = \sum_{k=1}^{N} (\langle \psi_{0,k} | h^{(0)} - \varepsilon^{(0)} | \psi_{0,k} \rangle + 2\langle \psi_{0,k} | h^{(1)} + \tfrac{1}{2} v_0^{(1)} | \chi_k^{(0)} \rangle), \tag{4}$$

$$L_1[\{n_{j-1,k}\}] = \sum_{k=1}^{N} (\{\chi_k^{(0)} \eta_{i-1,k} | h^{(0)} - \varepsilon_k^{(0)} | \eta_{i-1,k} \chi_k^{(0)} \rangle + 2\langle \psi_{i-1,k} | \eta_{i-1,k} | \chi_k^{(0)} \rangle), \tag{5}$$

$$L_2[\{\psi_{i,k}\}] = \sum_{k=1}^{N} \langle \psi_{i,k} | h^{(0)} - \varepsilon_k^{(0)} | \psi_{i,k} \rangle + 2\langle \psi_{i,k} | \tfrac{1}{2} v_i^{(1)} + \eta_{i-1,k} | \chi_k^{(0)} \rangle). \tag{6}$$

The quantity $v_i^{(1)}$ is defined as

$$v_i^{(1)} = 2 \sum_{l=1}^{N} \int \psi_{i,l}(2) \frac{\delta^2\{J[\varrho] + E_{xc}[\varrho])\}}{\delta\varrho(1)\,\delta\varrho(2)} \bigg|_{\substack{p = p^{(0)} \\ N}} \chi_l^{(0)}(2)\, d\tau_2, \tag{7}$$

where $J[\varrho]$ is the coulomb energy density functional and $E_{xc}[\varrho]$ is the exchange-correlation energy density functional. The functional derivative is performed keeping the number of electrons fixed and it is evaluated with the unperturbed electron density $\varrho^{(0)}$.

We prefer to determine the Cauchy moments by seeking variational solutions of the functionals defined in Eqs. (4)–(6). We show below that the variational process can lead to results equivalent to those obtained upon exactly solving the Euler–Lagrange equations. To insure that the variationally determined $\psi_{i,k}$ are orthogonal to the uperturbed functions $\chi_k^{(0)}$, we choose trial functions of the form

$$\psi_{i,k} \approx \tilde{\psi}_{i,k} = \tilde{\phi}_{i,k} - \sum_{l=1}^{N} \langle \tilde{\phi}_{i,k} | \chi_l^{(0)} \rangle \chi_l^{(0)}, \tag{8}$$

where the functions $\tilde{\phi}_{i,k}$, which are found by minimizing the functionals defined by Eqs. (4)–(6), need not satisfy any orthogonality relationships. In the current work, the functions $\tilde{\phi}_{i,k}$ and $\tilde{\eta}_{i,k}$ are approximated by

$$\tilde{\phi}_{i,k}(\mathbf{r}, \omega) = \sum_{j=1}^{M_k} \sum_{\lambda=0}^{l_k - |m_k|} C_{j,\lambda}^{(i,k)}(\omega) r^{j + l_k - 2\lambda} e^{-\beta_\lambda^{(k)} r} Y_{l_k + 1 - 2\lambda}^{m_k}, \tag{9}$$

$$\eta_{i,k}(\mathbf{r}, \omega) \approx \tilde{\eta}_{i,k}(\mathbf{r}, \omega) = \sum_{j=1}^{M'_k} \sum_{\lambda=0}^{l_k - |m_k|} D_{j,\lambda}^{(i,k)}(\omega) r^{j + l_k - 2\lambda - (n_k - 1)} \frac{Y_{l_k + 1 - 2\lambda}^{m_k}}{Y_{l_k}^{m_k}}. \tag{10}$$

Here n_k, l_k and m_k are the principle, angular momentum and magnetic quantum numbers, respectively, of the unperturbed functions $\chi_k^{(0)}$. The sum over λ defines the angular contributions to the $\tilde{\phi}_{i,k}$ and $\tilde{\eta}_{j,k}$, which are given by the spherical harmonics $Y_{l_k + 1 - 2\lambda}^{m_k}(\theta, \phi)$. These angular portions are fixed by the dipole selection rules. It is the radial portion of $\tilde{\phi}_{i,k}$ and $\tilde{\eta}_{i,k}$ which is varied. We thus minimize the functionals, defined by Eqs. (4)–(6), with respect to the linear variational parameters $\{C_{j,\lambda}^{(i,k)}\}$ and $\{D_{j,\lambda}^{(i,k)}\}$ as well as a nonlinear variational parameter $\beta_\lambda^{(k)}$ for each of the different angular contributions to $\tilde{\phi}_{i,k}$.

We found that trial functions of this form are sufficiently flexible to provide rapid convergence to the "exact" static polarizabilities. By "exact", we mean values of the polarizability calculated by directly solving the Euler–Lagrange equations for a given approximation to the exchange-correlation energy density functional. Table 1 provides a comparison of our variationally calculated static dipole polarizabilities with the "exact" results of Stott and Zaremba [16]. These authors solved the differential equation associated with the minimization of Eq. (4), in which they used the Gunnarsson–Lundqvist parameterization [17] at the $E_{xc}[\varrho]$. For the sake of comparison, we temporarily adopted the Gunnarsson–Lundqvist approximation to $E_{xc}[\varrho]$. With $M_k = 8$ linear variational parameters, convergence to three or four significant figures in the polarizability was achieved and, as seen from Table 1, we were able to reproduce the "exact" results. These variational results were obtained without completely optimizing the set of

Table 1. Static dipole polarizabilities[a]

Atom	He	Be	Ne	Mg	Ar
Differential equation[b]	1.63	43.0	3.00	69.8	11.8
Variational	1.63	43.0	3.00	69.8	11.8

[a] Results are in atomic units. The Gunnarsson–Lundqvist [17] form of the exchange-correlation functional was used in all calculations

[b] Results obtained by Stott and Zaremba [16]

nonlinear variational parameters. The set of nonlinear variational parameters used to obtain the results given in Table 1 were found by minimizing the uncoupled form of $L_0[\{\tilde{\psi}_{0,k}\}]$, which completely neglects $v_i^{(1)}$. Although polarizabilities calculated with the uncoupled equation provide poor estimates to the "exact" values, these uncoupled nonlinear optimizations are orders of magnitude faster than the fully coupled nonlinear optimizations and the $\beta_\lambda^{(k)}$ obtained are numerically similar. Since the values of the static dipole polarizabilities are not very sensitive to the set of $\beta_\lambda^{(k)}$, this procedure saves a considerable amount of computer time without a significant loss of accuracy. The observation that knowledge of the exact set of nonlinear parameters is not very critical in the calculated polarizabilities has also been reported in time-dependent Hartree–Fock calculations [18].

3. Results and discussion

Now that we have decided upon a method of solution, we must select the approximation to $E_{xc}[\varrho]$ that will be used in the minimization of Eqs. (4)–(6). Our choice for $E_{xc}[\varrho]$ is the gradient expansion developed previously by us [19]. Not only has this approximation yielded good numerical results in earlier work [19–22] but it does not suffer from the singularities which plague the usual graident expansion [23, 24] of $E_{xc}[\varrho]$. Also, our approximation to $E_{xc}[\varrho]$ gives reasonable results when the number of electrons is small, unlike most other approximations, and in the limit that the number of electrons becomes infinite, our approximation to $E_{xc}[\varrho]$ reduces to the Dirac functional [12]. Our earlier work employed variational trial functions that were too rigid for most atomic systems except for the rare gases. The current form of the trial functions is sufficiently flexible that convergence is rapid for all atoms considered. Thus, any error in the calculated numerical results should be attributed solely to the approximation to $E_{xc}[\varrho]$. To further establish the adequacy of our approximation to $E_{xc}[\varrho]$, we used Eq. (4) to variationally determine the mean dipole polarizabilities of the atoms H through Ar. These mean polarizabilities are weighted averages over the different M_L projections arising from the atomic ground states. The results are given in Tables 2–4. The variational functions contained $M_k = 8$ linear variational parameters and the nonlinear variational parameters $\beta_\lambda^{(k)}$ were

Table 2. Static dipole polarizabilities (in atomic units) of H and He

	H	He
Present work	5.189	1.363
Best theoretical	4.5	1.383[a]
Hartree–Fock	4.5	1.322[b]
Spin-polarized	4.436	

[a] Taken from [25]. Explicitly correlated wavefunctions were used in the calculation

[b] Taken from [28]

Table 3. Static dipole polarizabilities (in atomic units) of Li through Ne. These are weighted averages over the different M_L projections arising from the atomic ground states

	Li	Be	B	C	N	O	F	Ne
Present work	139.2	42.07	21.95	12.00	7.366	5.256	3.868	2.931
Best theoretical[a]	164.5	37.84	20.47	11.84	7.430	5.412	3.759	2.676
SCF[a]	170.3	45.63	22.16	12.07	7.365	4.772	3.291	2.368

[a] Taken from [26]

Table 4. Static dipole polarizabilities (in atomic units) of Na through Ar. These are weighted averages over the different M_L projections arising from the atomic ground states

	Na	Mg	Al	Si	P	S	Cl	Ar
Present work	153.5	73.00	76.46	45.33	29.53	21.18	15.75	12.07
Best theoretical[a]	165.0	71.32	56.27	36.32	24.52	19.60	14.71	11.10
SCF[a]	192.8	81.87	63.07	38.83	25.41	19.17	14.20	10.69

[a] Taken from [27]

determined from the minimization of the uncoupled functionals as described above. As with the above variational calculations, convergence was rapid. These variational solutions again should yield polarizabilities which are nearly identical to the polarizabilities found upon exactly solving the appropriate differential equations. The second row of these tables lists very accurate values of the mean polarizabilities, which were determined using wavefunction functional techniques. The wavefunction functional result for He, which employed a correlated wavefunction [25] is in exact agreement with experiment. The multiconfigurational perturbation results of Meyer and co-workers [26, 27] have an estimated accuracy of $\pm 2\%$. The third row of these tables contains mean dipole polarizabilities as predicted by coupled Hartree–Fock theory. We include the Hartree–Fock results since the computational difficulty of the present calculations (actually any orbital-density functional calculation) is between that experienced with the Hartree and the Hartree–Fock method. In addition, we believe that any viable method for calculating polarizabilities should be at least as good as Hartree–Fock, but preferably yield values that are closer to the accurate polarizabilities. As we see from these tables, this is generally the case for our density functional results. Except for H, Li, Al, Si and P, our results are in quite good agreement with the accurate mean polarizabilities. We believe that the poor agreement for H, Li and Al may be attributed to the absence of spin polarization in our calculations. That is, we did not explicitly take into account the partitioning of the density into spin-up and spin-down contributions. Writing our approximation to $E_{xc}[\varrho]$ in a spin (unrestricted) polarized form for H is straightforward. Thus, we performed a spin polarized calculation on H and found a marked improvement in the predicted dipole polarizability. The result is listed in Table 1. It is in good agreement with the exact dipole polarizability of H. Our poor value for the polarizability of Li may also be attributed to the neglect of electron spin. Unfortunately, expressing $E_{xc}[\varrho]$ in a spin polarized form for anything other than a one electron system is not simple since its inclusion will require extensive modification of the existing computer programs. We are currently studying this problem. Another source of error is the quality of the unperturbed solutions $\chi_k^{(0)}$, which is directly related to the error associated with the approximation to $E_{xc}[\varrho]$. Looking at some previous work along these lines for He [21], it appears that the expression for $\delta E_{xc}[\varrho]/\delta\varrho$, as calculated from our gradient expansion, deviates from the true first functional derivative more than the calculated $\delta^2 E_{xc}[\varrho]/\delta\varrho(1)\,\delta\varrho(2)$ deviates from the true second functional derivative. Thus, we may be able to obtain better results by focusing on corrections to our gradient expansion of $E_{xc}[\varrho]$ which contribute to the unperturbed energy. We are currently investigating the addition of terms to our proposed gradient expansion of $E_{xc}[\varrho]$, which may have the desired effect.

A much more sensitive test of our approximation to $E_{xc}[\varrho]$ comes from comparing the predicted dipole polarizability anisotropies, $\alpha(M_L = \pm 1) - \alpha(M_L = 0)$. Our calculated anisotropies are given in Table 5 as well as those calculated by Meyer and co-workers [26, 27]. Unfortunately, our results are not in good agreement with the wavefunction functional values. However, all our calculated anisotropies have the correct sign, which is not always the case with wavefunction functional calculations [26, 27].

Now that we have established a degree of confidence in our approximation to $E_{xc}[\varrho]$, we use it in Eqs. (4)–(6) to calculate dipole Cauchy moments for the atoms through Ar. Our results are given in Tables 6–9. The spatial part of the

Table 5. Static dipole polarizability anisotropies (in atomic units) $\alpha(M_L = \pm 1) - \alpha(M_L = 0)$

	B	C	O	F	Al	Si	S	Cl
Present work	−4.55	1.09	−1.29	0.762	−58.1	14.2	−4.66	2.70
Best theoretical[a]	−7.04	2.54	−0.948	0.439	−24.4	9.60	−4.88	2.16

[a] Taken from [26, 27]

Table 6. Dipole Cauchy moments of the atoms H through B.[a] The last row of the table provides an estimate of the first dipole excitation frequency ω_1, as obtained from the radius of convergence of the Cauchy series

	H[b]	H	He	Li	Be	B $M_L = 0$	B $M_L = \pm 1$
a_0	$4.43579180D+00$	$5.18940304D+00$	$1.36341378D+00$	$1.39230725D+02$	$4.20702252D+01$	$2.49792404D+01$	$2.04337738D+01$
a_1	$2.72752239D+01$	$3.85011093D+01$	$1.58169828D+00$	$2.02729416D+04$	$9.69960366D+02$	$8.62296534D+02$	$2.20949895D+02$
a_2	$1.89114902D+02$	$3.26621103D+02$	$2.26998577D+00$	$2.99368902D+06$	$2.33573254D+04$	$4.28913980D+04$	$3.81920127D+03$
a_3	$1.39138562D+03$	$2.96350262D+03$	$3.64029813D+00$	$4.44525346D+08$	$5.76143819D+05$	$2.44012996D+06$	$9.76405873D+04$
a_4	$1.05965106D+04$	$2.79777002D+04$	$6.24748750D+00$	$6.61755888D+10$	$1.44148543D+07$	$1.47279437D+08$	$3.11028755D+06$
a_5	$8.25132751D+04$	$2.71085951D+05$	$1.12221368D+01$	$9.86337253D+12$	$3.63749677D+08$	$9.15594045D+09$	$1.10441121D+08$
a_6	$6.52356022D+05$	$2.67479239D+06$	$2.08215921D+01$	$1.47097519D+15$	$9.22673728D+09$	$5.78528544D+11$	$4.16351023D+09$
a_7	$5.21347514D+06$	$2.67431505D+07$	$3.95571010D+01$	$2.19435562D+17$	$2.34782665D+11$	$3.69080221D+13$	$1.62978266D+11$
a_8	$4.19909360D+07$	$2.70026912D+08$	$7.64724153D+01$	$3.27291690D+19$	$5.98577984D+12$	$2.36870938D+15$	$6.54159429D+12$
a_9	$3.40137024D+08$	$2.74673814D+09$	$1.49746632D+02$	$4.88491395D+21$	$1.52786788D+14$	$1.52605871D+17$	$2.67022092D+14$
a_{10}	$2.76668576D+09$	$2.80968846D+10$	$2.95996071D+02$	$7.28886815D+23$	$3.90267165D+15$	$9.85659136D+18$	$1.10223715D+16$
a_{11}	$2.25729609D+10$	$2.88626930D+11$	$5.89081098D+02$	$1.08760209D+26$	$9.97304691D+16$	$6.37693453D+20$	$4.58354358D+17$
a_{12}	$1.84579703D+11$	$2.97442294D+12$	$1.17814375D+03$	$1.62286824D+28$	$2.54923135D+18$	$4.13035063D+22$	$1.91518044D+19$
ω_1	0.349	0.310	0.703	0.0819	0.198	0.124	0.154

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[a] Results are in atomic units. The Cauchy moments are given in scientific notation where "$D+$" followed by a number denotes the power of ten which the number is multiplied

[b] Spin-polarized calculation

Table 7. Cauchy moments of the atoms C through F.[a] The last row of the table provides an estimate of the first dipole excitation frequency ω_1, as obtained from the radius of convergence of the Cauchy series

	C $M_L = 0$	C $M_L = \pm 1$	N	O $M_L = 0$	O $M_L = \pm 1$	F $M_L = 0$	F $M_L = \pm 1$
a_0	1.12723439*D* + 01	1.23594395*D* + 01	7.36577478*D* + 00	6.11880541*D* + 00	4.82431321*D* + 00	3.35986742*D* + 00	4.12163940*D* + 00
a_1	5.88773160*D* + 01	1.48990593*D* + 02	4.14942136*D* + 01	2.22305751*D* + 01	1.48589667*D* + 01	6.24999183*D* + 00	8.98259022*D* + 00
a_2	5.04429855*D* + 02	2.85067837*D* + 03	3.90292520*D* + 02	1.32692068*D* + 02	7.89185704*D* + 01	2.05126197*D* + 01	3.32363917*D* + 01
a_3	6.10361348*D* + 03	6.57655420*D* + 04	4.57758072*D* + 03	9.63687727*D* + 02	5.34688581*D* + 02	8.72966769*D* + 01	1.52353736*D* + 02
a_4	8.88951983*D* + 04	1.65210352*D* + 06	5.95834322*D* + 04	7.65454021*D* + 03	4.07753113*D* + 03	4.22733835*D* + 02	7.71146732*D* + 02
a_5	1.42695752*D* + 06	4.33315437*D* + 07	8.18474953*D* + 05	6.36948586*D* + 04	3.30948301*D* + 04	2.19375618*D* + 03	4.11112541*D* + 03
a_6	2.42602727*D* + 07	1.16404991*D* + 09	1.15887551*D* + 07	5.44372055*D* + 05	2.78302075*D* + 05	1.18467621*D* + 04	2.25845277*D* + 04
a_7	4.28078723*D* + 08	3.17214337*D* + 10	1.67107470*D* + 08	4.72996335*D* + 06	2.39121814*D* + 06	6.55542317*D* + 04	1.26402747*D* + 04
a_8	7.74287232*D* + 09	8.72266781*D* + 11	2.43775650*D* + 09	4.15403575*D* + 07	2.08299687*D* + 07	3.68477763*D* + 05	7.16117544*D* + 05
a_9	1.42368489*D* + 11	2.41270086*D* + 13	3.58343951*D* + 10	3.67443499*D* + 08	1.83105440*D* + 08	2.09290573*D* + 06	4.09037793*D* + 06
a_{10}	2.64605150*D* + 12	6.69988321*D* + 14	5.29472111*D* + 11	3.26605784*D* + 09	1.61948620*D* + 09	1.19718561*D* + 07	2.34947204*D* + 07
a_{11}	4.95227773*D* + 13	1.86547684*D* + 16	7.85074954*D* + 12	2.91277517*D* + 10	1.43838486*D* + 10	6.88150726*D* + 07	1.35472402*D* + 08
a_{12}	9.30994914*D* + 14	5.20360736*D* + 17	1.16688638*D* + 14	2.60369027*D* + 11	1.28123169*D* + 11	3.96883344*D* + 08	7.83230548*D* + 08
ω_1	0.230	0.189	0.259	0.334	0.334	0.415	0.415

[a] Results are in atomic units. The Cauchy moments are given in scientific notation where "*D*+" followed by a number denotes the power of ten which the number is multiplied

Table 8. Cauchy moments of the atoms Ne through Si.[a] The last row of the table provides an estimate of the first dipole excitation frequency ω_1, as obtained from the radius of convergence of the Cauchy series

	Ne	Na	Mg	Al $M_L = 0$	Al $M_L = \pm 1$	Si $M_L = 0$	Si $M_L = \pm 1$
a_0	2.93085650D + 00	1.53482445D + 02	7.30047341D + 01	1.15174917D + 02	5.71068003D + 01	3.58574115D + 01	5.00737798D + 01
a_1	4.10983253D + 00	2.53202621D + 04	2.93200655D + 03	1.35582560D + 04	2.06401384D + 03	5.58343096D + 02	1.63166975D + 03
a_2	1.00352732D + 01	4.30838195D + 06	1.23330267D + 05	2.08998715D + 06	1.26826848D + 05	1.34768193D + 04	7.57096210D + 04
a_3	3.07997492D + 01	7.41508241D + 08	5.30081106D + 06	3.57595163D + 08	9.92395480D + 06	4.08346156D + 05	4.16477642D + 06
a_4	1.05216966D + 02	1.28340871D + 11	2.30659327D + 08	6.39106994D + 10	8.51597846D + 08	1.36397118D + 07	2.48362975D + 08
a_5	3.80327768D + 02	2.22772586D + 13	1.01097296D + 10	1.16481696D + 13	7.62055373D + 10	4.76019275D + 08	1.54068418D + 10
a_6	1.42059622D + 03	3.87262520D + 15	4.45011170D + 11	2.14284756D + 15	6.97666859D + 12	1.69857402D + 10	9.75229505D + 11
a_7	5.41577616D + 03	6.73732554D + 17	1.96387260D + 13	3.96037003D + 17	6.47317098D + 14	6.13532846D + 11	6.23970893D + 13
a_8	2.09246347D + 04	1.17259301D + 20	8.67999727D + 14	7.33679181D + 19	6.05397725D + 16	2.23154699D + 13	4.01578406D + 15
a_9	8.15767049D + 04	2.04127066D + 22	3.83992497D + 16	1.36084548D + 22	5.68871507D + 18	8.14916542D + 14	2.59293499D + 17
a_{10}	3.20000486D + 05	3.55388324D + 24	1.69966416D + 18	2.52574930D + 24	5.36039891D + 20	2.98281391D + 16	1.67728254D + 19
a_{11}	1.26060888D + 06	6.18773475D + 26	7.52567165D + 19	4.68941411D + 26	5.05930262D + 22	1.09325394D + 18	1.08609514D + 21
a_{12}	4.98065287D + 06	1.07739241D + 29	3.33282198D + 21	8.70812410D + 28	4.77969813D + 24	4.01007264D + 19	7.03691316D + 22
ω_1	0.501	0.0758	0.150	0.0734	0.103	0.165	0.124

[a] Results are in atomic units. The Cauchy moments are given in scientific notation where "D + " followed by a number denotes the power of ten which the number is multiplied

Table 9. Cauchy moments of atoms P through Ar.[a] The last row of the table provides an estimate of the first dipole excitation frequency ω_1, as obtained from the radius of convergence of the Cauchy series

	P	S	S	Cl	Cl	Ar
		$M_L = 0$	$M_L = \pm 1$	$M_L = 0$	$M_L = \pm 1$	
a_0	2.95347635*D* + 01	2.42890665*D* + 01	1.96276601*D* + 01	1.39510953*D* + 01	1.66478831*D* + 01	1.20749398*D* + 01
a_1	4.10766025*D* + 02	2.00196569*D* + 02	1.42788547*D* + 02	5.98200362*D* + 01	7.99922164*D* + 01	3.67095891*D* + 01
a_2	8.36537695*D* + 03	2.43707390*D* + 03	1.54258235*D* + 03	3.84817211*D* + 02	5.79431232*D* + 02	1.70845814*D* + 02
a_3	2.09545535*D* + 05	3.60005454*D* + 04	2.09354139*D* + 04	3.15140424*D* + 03	5.19539166*D* + 03	9.98986164*D* + 02
a_4	5.84772930*D* + 06	5.85105720*D* + 05	3.22439196*D* + 05	2.96598932*D* + 04	5.19528478*D* + 04	6.58478095*D* + 03
a_5	1.72737332*D* + 08	9.99432417*D* + 06	5.32780939*D* + 06	3.02592139*D* + 05	5.50779585*D* + 05	4.63518704*D* + 04
a_6	5.26267990*D* + 09	1.75471241*D* + 08	9.16322329*D* + 07	3.23822935*D* + 06	6.03560399*D* + 06	3.38930986*D* + 05
a_7	1.63135121*D* + 11	3.12991013*D* + 09	1.61318469*D* + 09	3.56667625*D* + 07	6.74394865*D* + 07	2.53536594*D* + 06
a_8	5.10723825*D* + 12	5.63516376*D* + 10	2.87938698*D* + 10	3.99754847*D* + 08	7.62372195*D* + 08	1.92296279*D* + 07
a_9	1.60808536*D* + 14	1.02021339*D* + 12	5.18158195*D* + 11	4.52799206*D* + 09	8.67899322*D* + 09	1.47080829*D* + 08
a_{10}	5.08014616*D* + 15	1.85317292*D* + 13	9.36980319*D* + 12	5.16154753*D* + 10	9.92230627*D* + 10	1.13074607*D* + 09
a_{11}	1.60799657*D* + 17	3.37289856*D* + 14	1.69921602*D* + 14	5.90627826*D* + 11	1.13727902*D* + 12	8.72015873*D* + 09
a_{12}	5.09548355*D* + 18	6.14620855*D* + 15	3.08679887*D* + 15	6.77395783*D* + 12	1.30554452*D* + 13	6.73755211*D* + 10
ω_1	0.178	0.234	0.234	0.295	0.295	0.359

[a] Results are in atomic units. The Cauchy moments are given in scientific notation where "*D*+" followed by a number denotes the power of ten which the number is multiplied

amplitudes $\tilde{\phi}_{i,k}$ were given by Eqs. (8) and (9) and the spatial part of the phase $\tilde{\eta}_{i,k}$ was given by Eq. (10). Eight linear variational parameters ($M_k = M'_k = 8$) were used for each symmetry type, as was one nonlinear variational parameter. These nonlinear variational parameters $\beta_1^{(k)}$ were determined from the minimization of $L_0[\{\tilde{\psi}_{0,k}\}]$, Eq. (4). In other words, the nonlinear parameters used in the time-dependent calculations were determined from calculations of static (time-independent) polarizabilities. This simplification should not dramatically alter the calculated Cauchy moments. Also given in these tables are the predicted first dipole excitation frequencies, ω_1. These values of ω_1 were obtained from the radius of convergence of the Cauchy series [1–5], namely

$$\omega_1^2 = \lim_{i \to \infty} a_{i-1}/a_i. \tag{11}$$

Since convergence of the ratio was rapid, we were able to obtain convergence to 4 or 5 significant figures in the ω_1 when $i = 25$.

Dipole Cauchy moments are directly related to the dynamic dipole polarizabilities (for $\omega < \omega_1$) through Eq. (1) and they are directly related to some dipole spectral sums [29, 30]

$$S(i) = \sum_{j=1} f_j \omega_j^i, \tag{12}$$

through the relationship [1–5] $S(-2i-2) = a_i$. Here, the f_j are oscillator strengths and the ω_j are transition frequencies. The Cauchy moments may also be used to calculate other properties related to the linear interaction of chemical systems with time varying external fields. For instance, using Padé summation techniques, the convergence of the Cauchy series, Eq. (1), can be improved [1–5]. The Padé approximant sums the series within its radius of convergence and furnishes an analytic continuation outside the radius of convergence. Further, the Padé approximants provide convenient methods for obtaining bounds to the dipole polarizabilities and dispersion coefficients [2, 5]. The Padé approximant defines a fictitious finite spectrum which approximates the exact spectrum of the atom. It is this fictitious (pseudo) spectrum that allows us to calculate other properties of the atom. These are properties such as spectral sums [29, 30], dynamic dipole polarizabilities [31], dipole two- and three-body long range interactions [32, 33], relativistic corrections to the van der Waals interaction [34] and Verdet constants [35].

Since the nonlinear variational parameters in the $\tilde{\phi}_{i,k}(r, \omega)$ are determined from calculations of $a_0 = \alpha(0)$, the rate of convergence in the higher moments (a_i for $i > 0$) depends critically upon the number of linear variational parameters. Within the context of wavefunction functional theory, Langhoff and Karplus [2] give a thorough discussion of this problem. Following their analysis, one would expect to find smooth convergence to the a_i. Indeed, this is the case. For a small set of atoms selected to test convergence in the present work, rapid convergence is found in the first few moments. However, the rate of convergence gets progressively worse as one goes to the higher moments. In order to obtain the same high rate of convergence found in the static calculations, it will be necessary to employ a set of nonlinear parameters for each of the $\tilde{\phi}_{i,k}(\mathbf{r}, \omega)$. In many applications, converged values of the higher moments are not necessary to obtain good convergence in other properties. Although we have not found the exact solutions of the relevant differential equations for the $\tilde{\phi}_{i,k}$ and $\tilde{\eta}_{i,k}$, the variationally determined Cauchy moments are sufficient to yield values for the van der Waals coefficients that have converged to 3 significant figures. This is acceptable considering the error introduced by the approximate $E_{xc}[\varrho]$ may be more significant. We believe that the overall quality of the calculated dipole Cauchy moments is good, especially the lower moments, and they should lead to reasonable values for a number of generated properties. In general, they are better than Hartree–Fock moments and in some cases they are in good agreement with the correct values. Using the dipole oscillator strength distribution generated by the Hartree–Slater method, Dehmer et al. [36, 37] systematically calculated various spectral moments $S(i)$, where $-6 \leqslant i \leqslant 1$, for the atoms He through Ar. They did an impressive in-depth study, including logarithmic spectral sums. Comparing values of $S(-2) = \alpha(0)$, our results are, for the most part, in closer agreement with accepted polarizabilities.

As with the anisotropies discussed above, the calculated first transition frequencies provide a very sensitive test of our approximation to $E_{xc}[\varrho]$. Comparing our values of ω_1 to accepted values [38] shows that higher order terms are necessary in our gradient expansion. The calculated van der Waals dispersion coefficient C_6 for hydrogen again show the importance of spin polarization. Using the nonspin polarized a_i to construct a $[5, 4]_\beta$ Padé approximant, we find $C_6 = 7.83$. However, the spin polarized a_i yield $C_6 = 6.25$. This is in much better agreement with the correct values [39] $C_6 = 6.50$. Further evidence of the importance of the consideration of spin is found upon comparing the values of ω_1 for the two cases.

The dipole Cauchy moments tabulated here should be helpful to anyone interested in properties which are manifested by the linear interaction of atoms with a time varying electric field. Since we have performed a systematic set of calculations of the atoms through Ar, our data may also be useful in studying the variations or trends in linear optical properties. This work has also identified deficiencies in our gradient expansion of $E_{xc}[\varrho]$. However, it has provided insight on how we might correct some of the problems. Work is in progress to expand the current set of calculations to the transition metals, higher multipoles and an improved gradient expansion.

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