

A COMPARISON OF MØLLER–PLESSET AND COUPLED CLUSTER LINEAR RESPONSE THEORY METHODS FOR THE CALCULATION OF DIPOLE OSCILLATOR STRENGTH SUM RULES AND C_6 DISPERSION COEFFICIENTS

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Four correlated linear response theory methods – the second order polarization propagator approximation (SOPPA), the second order polarization propagator approximation with coupled cluster singles and doubles amplitudes, SOPPA(CCSD), the CC2 and coupled cluster singles doubles (CCSD) linear response theory – were used to determine the dipole oscillator strength sum rules of the hydrogen halides HX (with X = F, Cl, Br and I) and the C_6 dispersion coefficient for all pairs of interacting HX molecules via numerical integration of the Casimir–Polder formula. The dependence of the polarizabilities, their frequency dependence and the C_6 coefficients on the level of correlation and the dependence of the C_6 coefficients on the two intramolecular bond lengths were studied.

Keywords: van der Waals complexes; Dispersion coefficients; Dipole oscillator strength sum rules; Coupled clusters linear response method; Møller–Plesset perturbation theory linear response method.

The dispersion-energy coefficients which govern the interaction energy of nonpolar species at long separation (see e.g.^{1–4}) are of great interest for atomic and molecular physics in particular at low temperature. Accurately calculated values of dispersion coefficients are needed for, e.g., the interpretation of experiments concerning total and differential cross-sections from low-angle scattering⁵. The anisotropic part of the dispersion interaction energy plays an important role in, e.g., molecular dynamics simulations of

molecules, where the mutual orientation has to be taken into account⁶, or in molecular modelling of crystal structures⁷.

The long-range asymptotic part of the weak interaction of van der Waals complexes is determined by the electric polarizability. While the asymptotic induction energy can be calculated from static multipole polarizabilities and multipole moments, the dispersion energy is described in terms of dispersion coefficients which are related to the dynamic multipole polarizabilities at imaginary frequencies via integration in the Casimir-Polder formula².

Frequency dependent multipole polarizabilities can in general be obtained from polarization propagators⁸⁻¹⁰ or linear response functions^{11,12}. In principle the polarizability for imaginary frequencies could be obtained with this formalism by using complex arithmetic^{13,14}. However, this is often avoided by using a moment expansion of the polarizability¹⁵⁻¹⁸ or an expansion in the dipole oscillator strength sum rules, $S(k)$ or Cauchy moments¹⁹. The $S(k)$ sum rules are also related to many other properties, e.g. the Verdet constant²⁰ or mean excitation energies²¹⁻²³, and have therefore been calculated using various *ab initio* methods such as e.g. time-dependent coupled Hartree-Fock^{21,23-25}, multiconfigurational self-consistent field linear response¹⁷, SOPPA^{26,27}, SOPPA(CCSD)²⁷, time-dependent second-order Møller-Plesset perturbation theory²⁸ and various coupled cluster linear response functions²⁹⁻³².

We have recently published³³ the first application of the SOPPA(CCSD) method to the calculation of the C_6 dispersion coefficients with particular emphasis on basis set and zero-point vibrational averaging effects as well as the possible usage of relativistic effective large-core potentials. In the present study we concentrate now on the comparison of Møller-Plesset perturbation theory and coupled cluster linear response functions in the calculation of dipole oscillator strength sum rules and dispersion coefficients.

In most currently available intermolecular potential energy surfaces (PES) the interacting molecules are treated as rigid bodies in either their equilibrium or vibrationally averaged geometries. However, several authors³⁴ have recently underlined the increasing need for potential energy surfaces with intramolecular-coordinate dependence, which are necessary for theoretical studies of a number of important phenomena as e.g. intramolecular frequency shifts, vibrational predissociation, intramolecular vibrational distribution, etc. We will therefore present also C_6 coefficients surfaces for the mixed pairs of hydrogen halides as a function of the two intramolecular bond lengths.

In the following sections we will firstly review the definitions of dispersion coefficients and sum rules employed in this work, then describe the details of our calculations and finally present and discuss the calculated sum rules and dispersion coefficients.

THEORETICAL BACKGROUND

Wormer and co-workers^{15,16,35–38} expand the second order dispersion energy between two diatomic molecules A and B as

$$\Delta E_{\text{disp}}^{\text{AB}}(\theta_A, \phi_A, \theta_B, \phi_B, \mathbf{R}) = \sum_{L_A, L_B, L} \Delta E_{L_A L_B L}(\mathbf{R}) A_{L_A L_B L}(\theta_A, \phi_A, \theta_B, \phi_B) \quad (1)$$

where $A_{L_A L_B L}(\theta_A, \phi_A, \theta_B, \phi_B)$ is an angular function¹⁵, which can be defined in terms of the normalized spherical harmonics functions $Y_L^M(\theta, \phi)$ as

$$\begin{aligned} A_{L_A L_B L}(\theta_A, \phi_A, \theta_B, \phi_B) &= \\ &= \sum_M \begin{pmatrix} L_A & L_B & L \\ M & -M & 0 \end{pmatrix} \sqrt{\frac{4\pi}{2L_A + 1}} Y_{L_A}^M(\theta_A, \phi_A) \sqrt{\frac{4\pi}{2L_B + 1}} Y_{L_B}^{-M}(\theta_B, \phi_B). \end{aligned} \quad (2)$$

The expansion coefficients $\Delta E_{L_A L_B L}(\mathbf{R})$ are given as

$$\Delta E_{L_A L_B L}(\mathbf{R}) = -\sum_n \frac{C_n^{L_A L_B L}}{R^n}. \quad (3)$$

In case of the dipole-dipole dispersion interaction this leads to six C_6 coefficients, of which, however, only four are independent.

$$C_6^{000} = \frac{2}{3} (C_{\parallel, \parallel} + 2C_{\perp, \parallel} + 2C_{\parallel, \perp} + 4C_{\perp, \perp}) \quad (4)$$

$$C_6^{022} = \frac{2}{3} \sqrt{5} (C_{\parallel, \parallel} + 2C_{\perp, \parallel} - C_{\parallel, \perp} - 2C_{\perp, \perp}) \quad (5)$$

$$C_6^{202} = \frac{2}{3} \sqrt{5} (C_{\parallel, \parallel} - C_{\perp, \parallel} + 2C_{\parallel, \perp} - 2C_{\perp, \perp}) \quad (6)$$

$$C_6^{220} = \frac{2}{3} \frac{1}{\sqrt{5}} (C_{\parallel,\parallel} - C_{\perp,\parallel} - C_{\parallel,\perp} + C_{\perp,\perp}) \quad (7)$$

$$C_6^{222} = \frac{10}{\sqrt{14}} C_6^{220} \quad (8)$$

$$C_6^{224} = \frac{54}{5} C_6^{222} \quad (9)$$

The coefficients C_6^{022} and C_6^{202} become equal, if the molecules A and B are the same. Instead of the anisotropic coefficients C_6^{022} to C_6^{224} one often reports dimensionless anisotropy factors $\gamma_n^{L_A L_B L}$ defined as

$$\gamma_n^{L_A L_B L} = \frac{C_n^{L_A L_B L}}{C_n^{000}}. \quad (10)$$

The coefficients $C_{\parallel,\parallel}$, $C_{\perp,\parallel}$, $C_{\parallel,\perp}$ and $C_{\perp,\perp}$ can be obtained from electric dipole polarizabilities $\alpha^{A/B}$ of the two molecules via integration over imaginary frequencies³⁹ $i\omega$ according to the Casimir-Polder formula²

$$C_{\parallel,\parallel} = \frac{1}{2\pi} \int_0^\infty \alpha_{\parallel}^A(i\omega) \alpha_{\parallel}^B(i\omega) d\omega \quad (11)$$

$$C_{\perp,\parallel} = \frac{1}{2\pi} \int_0^\infty \alpha_{\perp}^A(i\omega) \alpha_{\parallel}^B(i\omega) d\omega \quad (12)$$

$$C_{\parallel,\perp} = \frac{1}{2\pi} \int_0^\infty \alpha_{\parallel}^A(i\omega) \alpha_{\perp}^B(i\omega) d\omega \quad (13)$$

$$C_{\perp,\perp} = \frac{1}{2\pi} \int_0^\infty \alpha_{\perp}^A(i\omega) \alpha_{\perp}^B(i\omega) d\omega \quad (14)$$

where $\alpha_{\parallel}^{A/B}$ and $\alpha_{\perp}^{A/B}$ are the components of the polarizability tensor parallel and perpendicular to the molecular axis of molecule A or B, respectively.

The definition in Eq. (1) should be distinguished from the “LLM” definition in terms of associated Legendre functions as employed by Langhoff, Gordon and Karplus⁴ and others^{40,41}. However, the following simple relations connect the “LLL” coefficients of Wormer and co-workers to the C_{AB} , Γ_{BA} and Δ_{AB} coefficients of Langhoff, Gordon and Karplus⁴ or the C_6 , γ_6^{200} and γ_6^{220} coefficients of Meyer⁴¹.

$$C_6^{000} = C_{AB} = C_6 \quad (15)$$

$$\gamma_6^{202} = \sqrt{5} \Gamma_{BA} = \sqrt{5} \gamma_6^{202} \quad (16)$$

$$\gamma_6^{220} = \frac{1}{\sqrt{5}} \Delta_{AB} = \frac{1}{3\sqrt{5}} \gamma_6^{220} \quad (17)$$

The Casimir–Polder integrals, Eqs (11)–(14), are typically evaluated numerically either with a transformed Gauss–Legendre scheme⁴² or with a Gauss–Chebyshev quadrature³⁶. In the present study we have employed the latter approach with a grid of 10 imaginary frequencies³⁶.

Components of the frequency dependent polarizabilities

$$\alpha_{ij}(\mathbf{i}\omega) = \frac{2}{\hbar} \sum_{n \neq 0} \frac{\omega_{0n} \langle \Psi_0^{(0)} | \hat{\mu}_i | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{\mu}_j | \Psi_0^{(0)} \rangle}{\omega_{0n}^2 - \omega^2} \quad (18)$$

where $\hbar\omega_{0n} = E_n^{(0)} - E_0^{(0)}$ is the excitation energy from state $|\Psi_0^{(0)}\rangle$ to $|\Psi_n^{(0)}\rangle$ and $\hat{\mu}_i$ the i -th cartesian component of the electric dipole moment operator, could in principle also for imaginary frequencies be obtained from linear response functions or polarization propagators

$$\alpha_{ij}(\omega) = -\langle\langle \hat{\mu}_i ; \hat{\mu}_j \rangle\rangle_{\omega} \quad (19)$$

using complex arithmetic. However, for multiconfigurational linear response functions^{9,11} or polarization propagators based on Møller–Plesset perturbation theory^{9,43,44} this can be avoided by a moment expansion of the linear response function^{15–17} which leads to a set of pseudostates which can be used to calculate the polarizability for the imaginary frequencies according to Eq. (18) as described elsewhere^{17,33}.

Alternatively one can make use of the fact, that the frequency dependence of the polarizability can be expressed in terms of dipole oscillator strength sum rules¹⁹,

$$S_{ij}(\mathbf{k}) = \frac{2}{\hbar} \sum_{n \neq 0} \omega_{0n}^{k+1} \langle \Psi_0^{(0)} | \hat{\mu}_i | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{\mu}_j | \Psi_0^{(0)} \rangle \quad (20)$$

in the following form

$$\alpha_{ij}(\omega) = \sum_{k=0}^{\infty} S_{ij}(-2k-2) \omega^{2k} \quad (21)$$

where $S(-2)_{ij}$ are components of the static polarizability α_{ij} and the higher negative even sum rules determine thus the frequency dependence of the polarizability. This expansion, however, converges only for frequencies below the first excitation energy, i.e. $\hbar\omega < \min\{E_n^{(0)} - E_0^{(0)}\}$. Nevertheless the expansion can be extended beyond this convergence radius and in particular into the complex plane by using well known analytical continuation techniques based on Padé approximants $[n, m]_{\alpha}$ to the frequency dependent polarizability α ^{45,46} as given in Eq. (21). In particular the $[n, n-1]_{\alpha}$ Padé approximant to $\alpha(i\omega)$ expressed by the sum rules, Eq. (21), can be used as lower bound⁴⁶.

$$\alpha_{ij}(i\omega) \geq [n, n-1]_{\alpha} \quad (22)$$

An upper bound⁴⁶ can be obtained via the same type of Padé approximant $[n, n-1]$ but now to $S_{ij}(0) - \omega^2\alpha(i\omega)$ instead of to $\alpha(i\omega)$. This approximant is usually denoted as $[n, n-1]_{\beta}$. The upper bound to $\alpha(i\omega)$ is then given as

$$\alpha_{ij}(i\omega) \leq \frac{S_{ij}(0) - [n, n-1]_{\beta}}{\omega^2}. \quad (23)$$

A variety of approximate linear response or polarization propagator methods have been derived¹⁰. The simplest response functions is based on a self-consistent-field (SCF) reference wavefunction¹¹. This is equivalent to the random phase approximation^{47,48} or time dependent Hartree-Fock^{49,50}. In SOPPA^{43,44} a Møller-Plesset perturbation theory expansion of the wave function⁵¹ is employed together with single and double excitation and de-

excitation operators. All terms involving only single (de-)excitation operators are then evaluated to second order in Møller–Plesset perturbation theory, whereas terms involving single and double (de-)excitation operators are evaluated to first order and pure double (de-)excitation terms only to zeroth order. With this definition the SOPPA method gives single excitation dominated excitation energies and transition moments correct to second order⁵², whereas response functions like the frequency dependent polarizability are correct through second order⁴³, meaning that in addition to all second-order terms also some higher-order terms are included. The SOPPA response function, however, is not the response of a second-order wavefunction⁵³.

In the SOPPA(CCSD) method⁵⁴ the Møller–Plesset correlation coefficients are replaced in all SOPPA matrix elements by the corresponding coupled cluster singles and doubles amplitudes in contrast to the earlier CCSDPPA method⁵⁵, where only some of the Møller–Plesset correlation coefficients were replaced. Although SOPPA(CCSD) is based on a CCSD wavefunction, it is still only correct through second order and not the linear response of a CCSD wavefunction. Since the MP2 correlation coefficients are the result of the first iteration for the CCSD amplitudes, the CCSD amplitudes give a more accurate description of the connected doubles contribution to electron correlation. Thus it is often found that SOPPA(CCSD) give a better description of electron correlation than SOPPA^{27,56–58}.

In the CCSD linear response function^{12,59–61}, which is the proper response of a time-dependent CCSD wavefunction, the singles dominated excitations and transition moments are still only correct to second order but the doubles dominated excitations are now correct to first order. The response functions like the frequency dependent polarizability are, however, still only correct through second order⁶².

The CC2 linear response function⁶², finally, is an approximation to the CCSD response function in the sense that the doubles equations in (i) the non-linear ground state amplitude equations and (ii) the linear response equations are approximated by the first order terms only, whereas the singles equations are kept unchanged. The equations for the ground state doubles amplitudes in CC2 are then almost equal to the MP2 expressions for the doubles correlation coefficients with the important modification that the two electron integrals are transformed with single excitation cluster operator T_1 . Like in SOPPA, the singles dominated CC2 excitation energies are correct to second order and the doubles dominated excitations are only correct to zeroth order. However, contrary to SOPPA the transition moments

and response functions like the frequency dependent polarizability are only correct through first order⁶².

COMPUTATIONAL DETAILS

All calculations of frequency dependent polarizabilities for imaginary frequencies and sum rules were carried out with the Dalton 2.0 program^{17,18,30,37,54,61,63,64}. The calculation of the C_6 dispersion coefficients via a Gauss–Chebyshev quadrature with 10 grid points, as described in reference³⁶, and angular momentum re-coupling techniques were done with the DISPER program of Wormer^{15,38}.

Experimental equilibrium geometries⁶⁵, $R_{\text{eq}} = 0.09169$ nm (HF), 0.12746 nm (HCl), 0.14145 nm (HBr) and 0.16090 nm (HI) were used in the single point calculations. For the calculation of the C_6 coefficients surfaces we have varied the two bond lengths by ± 0.02 nm.

In order to allow for a meaningful comparison with experimental data we have used these polarizability, sum rule and C_6 coefficient radial functions and calculated the corresponding values of these properties in the vibrational ground state $|\Theta_{v=0,J}(R)\rangle$, e.g.

$$a_{ij}^{v=0} = \langle \Theta_{v=0,J} | a_{ij}(R) | \Theta_{v=0,J} \rangle. \quad (24)$$

For diatomic molecules, the vibrational wavefunctions can be obtained numerically by the Cooley–Numerov technique⁶⁶ as solution of the one-dimensional Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dR^2} + \frac{J(J+1)}{R^2} \right) + \frac{e^2}{4\pi\epsilon_0} \frac{Z_K Z_L}{R} + E_0(R) \right\} |\Theta_{v,J}\rangle = E_{v,J} |\Theta_{v,J}\rangle \quad (25)$$

where J is the rotational quantum number and $E_0(R)$ is the electronic energy radial function. The vibrational averaging in Eq. (24) can then be carried out numerically using the pointwise calculated property radial functions. As electronic energy radial functions we have employed a RKR potential curve⁶⁷ for HF, a Morse potential fitted to experimental data for HCl⁶⁸, an *ab initio* potential curve for HBr⁶⁹, and for HI a curve fitted to experimental frequency data⁷⁰.

The convergence of the polarizabilities and C_6 coefficients with increasing cardinal number X and level n of augmentation with extra diffuse functions of the n -aug-cc-pVXZ series of basis sets⁷¹ has been investigated

thoroughly in our previous study³³. Based on the results of this study we employ in the present study the d-aug-cc-pVQZ basis set for HF, HCl and HBr. For HI we use the Stuttgart–Dresden–Bonn (SDB) energy-consistent relativistic effective large-core pseudopotential⁷² in combination with the augmented correlation consistent basis sets, SDB-aug-cc-pVQZ, of Martin and Sundermann⁷³. The additional functions for the double augmented basis set were generated in the usual way³³, i.e. the exponent of the most diffuse function was divided by the ratio between the exponents of the two most diffuse functions. This leads to the following exponents: $\zeta_s = 0.020387$, $\zeta_p = 0.013337$, $\zeta_d = 0.029982$, $\zeta_f = 0.083274$ and $\zeta_g = 0.124319$.

RESULTS AND DISCUSSION

Dipole Oscillator Strength Sum Rules

In Table I the results for the static average dipole polarizabilities $S(-2)$ and the frequency dependence, $S(-4)$ and $S(-6)$ are presented. Using the difference between the SCF and CCSD results as an estimate for the correlation contribution, we can see that the importance of electron correlation increases strongly from the $S(-2)$ to the $S(-6)$ sum rules but decreases strongly from HF to HI. For HF the correlation contributions relative to the SCF result are 14, 41 and 79% for $S(-2)$, $S(-4)$ and $S(-6)$, whereas for HI the changes are only 2, 3 and 6%. Taking the CCSD results now as reference, we find a very good agreement between the SOPPA(CCSD) and CCSD results for $S(-2)$. The difference is on average only 1%. The pure SOPPA results differ somewhat more with an average deviation of 2% and CC2 finally shows the largest deviation with 3% on average. This implies that for the static polarizability the usage of Coupled Cluster amplitudes in the SOPPA(CCSD) method represents an improvement over SOPPA, as has previously been observed for the indirect nuclear spin-spin coupling constants and rotational g -factors^{27,56–58}. Secondly SOPPA gives results in better agreement with CCSD than CC2. A similar better performance of SOPPA than CC2 for static properties has also already previously been observed in the calculation of nuclear magnetic shielding constants^{57,74} and optical rotary powers⁵⁸. However, for the frequency dependence, $S(-4)$ and $S(-6)$ the situation is reversed. SOPPA(CCSD) gives still the best agreement with the CCSD results but CC2 shows now a smaller deviation from the CCSD results than SOPPA.

Turning now to vibrationally averaged values, we can see that there is essentially no difference between the zero point vibrational corrections

TABLE I
Dipole oscillator strength sum rules (in a.u.) for HX molecules (X = F, Cl, Br, I) at experimental equilibrium geometries (R_{eq}) and including the zero point vibrational averaging correction ($\nu = 0$)

Molecule	Method	S(-2)		S(-4)		S(-6)	
		R_{eq}	$\nu = 0$	R_{eq}	$\nu = 0$	R_{eq}	$\nu = 0$
HF	SCF	4.91		8.62		24.76	
	SOPPA	5.88	6.00	14.58	15.44	62.37	69.15
	SOPPA(CCSD)	5.68	5.79	13.83	14.63	58.87	65.12
	CC2	5.98	6.11	14.53	15.34	59.91	65.88
	CCSD	5.58	5.69	12.13	12.77	44.42	48.66
	DOSD ^a		5.60		14.40		68.96
HCl	SCF	16.75		60.62		301.9	
	SOPPA	17.54	17.71	70.19	71.81	395.8	411.3
	SOPPA(CCSD)	17.29	17.45	68.14	69.66	377.0	391.1
	CC2	17.72	17.89	68.95	70.48	378.5	392.0
	CCSD	17.35	17.51	66.29	67.67	358.2	370.4
	DOSD ^a		17.39		67.12		389.3
	Expt. ^b		17.42		67.67		370.4
HBr	SCF	23.20		104.7		646.6	
	SOPPA	24.21	24.36	118.9	120.7	813.1	834.0
	SOPPA(CCSD)	23.87	24.00	116.2	117.8	785.2	804.1
	CC2	24.31	24.47	115.5	117.2	764.5	782.3
	CCSD	23.83	23.97	111.5	113.0	730.8	746.9
	DOSD ^a		23.74		116.9		827.9
	Expt. ^b		23.73		115.1		801.9
HI	SCF	35.30		216.4		1789.	
	SOPPA	36.32	36.55	234.5	237.8	2041.	2087.
	SOPPA(CCSD)	35.72	35.93	227.3	230.3	1943.	1982.
	CC2	36.60	36.84	228.1	231.1	1925.	1962.
	CCSD	35.94	36.15	223.2	225.8	1893.	1926.
	Expt. ^b		35.33		225.2		1959.

^a Empirical dipole oscillator strength distribution values from ref.⁷⁵; ^b experimental values from ref.⁷⁶

(ZPVCs) obtained with the different response methods. This is partially due to the fact that we have employed the same potential energy radial functions for all methods, but must also imply that the property surfaces obtained with the different response function methods are essentially parallel around the equilibrium geometry. The importance of the zero point vibrational corrections (ZPVC) diminishes from HF to HI. The ZPVCs to $S(-2)$, i.e. the static polarizability, are thus in the order of 2% for HF and smaller for the other molecules. Going to the higher sum rules $S(-4)$ and $S(-6)$ the ZPVCs increase by roughly a factor of two each time.

Compared with the experimental based dipole oscillator strength distribution (DOSD) values by Kumar and Meath⁷⁵ or the experimental data compiled by Olney et al.⁷⁶ we find very nice agreement of our CCSD and even SOPPA(CCSD) results (equilibrium geometry as well as vibrational ground state values) with the DOSD values for the static polarizability (averaged deviation less than 1%), followed by SOPPA and then CC2. For the frequency dependence, the $S(-4)$ and $S(-6)$ sum rules, the agreement is less satisfying despite the fact that vibrationally averaging improves the agreement. Actually, some of the second order methods seem to give better agreement with the experimental values than CCSD. However, we observe also that for HCl and HBr the experimental and DOSD values differ almost as much from each other as the CCSD results from them, which makes the comparison somewhat vague. Nevertheless there is clearly room for improvement and it would be interesting to see how large triples corrections to these properties might be.

We can also compare our results for the static dipole polarisability of HF with results from previous CC2 calculations (5.72 a.u. using aug-cc-pVTZ⁷⁷, 5.27 a.u. using aug-cc-pVDZ⁷⁸, 5.47 a.u. using a large uncontracted basis set⁷⁹, 6.04 a.u. using t-aug-cc-pVTZ⁸⁰) and with a selection of the previous CCSD calculations (5.86 a.u. using Sadlej's polarized VTZ basis set⁶⁰, 5.38 a.u. using aug-cc-pVTZ⁷⁷, 4.99 a.u. using aug-cc-pVDZ⁷⁸, 5.64 a.u. using t-aug-cc-pVTZ⁸⁰, 5.09 a.u. using aug-cc-pVDZ³¹). Considering that the basis sets in these previous studies apart from the study by Maroulis⁷⁹ are of only polarized valence double or triple zeta quality one can say that the agreement is good.

For HCl we are only aware of four CCSD calculations: 17.53 a.u. using Sadlej's polarized VTZ basis set⁶⁰, 17.23 or 17.32 a.u. using basis sets of polarized VQZ quality⁸¹, 17.29 a.u. using the d-aug-cc-pV5Z basis set⁸² and 17.2 a.u. using the aug-cc-pVQZ basis set and an orbital relaxed version of CCSD³², which are all very close to our result.

Padé Approximants

In Table II the dependence of the homomolecular C_6^{000} coefficients on the order n of the lower, Eq. (22), and upper bound, Eq. (23), Padé approximants is shown for the CC2 and CCSD calculations. At order $n = 7$ the gap between the upper and lower bound is less than or equal 0.5% for all molecules with the exception of the CCSD results for HF–HF where it amounts to 0.8%. We will therefore use in the following the $n = 7$ lower bound as our result for the C_6 coefficients. One should note, however, that a smooth convergence of the results with the order n is only obtained if the calculations are carried out with a very strict convergence threshold.

Dispersion Coefficients

We can thus turn our attention to the C_6 dispersion coefficients in Tables III and IV. Using the difference between the SCF and CCSD results as an estimate for the correlation contribution, we can see that the relative importance of electron correlation for the isotropic C_6 coefficient decreases again from HF (17%) to HI (3%) similar to the polarizabilities in Table I. For the anisotropic coefficients, on the other hand, no clear trend is observed. Taking now again the CCSD results as reference we observe that in case of the isotropic C_6^{000} coefficients the SOPPA(CCSD) results are always smaller and on average 2% or 3.7 a.u. below the CCSD results. The SOPPA C_6^{000} coefficients are either essentially equal to or larger than the CCSD values and on average 2% or 1.2 a.u. above the CCSD results. The SOPPA and SOPPA(CCSD) values thus bracket the CCSD results. It is interesting to note that for the dimers involving HF the SOPPA(CCSD) results are closer to the C_6^{000} coefficients than the SOPPA values, whereas for all the other dimers SOPPA gives actually the results which are closest to the CCSD values. CC2, on the other hand predicts always coefficients which are significantly larger than the CCSD values (on average 5% or 6 a.u.). Furthermore CC2 shows always larger deviations than the two perturbation theory methods.

For the anisotropic coefficients, C_6^{022} , C_6^{202} and C_6^{224} , similar trends are observed with SOPPA(CCSD) always underestimating and CC2 always overestimating the CCSD results, whereas SOPPA predicts with a few exceptions for the HF containing dimers also mostly values below the CCSD results. For the non-HF containing dimers SOPPA again outperforms CC2 as well as SOPPA(CCSD).

Compared with the DOSD results by Kumar and Meath⁷⁵ we find that CC2 as the only method consistently predicts to large values with a average

TABLE II
Dependence of the C_6^{000} coefficients (in a.u.) on the order n of the Padé approximants in CC2 and CCSD calculations

Method	Padé n	HF-HF		HCl-HCl		HBr-HBr		HI-HI		
		lower	upper	lower	upper	lower	upper	lower	upper	
CC2	3	20.753	22.131	131.81	137.41	224.43	237.99	439.96	446.18	
	4	20.995	21.594	132.44	134.61	225.76	231.13	442.24	444.33	
	5	21.117	21.419	132.66	133.64	226.35	228.80	444.03	443.75	
	6	21.181	21.351	132.76	133.15	226.65	227.70	443.17	443.47	
	7	21.190	21.305	132.84	133.06	226.77	227.51	443.23	443.29	
	CCSD	3	19.003	20.228	127.61	133.15	217.60	231.18	426.19	432.59
		4	19.217	19.754	128.24	130.41	218.94	224.38	428.55	430.71
5		19.332	19.602	128.46	129.43	219.54	221.99	429.38	430.11	
6		19.390	19.538	128.56	128.95	219.85	220.87	429.53	429.82	
7		19.328	19.489	128.63	128.84	220.07	220.68	429.56	429.75	

TABLE III
 C_6 coefficients (in a.u.) for the homomolecular HX dimers (X = F, Cl, Br, I) at experimental equilibrium geometries (R_{eq}) and including the zero point vibrational averaging correction ($\nu = 0$)

Dimer	Method	C_6^{000}		C_6^{022}		C_6^{224}	
		R_{eq}	$\nu = 0$	R_{eq}	$\nu = 0$	R_{eq}	$\nu = 0$
HF-HF	SCF	16.54		2.65		1.17	
	SOPPA ^a	20.44	20.96	2.94	3.25	1.14	1.38
	SOPPA(CCSD) ^a	19.32	19.78	2.78	3.07	1.09	1.31
	CC2	21.19	21.53	2.95	3.31	1.10	1.35
	CCSD	19.33	19.67	2.81	3.15	1.10	1.34
	DOSD ^b		19.00				
HCl-HCl	SCF	122.2		10.59		2.43	
	SOPPA ^a	128.4	130.0	10.70	11.86	2.37	2.88
	SOPPA(CCSD) ^a	125.6	126.6	9.79	10.93	2.04	2.49
	CC2	132.8	134.3	11.75	13.10	2.74	3.35
	CCSD	128.6	129.9	11.03	12.28	2.50	3.04
	DOSD ^b		130.4				
HBr-HBr	SCF	211.1		17.63		3.90	
	SOPPA ^a	221.5	223.3	17.90	19.15	3.85	4.37
	SOPPA(CCSD) ^a	216.2	217.7	15.98	17.04	3.17	3.57
	CC2	226.8	227.7	19.80	21.36	4.55	5.23
	CCSD	220.1	220.7	18.37	19.87	4.05	4.68
	DOSD ^b		216.6				
HI-HI	SCF	415.7		29.77		5.72	
	SOPPA ^a	428.5	432.3	30.49	33.38	5.81	6.84
	SOPPA(CCSD) ^a	417.2	419.3	25.80	28.51	4.31	5.12
	CC2	443.2	446.4	34.09	37.70	7.01	8.38
	CCSD	429.6	432.2	31.19	34.35	6.10	7.23

^a Equilibrium geometry data from ref.³³, ^b empirical dipole oscillator strength distribution values from ref.⁷⁵

TABLE IV
 C_6 dispersion coefficients (in a.u.) for the heteromolecular dimers HX–HY (X, Y = F, Cl, Br, I) at experimental equilibrium geometries

	Method	C_6^{000}	C_6^{022}	C_6^{202}	C_6^{224}
HF–HCl	SOPPA	50.33	4.09	7.48	1.63
	SOPPA(CCSD)	48.33	3.67	7.23	1.48
	CC2	51.97	4.57	7.55	1.74
	CCSD	48.86	4.15	7.34	1.65
	DOSD ^a	48.85			
HF–HBr	SOPPA	65.53	5.18	9.79	2.07
	SOPPA(CCSD)	62.85	4.53	9.45	1.83
	CC2	67.47	5.69	9.82	2.19
	CCSD	63.28	5.30	9.56	2.10
	DOSD ^a	62.45			
HF–HI	SOPPA	89.26	6.29	13.48	2.52
	SOPPA(CCSD)	85.50	5.23	13.02	2.12
	CC2	92.03	7.70	13.48	2.89
	CCSD	86.74	6.46	13.22	2.57
HCl–HBr	SOPPA	168.5	13.59	14.06	3.02
	SOPPA(CCSD)	164.6	12.15	12.86	2.54
	CC2	173.3	14.89	15.41	3.50
	CCSD	167.7	14.13	14.45	3.20
	DOSD ^a	167.8			
HCl–HI	SOPPA	232.8	16.59	19.54	3.70
	SOPPA(CCSD)	227.2	14.08	17.86	2.96
	CC2	240.0	19.54	21.40	4.51
	CCSD	232.2	17.23	20.10	3.92
HBr–HI	SOPPA	307.1	21.86	24.92	4.73
	SOPPA(CCSD)	299.4	18.53	22.24	3.69
	CC2	315.2	25.49	27.23	5.70
	CCSD	306.1	22.52	25.71	5.01

^a Empirical dipole oscillator strength distribution values from ref.⁷⁵

deviation of 4% or 2.8 a.u., whereas the results of the other methods are scattered around the empirical values. For CCSD, SOPPA(CCSD) and SOPPA the average absolute deviations are thus 1% or 0.7 a.u., 1% or 1.0 a.u. and 2% or 1.4 a.u.

We are only aware of one earlier coupled cluster calculation³² of the C_6^0 dispersion coefficient of HCl–HCl or any other hydrogen-halide dimer. In this paper an isotropic C_6^{000} coefficient of 125.3 a.u. at the relaxed CCSD level was reported for HCl–HCl employing the aug-cc-pVQZ basis set. Also this result is in close agreement with our unrelaxed CCSD result in Table III.

Dispersion Coefficient Surfaces

The dispersion coefficient surfaces, i.e. the $C_6^{L_A L_B L}(\Delta R_{\text{HX}}, \Delta R_{\text{HY}})$, coefficients of a dimer HX–HY as function of the deviation of the two intramolecular bond lengths ΔR_{HX} and ΔR_{HY} from their equilibrium values, are essentially flat as illustrated in Fig. 1 for HF–HF and HF–HCl.

We have therefore fitted them by using the Levenberg–Marquart method to a bilinear form

$$C_6^{L_A L_B L}(\Delta R_{\text{HX}}, \Delta R_{\text{HY}}) = C_6^{L_A L_B L} + \alpha_{\text{HX}}^{L_A L_B L} \Delta R_{\text{HX}} + \alpha_{\text{HY}}^{L_A L_B L} \Delta R_{\text{HY}}. \quad (26)$$

In Table V, we report the values of the linear fit parameters, α_{HX}^{000} and α_{HY}^{000} of the isotropic component C_6^{000} for all dimers and methods.

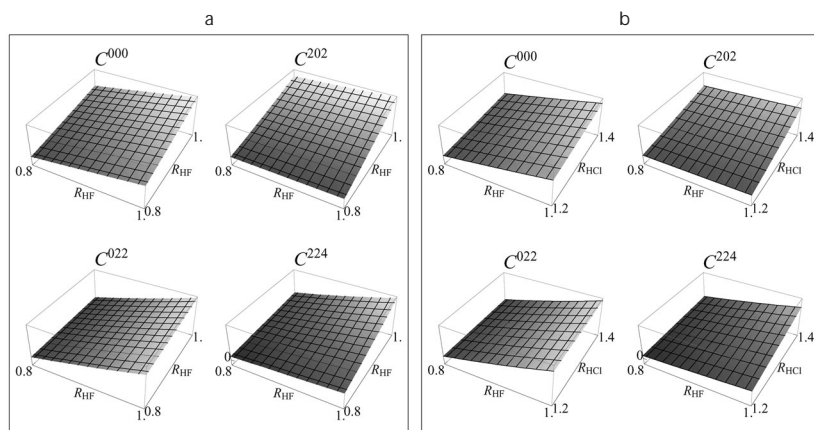


FIG. 1
Dispersion coefficient surfaces for HF–HF (a) and HF–HCl (b) obtained at the CCSD level

TABLE V
Coefficients (in a.u./Å) in the bilinear fit of the C_6 dispersion coefficients surfaces

	SOPPA	SOPPA(CCSD)	CC2	CCSD				
	C_6^{000}	C_6^{000}	C_6^{000}	C_6^{202}				
HF-HF	a_{HF}	13.74	12.93	14.40	12.25	1.47	12.49	4.28
HF-HCl	a_{HF}	37.36	35.63	39.21	34.41	2.87	35.21	8.59
	a_{HCl}	16.58	15.52	17.76	15.75	19.74	2.26	6.86
HF-HBr	a_{HF}	49.77	47.24	52.02	45.64	4.30	46.66	11.84
	a_{HBr}	17.92	16.68	19.31	16.92	21.80	3.05	7.88
HF-HI	a_{HF}	69.13	65.65	72.63	63.68	4.84	65.11	13.29
	a_{HI}	18.11	16.25	19.70	17.04	23.09	2.72	8.07
HCl-HCl	a_{HCl}	46.91	43.67	50.12	45.98	4.81	58.28	14.74
HCl-HBr	a_{HCl}	62.62	58.06	66.51	61.07	6.30	77.78	20.23
	a_{HBr}	50.98	46.50	54.71	49.65	64.73	6.34	16.48
HCl-HI	a_{HCl}	88.21	81.69	93.99	86.28	6.99	110.4	22.36
	a_{HI}	52.25	46.31	56.52	50.60	69.49	5.89	17.61
HBr-HBr	a_{HBr}	67.65	61.46	72.10	65.53	86.54	7.22	22.23
HBr-HI	a_{HBr}	95.81	86.87	102.43	93.08	8.09	123.5	24.70
	a_{HI}	69.87	61.70	75.09	67.30	93.27	7.22	24.19
HI-HI	a_{HI}	99.26	87.52	106.89	95.81	8.01	133.5	26.56

In order to allow for the construction of a fully dimensional R^6 part of the dispersion PESs, according to Eqs (1)–(3), we present in Table V also the fit parameters for all independent C_6 dispersion coefficients, C_6^{000} , C_6^{022} , C_6^{202} and C_6^{224} . Only the fits for the surfaces based on the CCSD results are given in Table V, because the overall shape of the surfaces obtained with the other methods, SOPPA, SOPPA(CCSD) and CC2, are quite similar to the CCSD surfaces.

In Table III, we present also values of the C_6 dispersion coefficients for the two molecules in their vibrational ground states. The changes in C_6^{000} are rather small – at most 2.5% for HF and on average only 1% similar to the static polarizability. The changes in the anisotropic coefficients are in absolute values even smaller.

SUMMARY

We have carried out correlated linear response calculations of the dipole oscillator strength sum rules of the hydrogen halides HX (with X = F, Cl, Br and I) and the C_6 dispersion coefficient for all pairs of interacting HX molecules. The two Møller–Plesset perturbation theory based methods SOPPA and SOPPA(CCSD) as well as two coupled cluster theory methods, CC2 and CCSD, were employed.

For the static polarizabilities we can conclude that SOPPA(CCSD) predicts values which are in closer agreement with the CCSD results than the SOPPA and CC2 results. Secondly SOPPA gives results in better agreement with CCSD than CC2. However, for the frequency dependence, the $S(-4)$ and $S(-6)$ sum rules, the situation is somewhat reversed. SOPPA(CCSD) gives still the best agreement with the CCSD results although with significantly larger differences than for the static polarizability. Furthermore the CC2 values differ now less from the CCSD results than SOPPA values. Zero point vibrational corrections to the static polarizability and sum rules changes the results by at most 3% with the exception of $S(-4)$ and $S(-6)$ in HF, where the correction can amount to 10%.

For the C_6 dispersion coefficients the picture is less clear. The SOPPA(CCSD) results for the isotropic and anisotropic coefficients are always smaller than the CCSD results, whereas CC2 clearly overestimates all dispersion coefficients. The SOPPA results, on the other hand, are depending on the dimer and coefficient larger or smaller than the CCSD values. For the dimers containing HF, the isotropic SOPPA(CCSD) C_6 coefficients are always closest to the CCSD results, whereas for the other dimers the SOPPA results for all coefficients are closest to the CCSD values. Overall, at

least one of the two Møller–Plesset perturbation theory based methods, SOPPA or SOPPA(CCSD), gives always a better agreement with CCSD than CC2 for the C_6 dispersion coefficients of the hydrogen halides.

Finally the variation of the dispersion coefficients with the two intramolecular distances is in the range close to the equilibrium structures essentially linear.

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