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Electric properties of hydrogen iodide: Reexamination of correlation and relativistic effects

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Abstract. The electric dipole moment and the static dipole polarizability of the hydrogen iodide molecule were studied using sophisticated correlated and relativistic methods. Both scalar and spin–orbit relativistic effects were carefully accounted for. We conclude that the large differences between the theoretical and experimental dipole moment, the dipole moment derivative and the polarizability cannot be reconciled by improved account of electron correlation and relativistic effects. The most striking difference between theory and experiment is observed for the polarizability anisotropy. We believe that experimental data, namely the experimental dipole moment (the most recent value is 0.176 au as compared to our best theoretical estimate, 0.154 ± 0.003 au), the parallel polarizability (44.4 and 38.47 ± 0.05 au) and the anisotropy (11.4 and 2.33 ± 0.05 au) must be inaccurate. Experimental and theoretical perpendicular polarizability components (33.0 and 36.14 ± 0.05 au,) and the mean polarizability (36.8 and 36.92 ± 0.05 au) agree better. Our vibrationally corrected relativistic CCSD(T) results represent the most sophisticated predictions of electric properties of HI obtained so far.

Keywords: Hydrogen iodide – Dipole moment – Dipole polarizability – Scalar relativistic effects – Spin-orbit relativistic effects

1 Introduction

The aim of this paper is to calculate electric properties of the hydrogen iodide molecule (X $^1\Sigma^+$), namely the dipole moment, both perpendicular and parallel components of the static dipole polarizability, and to analyze discrepancies between theoretical and experimental data. For this purpose, electron correlation effects as well as scalar and spin–orbit (SO) relativistic effects were thoroughly reexamined.

The first dielectric measurement of the dipole moment of HI was reported in 1924 by Zahn [1]. Experimental observations based on the Stark effect [2, 3] appeared in the second half of the twentieth century. Sophisticated theoretical calculations including electron correlation effects have been published in the last decade [4, 5, 6, 7]. More recent papers also treated relativistic effects that are expected to be important in compounds containing a relatively heavy atom [6, 8, 9, 10, 11, 12, 13].

Experimental values of the electric polarizability as published in standard reference books [14] result from the old work of Denbigh [15]. Theoretical results are presented in papers by Kellö and Sadlej [4, 5], and in the recent studies by Maroulis [7] and Norman et al. [13].

The current study was motivated by discrepancies between calculated and experimental values of the dipole moment and polarizabilities of the HI molecule. This is the heaviest diatomic hydrogen-halide compound for which these electric properties are experimentally known. A detailed discussion of this discrepancy was presented by Maroulis [7]. He suggested a more rigorous treatment of both scalar and SO relativistic effects combined with a highly sophisticated consideration of electron correlation. A few years ago, some of these properties, like the dipole moment [4, 5], were only considered using less sophisticated relativistic methods, like the mass–velocity–Darwin treatment. When this

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work was almost completed a very recent paper by Norman et al. [13] appeared. Relativistic effects are treated in this paper in great detail at the Hartree–Fock or the Dirac–Hartree–Fock level neglecting electron correlation. These results were helpful for our analysis. To reach accurate values one needs, however, to also consider basis set and electron correlation issues on the same footing along with scalar and SO relativistic effects. Thus, we hoped that our one- and two-component Douglas–Kroll–Hess [16, 17, 18] and more demanding four-spinor [19] investigation of relativistic effects combined with the coupled–cluster (CC) [20, 21, 22] and variational configuration interaction (CI) [23] treatment of the electron correlation should be capable of sheding light on the previously mentioned discrepancies. Of course, we will pay sufficient attention to the basis set effect issue, even if this point was analyzed carefully enough by Maroulis [7]. Finally, we compare our results with other reliable theoretical data.

2 Methods and computational details

The starting point in our calculations is a single-determinant Hartree–Fock self-consistent-field (SCF) wave function. Electron correlation is treated by second-order Møller–Plesset perturbation theory (MP2) and also by the CC method with iterative single and double excitations (CCSD) combined with the noniterative estimate of triple excitations using the converged single and double excitation amplitudes from CCSD, the CCSD(T) method [21].

Considering the relatively large nuclear charge of the iodine atom ($Z = 53$), the treatment of relativistic effects is necessary. Use of the Dirac–Coulomb–Breit Hamiltonian comprises the most rigorous treatment of relativity. However, four-component ab initio methods are computationally very demanding and thus we are restricted to relatively small basis sets and/or to a limited number of correlated electrons. Approximate one- or two-component methods are preferred instead, which are also known to describe valence properties with reasonable precision [24]. The Douglas–Kroll–Hess transformation of the Dirac–Coulomb–Breit Hamiltonian [16] is widely employed. It eliminates the positronic levels and leads to variationally stable scalar and spin–orbit terms. When including scalar relativistic effects, only modified one-electron atomic integrals are required. The corresponding two-electron corrections [17] do not contribute significantly here. Standard nonrelativistic quantum chemical codes are employed in that case. Relaxed scalar one-component molecular orbitals serve as a basis for subsequent correlated calculations. The estimation of the size of SO relativistic effects on the electric properties studied was one of our goals. This was achieved by four-component Dirac–Coulomb based methods, and by the so-called Douglas–Kroll–Hess mean-field SO approach [18].

All the basis sets utilized are summarized in Table 1 and are available upon request from the authors. In the present work we used five different basis sets:

1. Nonrelativistic contractions of Sadlej's polarized basis set [6.4/3.2] for hydrogen [25] and [19.15.12/11.9.6] for iodine [5] were used in the nonrelativistic calculations, while in Douglas–Kroll (DK) calculations we used the so-called no-pair contractions of these basis sets [27]. The acronym Pol is used here for both the nonrelativistic and DK contraction of these basis sets.
2. The acronym ExtPol was used for the basis set [8.4.1/5.2.1] for hydrogen and the [22.18.14.3/14.12.9.3] set for iodine. These sets are extensions of the Pol sets. In the hydrogen basis we added 2s1d functions with small exponents to the Pol set and similarly for iodine 3s3p2d1f functions to the HyPol set [26]. These additional diffuse functions were taken from Maroulis' basis sets [7]. The HyPol set was developed for calculations of hyperpolarizabilities and actually it is the Pol set extended by two f exponents while the two most diffuse d exponents are left uncontracted. As in item 1 the ExtPol sets were also used in the nonrelativistic or DK contractions depending on the type of calculations. The ExtPol basis sets were generated in order to mimic the previously used Maroulis basis sets [7].
3. The term unExtPol represents completely uncontracted ExtPol sets, (8.4.1) for hydrogen and (22.18.14.3) for iodine, respectively.
4. The term unPol222 represents the completely uncontracted Pol sets extended by 2d2f2g and 2f2g2h functions, resulting in the final (6.4.2.2.2) and (19.15.12.2.2.2) set for hydrogen and iodine, respectively. These were obtained by repeating the use of the two most diffuse p and d exponents of the hydrogen and iodine Pol basis set, respectively.
5. Contracted relativistic basis sets sp-apvtz for I (L:[22.18.13.2/8.9.5.2] S:[18.35.20.13.2/7.13.12.6.2]) and accpvtz for H (L:[6.3.2/4.3.2] S:[3.8.3.4/3.6.3.2] of Visscher et al. [28] were utilized in the correlated Dirac–Coulomb calculations. For these basis sets we use the acronym r-pvtz

The MOLCAS [29] program package was employed for the one-component CC calculations. The CI calculations were carried out with transformed molecular integrals and the corresponding SCF Molecular orbital vectors from the MOLCAS [29] package. The CI program LUCITA [30] was used for the spin-free scalar relativistic calculations, where nonrelativistic point group symmetry is conserved. The code employs the generalized active space concept [23], where the orbital space is subdivided into an arbitrary number of active spaces with predefined occupation constraints. In the present case, the atomic $4d$ shell of iodine forms the first space, and is either kept fully occupied (corresponding to CI with eight active elec-

Table 1. The used basis sets. For explanation see the text

Symbol	Atom	Primitives	Contraction	Type
Pol	H	(6s4p)	[3s2p]	Nonrelativisitic; DK
	I	(19s15p12d)	[11s9p6d]	Nonrelativisitic; DK
ExtPol	H	(8s4p1d)	[5s2p1d]	Nonrelativisitic; DK
	I	(22s18p14d3f)	[14s12p9d3f]	Nonrelativisitic; DK
unExtPol	H	(8s4p1d)	None	
	I	(22s18p14d3f)	None	
unPol222	H	(6s4p2d2f2g)	None	
	I	(19s15p12d2f2g2h)	None	
r-pvtz	H	L:(6.3.2) S:(3.8.3.4)	L:[4.3.2] S:[3.6.3.2]	Relativistic
	I	L:(22.18.13.2) S:(18.35.20.13.2)	L:[8.9.5.2] S:[7.13.12.6.2]	Relativistic

trons) or is opened for single and double excitations (18-electron CI). The second space, which contains the valence s and p functions, is opened for single and double excitations in all cases. Two further spaces comprise the virtual orbitals, split up for technical reasons.

The wave function is represented by a complete expansion within the given constraints, so no selection of determinants is carried out. It is justified to investigate the contribution of the SO coupling to the electric properties of the ground state in this approximation as this system is predominantly a closed-shell single-reference case. Thus, from a theoretical point of view, the interaction of excited triplet states with the singlet ground state can be best modeled by coupling single excitations with the double excitations in CISD required for the (leading) correlation contributions. It is clear that the inclusion of triple excitations from the valence shell leads to a strong increase of the computational demands, rendering an investigation including correlation of *d* electrons impossible with the current implementation. In the present study we determine the SO contribution with the extensive basis set ExtPol and correlating 18 electrons in the SO-CISD approximation as the highest-level approach.

For this, SO mean-field integrals were computed in the atomic approximation with the AMFI code of Schimmelpfennig [31]. These were used in the two-component CI program LUCIAREL [23], where identical active spaces with respect to LUCITA are constructed. Now, in contrast to the spin-free approach, all determinants with Kramers (time-reversal) spin projections differing from the reference state by two units (triplet configurations) were included in the trial wave function. This leads to larger expansion spaces compared to the spin-free case. The optimization was carried out fully variationally in configuration space in the totally symmetric boson irrep of the double group C_2^*.

The Dirac–Coulomb calculations were performed with the MOLFDIR [19] program suite, and the CC calculations in a four-spinor basis were carried out with the Kramers unrestricted code of Visscher et al. [22] connected to this package.

The electric properties were obtained using the finite-field method, applying weak homogeneous static electric fields of strengths of 0.0005 and 0.001 au (and 0.002 au in the SO-CI calculations) in one- and two-component calculations and orienting the molecule in the *z* direction. Possible inaccuracies in relativistic effects due to the change of the relativistic picture [32] are expected to be small for valence properties of HI [24]. In the four-component Dirac–Coulomb computations electric fields of strengths 0.0012 and 0.0006 were generated by four remote point charges [33] placed in *z* and *x* directions, respectively. A polynomial fit of the perturbed energies was used in the calculations of the dipole moments and polarizabilities.

Most calculations were performed at the experimental bond length, $R_e = 3.0409$ au [34]. Estimates of vibrational corrections to electric properties were based on a series of additional calculations for bond lengths in the interval of ±0.8 au around the equilibrium distance. T1 and T2 amplitudes were not larger than 0.013 and 0.086, respectively.

The atomic units used throughout the paper have conversion factors 1 au = 2.5418 D for the dipole moment and 1 au = 1.4818 $\times 10^{-25}$ cm^3 for the polarizability.

3 Results and discussion

One-component results for the dipole moment and the dipole polarizabilities using various basis sets are presented in Table 2. Additional results aimed at the analysis of the electron correlation effect dependence on the number of correlated electrons, i.e., effects of the

Table 2. Basis set effects on electric properties of HI. Nonrelativistic (NR), one component scalar-relativistic (SC) calculations with 18 correlated electrons. All calculations at the experimental HI bond length $R_e = 3.0409$ au. [34]. All values in atomic units

Method	Basis	μ		α_{zz}		α_{xx}		$\bar{\alpha}$	$\Delta\alpha$
		NR	SC	NR	SC	NR	SC	SC	SC
SCF	Pol	0.263	0.218	37.00	36.72	34.52	34.22	35.05	2.50
SCF	ExtPol	0.263	0.218	37.12	36.84	34.51	34.21	35.09	2.63
SCF	unPol222		0.217		36.87		34.21	35.10	2.66
MP2	Pol	0.231	0.189	37.38	37.09	34.95	34.81	35.57	2.28
MP2	ExtPol	0.226	0.185	37.92	37.62	35.64	35.48	36.19	2.14
MP2	unPol222		0.175		37.70		35.66	36.34	2.04
CCSD	Pol	0.218	0.175	37.29	36.97	35.05	34.88	35.58	2.09
CCSD	ExtPol	0.214	0.171	37.79	37.45	35.63	35.45	36.12	2.00
CCSD(T)	Pol	0.212	0.169	37.49	37.15	35.29	35.13	35.80	2.02
CCSD(T)	ExtPol	0.208	0.166	38.04	37.69	35.97	35.80	36.43	1.89
Other theoretical results									
SCF^a	[11.10.10/7.5.1]	0.263		37.12		34.44			
SCF^a	[11.10.10.3/7.5.1]	0.263		37.09		34.46			
SCF^a	[21.16.15.7/11.9.7.3]	0.256		37.12		34.50			
MP2^a	[11.10.10/7.5.1]	0.216		37.86		35.13			
MP2^a	[11.10.10.3/7.5.1]	0.217		37.91		35.60			
MP4^a	[11.10.10/7.5.1]	0.196		38.00		35.38			
CCSD(T)^a	[11.10.10/7.5.1]	0.197		37.98		35.41			
SCF^b	[11.9.6/3.2]	0.263	0.223	37.03	36.69	34.48	34.09	34.96	2.60
SCF^b	[11.9.6.2/3.2]	0.257	0.218	36.99	36.65	34.50	34.11	34.96	2.54
MP2^b	[11.9.6.2/3.2]	0.219		37.18		34.68			
MP4^b	[11.9.6.2/3.2]	0.199		37.34		35.02			
SCF^c	[23.18.9.2/7.4.2]	0.260	0.221	37.13	36.82				
MP4^c	[23.18.9.2/7.4.2]	0.192	0.152	38.15	37.84				

[a] Maroulis [7]

[b] First-order relativistic correction, Sadlej [5]

[c] First-order relativistic correction, valence correlation, Kellö and Sadlej [4]

core–valence correlation are presented in Table 3. Finally, the importance of SO effects is analyzed in Table 4.

3.1. Dipole moment

The first point to be discussed is the basis set effect. When we increase the basis set by adding diffuse functions and functions with higher angular momenta, a slight decrease of the dipole moment is observed (Tables 2, 4). This is especially significant at the correlated levels MP2, CCSD, CCSD(T), and (SO)CISD. Decontraction of the basis set leads to further lowering of μ (Table 3). We are unable to extrapolate our results to the basis set limit [36] with the basis sets used in this work, yet, the results are sufficiently transparent to demonstrate that the basis set issue at the scalar relativistic level is not the reason for the discrepancy between theoretical and experimental dipole moments from the Stark effect measurements [2]. This agrees with Maroulis' conclusions [7].

Table 3. Electric properties of HI: one component scalar-relativistic calculations. Effect of core–valence correlation. ExtPol basis sets, in *parentheses* results in unExtPol sets. All calculations at the experimental HI bond length $R_e = 3.0409$ au. [34]. All values in atomic units

Method	μ	α_{zz}	α_{xx}	$\bar{\alpha}$	$\Delta\alpha$
SCF	0.218 (0.217)	36.84 (36.86)	34.21 (34.23)	35.09 (35.11)	2.63 (2.63)
MP2-8	0.174 (0.167)	37.81 (37.80)	35.76 (35.74)	36.44 (36.43)	2.05 (2.06)
MP2-18	0.185 (0.178)	37.62 (37.60)	35.48 (35.46)	36.19 (36.17)	2.14 (2.14)
MP2-26	0.180 (0.173)	37.72 (37.70)	35.63 (35.61)	36.33 (36.31)	2.09 (2.09)
MP2-all	(0.174)	(37.70)	(35.59)	(36.29)	(2.11)
CCSD-8	0.166 (0.159)	37.59 (37.58)	35.71 (35.68)	36.34 (36.31)	1.88 (1.90)
CCSD-18	0.171 (0.165)	37.45 (37.44)	35.45 (35.42)	36.12 (36.09)	2.00 (2.02)
CCSD-26	0.168 (0.161)	37.55 (37.54)	35.59 (35.56)	36.24 (36.22)	1.96 (1.98)
CCSD(T)-8	0.160 (0.154)	37.83 (37.82)	36.04 (36.02)	36.64 (36.62)	1.79 (1.80)
CCSD(T)-18	0.166 (0.159)	37.69 (37.68)	35.80 (35.77)	36.43 (36.41)	1.89 (1.91)
CCSD(T)-26	0.162 (0.155)	37.79 (37.78)	35.95 (35.91)	36.56 (36.53)	1.84 (1.87)
Other theoretical results					
MP4[a]	0.157	37.34			
Our best theoretical values (vibrationally corrected values in parentheses)					
	0.153 (0.154)	37.82 (38.47)	35.89 (36.14)	36.53 (36.92)	1.93 (2.33)
Experiment	0.176[b] (0.15[e])	44.4[c]	33.0[c]	36.8[c], 36.71[d] 34.25-35.30[f]	11.4[c]

[a] Kellö and Sadlej [4] plus estimated core correlation contribution
[b] Stark effect measurement by Van Dijk and Dymanus [2]
[c] Denbigh [15]
[d] Dynamic value referenced by Hirschfelder et al. [35]
[e] Dielectric measurements by Zahn [1]
[f] Static value cited by Maroulis [7]

Table 4. Electric properties of HI. Comparison of scalar relativistic (SC) and spin-orbit (SO) values. All values in atomic units

Method	Basis	μ		α_{zz}		α_{xx}	
		SC	SO	SC	SO	SC	SO
SCF[a]	unExtPol	0.217	0.205	36.86	37.09	34.23	34.35
SCF[b]	r-pvtz		0.202		36.51		33.64
MP2[b]	r-pvtz		0.161		37.08		34.60
CCSD[b]	r-pvtz		0.154		36.79		
CCSD(T)[b]	r-pvtz		0.151		36.96		
(SO)CISD-8[c]	Pol	0.173	0.170	37.00	37.02		
(SO)CISD-18[c]	Pol	0.181	0.180	36.77	36.78		
(SO)CISD-8[c]	ExtPol	0.170	0.167	37.44	37.48		
(SO)CISD-18[c]	ExtPol	0.178	0.177	37.18	37.19		
Other theoretical results							
SCF[d]		0.210	0.197	37.45	37.69	34.31	34.43
RCI[e]			0.163				
(SO)CI[f]		0.189	0.181				
(SO)CI[g]		0.185	0.176				
ZORA[h]		0.17	0.16				
ACPF[i]		0.172	0.162				
CCSD(T)[i]		0.170	0.161				

[a] One-component scalar and four-component Dirac–Coulomb calculations
[b] Dirac–Coulomb calculations, eight correlated electrons
[c] One- and two-component configuration interaction calculations, 8 and 18 correlated electrons, respectively.
[d] Norman et al. [13]
[e] Chapman et al. [10]
[f] Chapman et al. [9, 10]
[g] Alekseyev et al. [12]
[h] Van Lenthe et al. [11]
[i] Dolg [6]

In general, electron correlation leads to a significant decrease of the dipole moment at both nonrelativistic and scalar relativistic levels (Table 2). Deeper analysis (Table 3) shows that the dipole moments oscillate slightly when one proceeds stepwise from correlating just eight valence electrons, adding 4*d* iodine electrons (a slight increase) and, continuing further, by taking deeper 4*s* and 4*p* shells into account (which leads back to a slight decrease). Comparing results with 26 and all electrons correlated at the MP2 level (Table 3) allows one to conclude that 26 correlated electrons is close to saturation. Thus, the number of correlated electrons does not affect the results significantly. The pattern is the same at MP2, CCSD, and CCSD(T) levels, however, the difference between MP2 and CCSD(T) dipole moments is typically about 0.018 au and is thus critical if accurate results have to be obtained. Triples contribute by about 0.005 au.

Scalar relativistic effects are important in HI. The reduction of the dipole moment (Table 2) is less than that due to electron correlation by about 0.04 au (26% of the final dipole moment), but is very important when theoretical and experimental values are compared. This was also found by Kellö and Sadlej [4] who calculated the relativistic correction perturbatively using mass–velocity and Darwin terms. The same ensues from the SCF results of Norman et al. [13].

SO relativistic effects, on the other hand, affect the dipole moment only slightly. Sophisticated SO-CI calculations give a negative contribution, −0.001 au or −0.003 au, depending on the number of correlated electrons (Table 4). We prefer data with eight correlated electrons over those with 18 electrons in our final estimates. The reason is the oscillatory character of the correlation contribution to the dipole moment (and in fact also to polarizabilities) when we increase the number of correlated electrons. Other calculations on the dipole moment of HI [6, 9, 10, 11, 12, 13] (Table 4) show a slightly larger SO contribution (up to −0.01 au). We note that the largest contribution is observed in the Dirac–Hartree–Fock calculations by Norman et al. [13]. We conclude that our SO-CI results are most appropriate for our purposes owing to the compatibility of the DK Hamiltonian and of the basis sets used in scalar relativistic calculations and also for considering electron correlation effects.

The bond-length dependence for the scalar relativistic CCSD(T) dipole moment calculated in ExtPol basis sets with 26 correlated electrons (in atomic units) is expressed as follows:

$$\mu(R) = 0.1620 - 0.0231(R - R_e) + 0.0339(R - R_e)^2 - 0.0201(R - R_e)^3 - 0.0006(R - R_e)^4 \ . \tag{1}$$

The dipole moment curves from scalar relativistic calculations are visualized in Fig. 1. The general shape is similar for SCF and CC calculations, whereas the MP2 curve differs significantly. Triples affect the shape of the dipole moment curve only slightly. Riris et al. [3] have experimentally measured the bond-length dependence of the dipole moment and obtained the first derivative $(\mathrm{d}\mu/\mathrm{d}R)_e = -0.0103$. From our dipole moment curves two dipole moment derivatives result, namely −0.0231 and −0.0218 for experimental and calculated values of R_e −3.0409 and 3.06 au, respectively. Clearly, this is in significant disagreement with the experimental value. Maroulis [7] obtained a similar theoretical value, $(\mathrm{d}\mu/\mathrm{d}R)_e = -0.0171$ from nonrelativistic calculations. We also fitted the fourth-order polynomials over other calculated dipole moment curves using the experimental R_e. The results of Chapman et al. [9] lead to the value of −0.0414 and −0.0518 from scalar and SO-CI calculations, respectively. On the other hand, Alekseyev et al. [12] presented $(\mathrm{d}\mu/\mathrm{d}R)_e = -0.0116$ and −0.0297 for spin-free and SO-corrected CI, respectively.

The zero-point vibrational (ZPV) correction obtained from the dipole moment curve given above is about

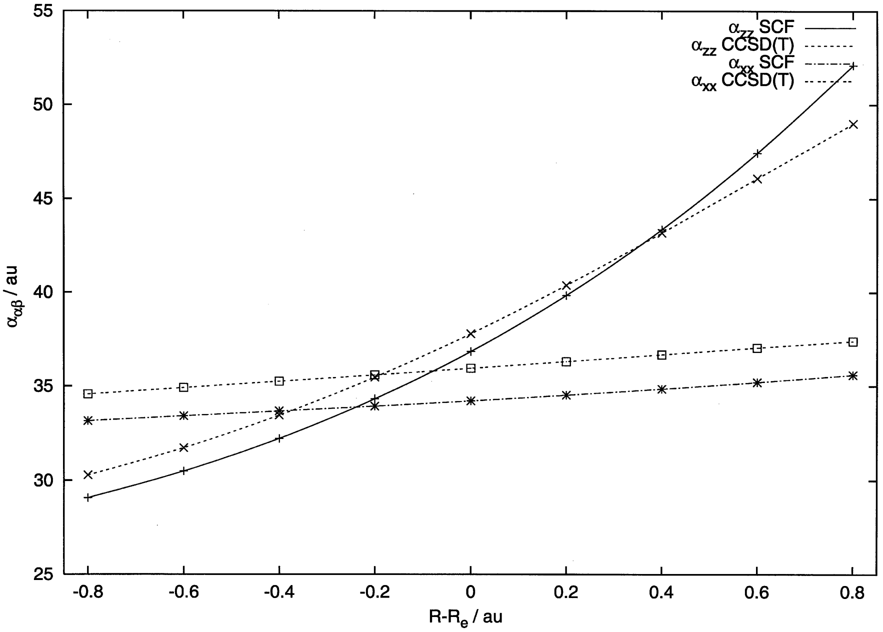

Fig. 1. Bond-length dependence of the dipole moment of the HI molecule. Scalar relativistic self-consistent-field (*SCF*), Second-order Møller–Plesset (*MP*2), Coupled cluster with iterative single and double excitations (*CCSD*) and CCSD combined with the noniterative estimate of triple excitations [*CCSD*(*T*)] calculations with 26 electrons correlated

+0.0007 au This is a negligible correction and was also found by Maroulis [7], who estimated it from the nonrelativistic CCSD(T) curve.

Using the calculated CCSD(T) dipole moment with the unExtPol basis set, 0.155 au, and correcting this value by core–valence correlation effects, ZPV, and the SO effect (0.001, 0.001, and −0.003, respectively, Tables 3, 4), we predict our best theoretical value for the dipole moment as 0.154 ± 0.003 au Alternatively, one could use the scalar CISD-8 value with the ExtPol basis set from Table 4, 0.167 au, as a basis for the final estimate. Its scalar counterpart (0.170 au) agrees to within 0.004 au with the scalar relativistic CCSD-8 value (0.166 au). Considering that the two methods in which triples are missing are conceptually different, this gives further confidence in our final estimate.

It remains unclear why our final estimate agrees reasonably with the old nonspectroscopic experiment of Zahn [1] and differs from the Stark effect measurements [2]. Our best theoretical estimate can also be supported by adding the SO contribution of −0.003 au to the best result of Kellö and Sadlej [4] (Table 3), which gives, again, a value of 0.154 au Also, when we add scalar and SO relativistic contributions of approximately −0.04 au to the best nonrelativistic result of Maroulis [7], 0.192 au, we again land near Zahn's experiment. And finally, the Dirac–Coulomb CCSD(T) value of 0.151 au with the relativistic r-pvtz basis set and eight electrons correlated gives us further confidence in our final prediction. A correction of this value by effects due to core-valence correlation would result in an increase by 0.001–0.002 au, again nearly resembling our best estimate.

3.2 Static dipole polarizabilities

The pattern of basis set effects within our rather limited selection of sets can be seen from the data in Table 2. Basis set enlargement from the Pol to the ExtPol basis leads to a slight and quite similar increase of both components of the polarizability and amounts to 0.54 and 0.67 au for the parallel and perpendicular polarizability, respectively, at the scalar CCSD(T) level. Thus, the anisotropy is rather insensitive to such a change of the basis as well. Decontraction of the ExtPol basis set affects the scalar relativistic CCSD(T) polarizabilities almost negligibly (Table 3). Combining our results with those presented by Maroulis [7] we conclude that the basis set issue is not a key problem in the accurate calculation of both components of the polarizabilities. This does not mean that there is no space for further improvement by expanding the basis set in a more systematic way that would allow extrapolation methods to polarizabilities [36].

Electron correlation increases both components of the polarizability by about 0.85 au (parallel component) and by 1.59 au (perpendicular component) using the scalar relativistic CCSD(T) values with the ExtPol basis set. The number of correlated electrons does not change the overall picture of the electron correlation in both components of the polarizability. Like with the dipole moment, correlating 8, 18, or 26 electrons is a bit oscillatory. Including the iodine 4*d* electrons in CCSD(T) lowers both polarizability components by less than 0.2 au, while considering also 4*s* and 4*p* electrons brings both components back by some 0.1–0.05 au In fact, the number of correlated electrons is by no means critical in an accurate calculation of the HI polarizability. Actually, correlating only eight valence electrons leads to results very close to those obtained from correlating 26 electrons. Since correlating all electrons, as demonstrated by an MP2 calculation, agrees perfectly with results from correlating 26 electrons and since the overall picture of electron correlation at the MP2 level is similar to that at the highly correlated CC level, the effect arising from the number of correlated electrons seems to be reliable enough. The slight difference between the final CCSD(T) and MP2 values with the unExtPol basis sets, 0.08 au (α_{zz}) and 0.32 au, (α_{xx}), respectively (Table 3), is unimportant, even if not completely negligible. What is important is that changes of this size cannot reconcile theory and experiment for example, $\Delta\alpha$.

The *R*- dependencies for the scalar relativistic CCSD(T) electric properties with the same basis sets and the same number of correlated electrons as for the dipole moment curves are

$$\alpha_{zz}(R) = 37.79 + 12.32(R - R_e) + 3.36(R - R_e)^2 - 0.97(R - R_e)^3 - 0.75(R - R_e)^4 \ , \tag{2}$$

$$\alpha_{xx}(R) = 35.95 + 1.80(R - R_e) + 0.13(R - R_e)^2 - 0.04(R - R_e)^3 - 0.11(R - R_e)^4 \ , \tag{3}$$

$$\bar{\alpha}(R) = 36.56 + 5.30(R - R_e) + 1.21(R - R_e)^2 - 0.35(R - R_e)^3 - 0.33(R - R_e)^4 \ , \tag{4}$$

$$\Delta\alpha(R) = 1.84 + 10.52(R - R_e) + 3.23(R - R_e)^2 - 0.92(R - R_e)^3 - 0.63(R - R_e)^4 \ . \tag{5}$$

The polarizability curves from DK SCF and CCSD(T) calculations are displayed in Figs. 2 and 3. The shape of the SCF and CC curves is quite similar for both polarizability components as well as for the mean polarizability and anisotropy. Vibrational corrections are 0.65 ± 0.05 and 0.25 ± 0.05 for the α_{zz} and α_{xx} components, respectively. We note that the pure vibrational contribution is included in the parallel component together with the ZPV contribution.

Table 3 shows a significant discrepancy between the experimental and all theoretical values of the parallel polarizability. Consequently, the anisotropy is much smaller than in experiment. Our original expectation, prompted to us by Maroulis [7], was that better treatment of relativistic effects and especially incorporating SO effects could eventually reconcile theoretical and experimental results. This turns out not to be true. The CISD and SO-CISD results in Table 4 clearly show that SO effects are small and can by no means increase the parallel polarizability to the extent which would lead to better agreement of the anisotropy with experiment. The

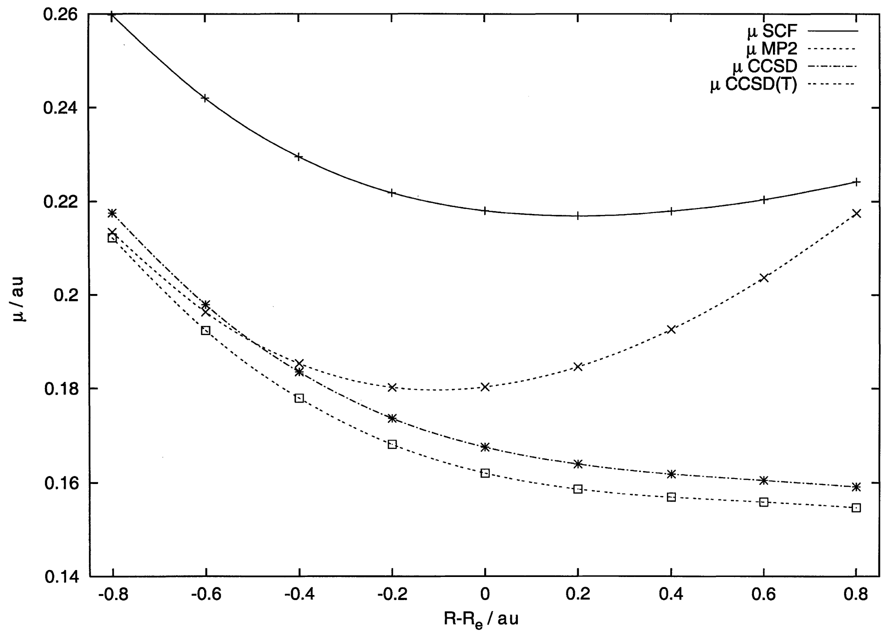

Fig. 2. Bond-length dependence of *zz* and *xx* components of the polarizability of the HI molecule. Scalar relativistic SCF and CCSD(T) calculations with 26 electrons correlated

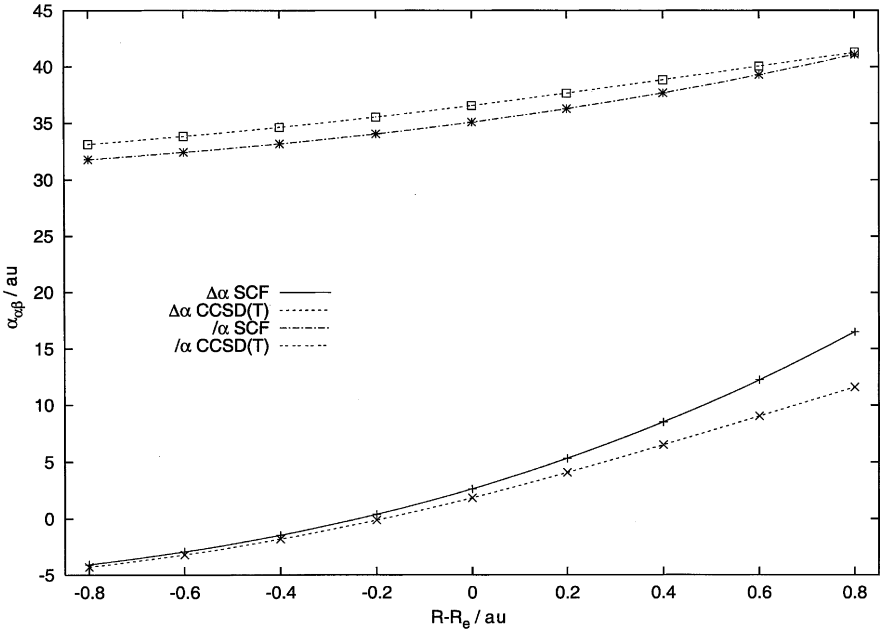

Fig. 3. Bond-length dependence of the mean polarizability and the polarizability anisotropy of the HI molecule. Scalar relativistic SCF and CCSD(T) calculations with 26 electrons correlated

SO contribution arising from the Dirac–Hartree–Fock calculation is larger than our (SO)CISD-18 value. Even if the SO effect from the Dirac–Hartree–Fock calculations is larger for the α_{zz} than for the α_{xx} component, the effect is too small to alleviate the disagreement between the theoretical and experimental anisotropy. Since one can hardly expect any reasonable change arising from further improvement of the basis sets and the treatment of electron correlation, we conclude that we see no way of bringing the theoretical parallel polarizability and the polarizability anisotropy into better agreement with experiment.

To estimate the best theoretical values for the parallel polarizability we proceed similarly as with the dipole moment. Using the CCSD(T) polarizability obtained with the unExtPol basis set (Table 3), α_{zz} = 37.78 au, and correcting this value by core–valence correlation effects, the vibrational correction, and the SO effect (0.00, +0.65, and +0.04, respectively, Tables 3, 4), we predict our best theoretical value for the parallel polarizability as 38.47 ± 0.05 au

Estimating SO corrections to the scalar CCSD(T) value for α_{xx} = 35.91 au is more complicated. Unfortunately, we were unable to obtain a correlated SO value for α_{xx} with the CC or SO-CISD method owing to technical problems when the symmetry is reduced after applying an external electric field. Core correlation effects and the vibrational correction are estimated as −0.02 and +0.25, respectively, (Table 3). SO effects are precisely calculated at the SCF level. Our Dirac–Coulomb SCF calculations and the results of Norman et al. [13] lead to the same value, +0.12 au. This is about half of the SO contribution to α_{zz} at the same level. We should realize that the SO contribution decreases significantly when electron correlation is included in α_{zz} (see SO-CISD data in Table 4). Our most sophisticated correlated value including SO effects is calculated using the MP2-8 Dirac–Coulomb method: $\alpha_{xx} = 34.60$ au with the relativistic r-pvtz basis set. This basis set, specifically designed for correlated Dirac–Coulomb calculations, underestimates the Dirac–Coulomb SCF α_{xx} value by 0.71 au in comparison with the unExtPol basis set. Even if possibly not so suitable for Dirac–Coulomb calculations, this last basis is more suitable for calculations of polarizabilities. For this reason we do not consider the difference between the scalar MP2-8 value and the CCSD(T)-26 for α_{xx}, which is available from Table 3. Thus, we do not use this difference as a correction for correlation (and basis set) effects to the MP2-8 Dirac–Coulomb result. We rather suppose that the SO correction is small for α_{xx} as was the case for the dipole moment and the parallel polarizability. Thus, starting from our $\alpha_{xx} = 35.89$ au value and considering the vibrational correction, our best estimate is $\alpha_{xx} = 36.14 \pm 0.05$ au. Using these values we arrive at the mean scalar polarizability and the anisotropy of the polarizability, $\bar{\alpha} = 36.53 \pm 0.05$ and $\Delta\alpha = 1.93 \pm 0.05$ au The vibrationally corrected values are $\bar{\alpha} = 36.92 \pm 0.05$ and $\Delta\alpha = 2.33 \pm 0.05$ au.

4 Conclusions

In the present study we have carefully explored basis set effects by adding diffuse functions and by decontraction of basis sets, correlation effects by using the MP2, CISD, CCSD, and CCSD(T) sequence of methods and by also taking deeper electrons into account, and scalar and SO relativistic effects by using Douglas–Kroll–Hess and Dirac–Coulomb Hamiltonians.

Disagreement between theory and experiment is frequently caused by deficiencies in basis sets. One might suspect that the original Maroulis basis sets lead to some “overpolarization” of the molecule owing to inconsistency of the H and I basis sets. As a matter of fact, our series of basis sets leads to results which are not too different from previously published data. Thus, the choice of basis set does not seem to be a reason for the observed discrepancy between theory and experiment. Of course, an improvement could be achieved by using more systematically extended series that would allow an extrapolation to the basis set limit.

Electron correlation effects from scalar relativistic CCSD(T) calculations with the ExtPol basis set and 18 electrons correlated are approximately the same as at the nonrelativistic level (values in parentheses): for the dipole moment, parallel, and perpendicular polarizability they are −0.52 (−0.55), +0.85 (+0.92), and +1.59 (+1.46) au, respectively and are thus inevitable if accurate properties shall be obtained. This means that correlation and scalar relativistic effects are approximately additive. Scalar relativistic contributions to the three properties from the ExtPol CCSD(T) calculations are −0.042, −0.35 and 0.17 au, respectively. Even if much smaller than electron correlation effects, one cannot neglect scalar relativistic effects that are very important in comparison of the theoretical dipole moment with its experimental value. SO effects at the Dirac–Coulomb SCF level for the dipole moment, parallel, and perpendicular polarizabilities are -0.012, +0.23, and +0.12 au, respectively. At the SO-CISD correlated level SO corrections are negligible for the dipole moment and the parallel polarizability. Correlated Dirac–Coulomb calculations for the perpendicular polarizability could only be obtained at the MP2 level. Even if there is space for further improvement we doubt that any more precise calculation of correlation and relativistic effects can change the results significantly.

Our final theoretical values, including vibrational corrections, are (in atomic units) dipole moment $\mu = 0.154 \pm 0.003$ (experimental value is 0.176 from the Stark spectra and 0.15 from dielectric measurements), static dipole polarizabilities $\alpha_{zz} = 38.47 \pm 0.05$ (experimental value is 44.4), $\alpha_{xx} = 36.14 \pm 0.05$ (experimental value is 33.0), $\bar{\alpha} = 36.92 \pm 0.05$ (experimental value is 36.8), and $\Delta\alpha = 2.33 \pm 0.05$ (experimental value is 11.4).

In spite of the significant improvement of theoretical treatments used in the present work, principal discrepancies between theory and experiment, as stressed by Maroulis [7], still persist. The dipole moment as predicted from scalar relativistic CCSD(T) calculations is significantly lower than the experimental value from the Stark spectra. Our study corroborates the suspicion that the experimental values for α_{zz} and α_{xx} [15] are inaccurate. In fact, the large difference between the experimental α_{zz} and α_{xx} neither finds support through all theoretical treatments mentioned here (including our own) nor through physical reasoning. The polarizability and its anisotropy are strongly sensitive to details in the valence structure of the wave function. Intuitively, a large anisotropy of HI is not expected on these grounds. The expected anisotropy should instead be roughly similar to that resulting from sophisticated correlated relativistic calculations. A supporting argument for this claim follows from analogous data for HCl. The static anisotropy of the polarizability for this species, calculated with similar correlated methods as those used in the present work [38], is small, 1.6 au, which agrees with experiment fairly well. A common complicating factor with accurate experimental data for polarizabilities and comparisons with theoretical values is also the frequency dependence of this property and extrapolation to static limits.

We conclude that the main message of this paper is not the disagreement between theory and experiment for selected electric properties of HI. this was already known from other papers. Our results rather represent the most sophisticated predictions of accurate data for this species obtained so far.

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Note added in proof Meanwhile we performed the relativistic Dirac-Coulomb CCSD(T) calculations in the unExPol basis set with eight correlated electrons and 38% of the highest virtual space was deleted. The obtained dipole moment value is 0.143 au, what is lower than the corresponding one in the contracted r-pvtz basis, 0.151 au (Table 4). By subtracting the scalar relativistic CCSD(T)-8 value of 0.154 au (Table 3) from the new one we calculate larger SO contribution to the dipole moment, which isi now -0.011 au. Employing the new data we land at the value of 0.146 ± 0.011 au for the final prediction of the dipole moment of the HI molecule.