

Regular article

Toward spectroscopic accuracy of *ab initio* calculations of vibrational frequencies and related quantities: a case study of the HF molecule*

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Abstract. Calculations at various coupled-cluster (CC) levels with and without the inclusion of linear r_{ij} -dependent terms are performed for the HF molecule in its ground state with a systematic variation of basis sets. The main emphasis is on spectroscopic properties such as the equilibrium distance r_e and the harmonic vibration frequency ω_e . Especially with the R12 methods (including linear r_{ij} -dependent terms), convergence to the basis set limit is reached. However, the results (at the basis set limit) are rather sensitive to the level of the treatment of electron correlation. The best results are found for the CCSDT1-R12 and CCSD[T]-R12 methods (CCSD[T] was previously called CCSD + T(CCSD)), while CCSD(T) overestimates ω_e by $\approx 6 \text{ cm}^{-1}$. The good agreement of conventional CCSD(T) with experiment for basis sets far from saturation (e.g. truncated at g -functions) is probably the result of a compensation of errors. The contribution of core-correlation is non-negligible and must be included (effect on $\omega_e \approx 5 \text{ cm}^{-1}$). Relativistic effects are also important ($2\text{--}3 \text{ cm}^{-1}$), while adiabatic effects are much smaller ($< 1 \text{ cm}^{-1}$) and non-adiabatic effects on ω_e can be simulated in replacing nuclear by atomic masses; for rotation nuclear masses appear to be the better choice, at least for hydrides. From a potential curve based on calculations with the CCSDT1-R12 method with relativistic corrections, the IR spectrum is computed quantum-mechanically. Both the band heads and the rotational structures of the observed spectra are reproduced with a relative error of $\approx 10^{-4}$ for the three isotopomers HF, DF, and TF.

Key words: Explicitly correlated wave functions – Coupled-cluster methods – Relativistic effects – Rovibrational spectra – Hydrogen fluoride and its isotopomers

1. Introduction

“Spectroscopic accuracy” has always been a challenge to quantum chemistry. Although this term is not uniquely defined, there appears to be agreement that spectroscopic accuracy is achieved for a vibration frequency if it is certain within at least 1 cm^{-1} . This accuracy has been realized for H_2 for quite some time [1–4] and recently for H_3^+ [5–10]. Among the molecules that are built not only from H atoms, HF is certainly one of the simplest, although it has 10 electrons and is much more complicated than the two-electron systems H_2 and H_3^+ . Only LiH and Li_2 are probably simpler. In fact we have, in a recent study, computed ω_e of LiH with 1 cm^{-1} accuracy, using CC wavefunctions with linear R12 terms [11]. It is the concern of the present paper to find out which level of sophistication is necessary to compute the vibrational frequencies and related quantities such as the equilibrium distance (r_e) and the rotational structure of the vibrational bands with spectroscopic accuracy. To arrive there one has to do much more than just apply standard high-level methods, although by applying such methods one may get seemingly good results just due to a fortunate compensation of errors.

If one strives at accurate results of quantum chemical calculations one has to be sure that one

1. has reached the basis set limit;
2. is at a sufficiently high level of the treatment of electron correlation;
3. has taken care of relativistic, adiabatic, and non-adiabatic corrections.

Of course, one has to compare either theoretical harmonic frequencies ω_e with harmonized experimental ones, or transition energies $\nu_{v \leftarrow 0}$ between vibrational levels with their experimental counterparts, and be sure that the quantities that one compares are defined in the same way.

The direct comparison of the observed infrared (IR) frequencies with their theoretical counterparts is cer-

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tainly the better choice. Nevertheless, we have first studied ω_e as a useful quantity to compare various theoretical calculations with each other, keeping in mind that the comparison of theoretical and experimental ω_e may not be too meaningful. It turns out that reliable information on the accuracy of quantum chemical calculations is only obtained if one considers vibration-rotation spectra explicitly.

The earliest approach towards spectroscopic accuracy for HF and other diatomic hydrides was probably the CEPA study by Meyer and Rosmus [12]. Considering that these authors obtained r_e , D_e , ω_e , $\omega_e x_e$ with respective errors of < 0.1 pm, ≈ 0.3 eV, ≈ 30 cm $^{-1}$, and ≈ 0.3 cm $^{-1}$, the progress that has been achieved in the past 25 years may appear rather modest.

Recently, Martin and Taylor [13] have studied how extension of the basis and change of the level of the treatment of electron correlation affect ω_e and r_e for HF. The subtitle of their paper “Are h -functions enough” manifests that their conclusions are rather pessimistic. We confirm the poor convergence with extension of the basis for “conventional” calculations, while it is relatively easy to reach the basis set limit if one uses R12 methods, such that we can make statements at the basis set limit. There has been a complementary study by Feller and Peterson [14] with the main message that one should use Dunning-type basis extrapolations, while less clear-cut conclusions were possible as to the level of correlation needed (see [15]). In a more general context Lee and Scuseria [16] have found that for molecules of first-row atoms using the CCSD(T) approach with basis sets including up to g -functions, vibrational frequencies for molecules of first-row atoms are obtained with an error of ≈ 8 cm $^{-1}$. This optimistic message may, as our present study indicates, to some extent be based on a fortunate compensation of errors. To arrive at an intrinsic spectroscopic accuracy (not relying on an error compensation) is actually much harder than is often believed.

We shall see that in conventional calculations of the MP2, CCSD, CCSD(T) or CCSD[T] type [the last was formerly called CCSD+T(CCSD)], basis functions at least up to h ($l = 5$) on F are necessary in order to get converged results (on the cm $^{-1}$ level), while with R12 methods, to include up to f in the basis is practically sufficient.

While it appears possible to come sufficiently close to the basis set limit, the dependence of the results on the level of the treatment of electron correlation suggests that one is still too far from the limit of the corresponding hierarchy. The large differences between the CCSD results, on one side, and CCSD(T) or CCSD[T], on the other, indicate that triple substitutions are very important, but the substantial differences between CCSD(T) and CCSD[T] mean that the way how the contributions of the triples are evaluated matters a lot. Fortunately we could – for an acceptable basis set – afford iterative non-perturbative CCSDT1-R12 calculations. The closeness of the result of this approach with experiment and with those for CCSD[T]-R12 appears to indicate that CCSD[T] is actually a better approximation – at least in the present case – than the more widely used CCSD(T).

The good agreement of the CCSDT1-R12 potential curve (with relativistic corrections) with experiment is an indication that quadruple excitations are not important in this case, provided that one treats the triples at the CCSDT1-R12 level – or that this level simulates quadruple excitations to some extent. More studies are necessary to find out whether this is more general or just a special feature of HF.

Relativistic effects matter roughly 2–3 cm $^{-1}$ for ω_e , adiabatic corrections less than 1 cm $^{-1}$, such that the latter corrections are relatively unimportant, as long as the errors in the correlation effects are much larger.

Density functional methods yield results that scatter over a large range depending on the chosen functional, and have no chance to compete with genuine ab initio methods.

2. Methods, basis sets, and computer programs

We have performed both conventional MP2 (Møller-Plesset perturbation theory to second order), CCSD (coupled cluster with single and double substitutions), CCSD(T) and CCSD[T] (i.e. CCSD with approximate non-iterative inclusion of triples) calculations, and calculations with the same methods including linear terms in the electronic coordinates, i.e. MP2-R12, CCSD-R12, CCSD(T)-R12, and CCSD[T]-R12. Additional calculations were done with the iterative CCSDT1A and CCSDT1-R12 methods, the latter being the R12 counterpart of the former. What is now named CCSD[T] has previously been called CCSD+T(CCSD). These methods have been described elsewhere in detail [17–19]. We use the modification [18] taking advantage of extremal electron pairs [20] that has turned out to be numerically more stable than the older orbital-invariant approach [21].

For the R12 methods one can choose between the standard approximations A and B, with B generally more accurate. In all previous calculations B was used, except for MP2, where calculations with both MP2-R12/A and MP2-R12/B were reported. In the present study all calculations were done with the standard approximation B. Only occasionally we report on the difference of the results of MP2-R12/A and MP2-R12/B, which is a measure of the saturation of the basis.

Most of the basis sets which we have used are based on the correlation consistent basis sets of Dunning [22]. These are for F: aug-cc-pVXZ

$$\begin{aligned} X = T: & 11s6p3d2f \\ X = Q: & 13s7p4d3f2g \\ X = 5: & 15s9p5d4f3g2h \\ X = 6: & 17s11p6d5f4g3h2i \end{aligned}$$

for H: cc-pVXZ

$$\begin{aligned} X = T: & 5s2p1d \\ X = Q: & 6s3p2d1f \\ X = 5: & 8s4p3d2f1g \\ X = 6: & 10s5p4d3f2g1h \end{aligned}$$

We have modified these basis sets in the following way:

1. All basis sets are completely decontracted.
2. Except for the aug-cc-pVTZ basis, a steep function per l -value was added to the F basis, with an exponent extrapolated logarithmically. It had been shown earlier that the addition of more than one steep and diffuse function does not alter the results for correlation energies of first-row elements by more than a few microhartrees [23].
3. In some cases, functions with high l -values were omitted. This is indicated in the tables, e.g. aug5-fd means an aug-cc-pV5Z

basis truncated at f for F and at d for H. (with the additional steep functions mentioned under 2.)

4. In some cases, more additional functions are added. These are indicated by adding D (for diffuse) or S (for steep) to the basis name.

The exponents of the additional basis functions are in Table 1.

On the whole the aug basis sets used here differ from those of Dunning [22] in an improvement for the low angular momenta, but truncation at lower l . Such basis sets are especially appropriate for calculations with R12 methods, but they are not too bad for conventional calculations.

The basis sets aug5-gd ($N = 168$) and aug6-gd + DS ($N = 270$) have been used before in our study of the Ne atom and the molecules HF, H₂O, NH₃, and CH₄ at their equilibrium geometries [23].

We have further used basis sets constructed differently, namely

1. ET-A: an even tempered basis based on the 22s15p basis of Schmidt and Ruedenberg [24] with the parameters reoptimized at the MP2-R12-B level, with even-tempered $6d$ and $4f$ added, optimized at the same level.
2. ET-B: like ET-A in the s, p part, but with a set of $13d$ and $11f$ functions, optimized in the same way.
3. ET-C: as ET-B, but with the most diffuse d and f functions deleted, and 8 even-tempered g functions are added.

The parameters of the ET basis sets are found in Table 2.

For the evaluation of r_e and ω_e the energy was computed for $r = 1.65, 1.68, 1.70, 1.71, 1.72, 1.73, 1.74, 1.75$, and $1.80 a_0$. A polynomial fit of maximum degree 6 was used. For the calculation of ω_e , atomic (rather than nuclear) masses were used. There is evidence that this simulates non-adiabatic effects [25–28].

The “full” potential curves for the construction of IR spectra were based on the points

1.1, 1.2, 1.3, 1.4, 1.5, 1.55, 1.6, 1.65, 1.7, 1.7328, 1.75, 1.8, 1.85, 1.9, 1.95, 2.0, 2.2, 2.4, 2.6, 2.8, and $3.5 a_0$

In a fit through these points by an extended Rydberg ansatz [29, 30]

$$V(x) = -D_e(1 + a_1x + a_2x^2 + \dots)e^{-ax}; \quad x = r - r_e \quad (1)$$

information on the experimental dissociation energy D_e was included.

The fit to 22 points contained 11 parameters. The standard deviation of the fit is $10^{-6} E_h$. From this fit the rovibronic states

were calculated with a finite-element method [31], in the range 0.1 – $12 a_0$, with 80 elements and polynomials of degree 5. The intrinsic error of the term values is $< 10^{-3} \text{ cm}^{-1}$. For the vibrations, atomic masses were used, but for the rotation nuclear masses. This has turned out to be a good choice in previous calculations, at least for systems, where the relative nuclear motion is dominated by a hydrogen atom [25–28].

All non-relativistic ab initio calculations have been performed with the direct coupled cluster program DIRCCR12-95 [32]. The two-electron integrals required by R12 methods were calculated by an extended [33] version of the HERMIT program [34–36]. The relativistic calculations were carried out with the MPGRADRE program [37], an extension of the nonrelativistic program MPGRAD [38], of the TURBOMOLE package [39] to calculate relativistic corrections to the SCF and MP2 energy in the framework of direct perturbation theory (DPT) [40]. For the velocity of light a value of 137.0359895 au [41] is used in the MPGRADRE program. All DFT calculations have been performed with the Gaussian 94 [42] suite of programs. For the quantum-mechanical computation of the IR spectrum, two codes have been used: the program FITNONLIN [43] for the fit of the potential curve according to the extended Rydberg ansatz [29] (for a detailed review of different fit ansätze, see [30]), and D1FEM [44] for the solution of the one-dimensional Schrödinger equation with the finite element method [31]. The computations reported in this work were performed partly on IBM RS/6000 workstations of the Lehrstuhl für Theoretische Chemie in Bochum and mainly on the SGI PowerChallenge-XL-12 of the Computer center of the Ruhr-Universität Bochum.

3. Discussion of the results

3.1. The energy

In Table 3 the Hartree-Fock energy of HF at the distance $r = 1.7328 a_0 = 0.9170 \text{ \AA} \approx r_e$ is tabulated for various basis sets. Our best result (ET-C) differs from the numerically exact Hartree-Fock energy of Laaksonen et al. [46] by $\approx 30 \mu E_h$, but all values in Table 1, except those for the four smallest basis sets (of aug3- and

Table 1. Exponents of the additional functions in the various basis sets for F and H

	Basis	Origin	Exponents of the additional functions					
			s	p	d	f	g	h
F	aug4	aug-cc-pVQZ	–	–	14.57	11.05	6.110	–
	aug5	cc-pV5Z	0.0917	0.0593	19.86	14.02	12.44	8.587
					0.1809	0.308	0.5277	0.1045
F	aug6	cc-pV6Z	0.08494	0.05191	127.3	39.01	16.30	–
			0.03618	0.02164	55.54	17.17	0.4757	
					24.23	0.2838		
				0.1671	0.1249			
				0.07288				
H	aug6	cc-pV6Z	–	21.33	11.17	–	–	–
				9.82				

Table 2. Values of the optimized even-tempered parameters α and β for F in the ET basis sets^a

		s	p	d	f	g
ET-A	α	0.09860	0.0393	0.05011	0.1815	–
	β	2.1230	2.2010	3.000	2.295	–
ET-B	α	0.09860	0.0393	0.02383	0.3537	–
	β	2.1230	2.2010	1.930	2.050	–
ET-C	α	0.09860	0.0393	0.0460	0.725	0.119
	β	2.1230	2.2010	1.930	2.050	2.273

^aThe even-tempered parameters are defined by the rule $\zeta = \alpha \beta^{n-1}$, ($n = 1, 2, 3, \dots, N_i$)

Table 3. Hartree-Fock energies for HF at $r = 1.7328 a_0$ (91.70 pm) for various basis sets^a (in hartree)

Basis		Basis set discription		HF
Name	N^b	F	H	SCF
aug3-fd	74	11s6p3d2f	5s2p1d	-100.061 024
aug4-fd	112	13s7p5d4f	6s3p2d	-100.068 501
aug4-gd	139	13s7p5d4f+3g	6s3p2d	-100.068 520
aug4-gf	146	13s7p5d4f+3g	6s3p2d1f	-100.068 550
aug5-fd ^c	132	15s9p6d5f	6s3p2d	-100.070 431
aug5-ft ^c	139	15s9p6d5f	6s3p2d1f	-100.070 458
aug5-gd ^c	168	15s9p6d5f+4g	6s3p2d	-100.070 460
aug5-gf ^c	175	15s9p6d5f+4g	6s3p2d1f	-100.070 471
aug5-hd ^c	201	15s9p6d5f+4g+3h	6s3p2d	-100.070 463
aug5-hf ^c	208	15s9p6d5f+4g+3h	6s3p2d1f	-100.070 472
aug5-fd	142	15s9p6d5f	8s4p3d	-100.070 526
aug5-gd	178	15s9p6d5f+4g	8s4p3d	-100.070 558
aug5-hd	211	15s9p6d5f+4g+3h	8s4p3d	-100.070 564
aug5-hg	234	15s9p6d5f+4g+3h	8s4p3d2f1g	-100.070 575
aug6-fd	172	17s11p7d6f	10s5p4d	-100.070 711
aug6-fd+D	188	18s12p8d7f	10s5p4d	-100.070 722
aug6-fd+DS	216	18s12p10d8f	10s7p5d	-100.070 735
aug6-gd+DS	270	18s12p10d8f+6g	10s7p5d	-100.070 764
ET-A	173	22s15p6d4f	7s4p3d2f	-100.070 653
ET-B	285	22s15p13d11f	9s7p5d3f	-100.070 778
ET-C	335	22s15p12d10f+8g	10s5p4d3f	-100.070 788
SCF limit ^d				-100.070 82

^aThe basis sets are described in Sect. 2^bNumber of basis functions^cBasis for H is cc-pVQZ instead of cc-pV5Z^d[47]

aug4-type) are in error by less than $1 mE_h$. The SCF results for F^- are given in Table 4 for comparison. Our best value differs by $\approx 10 \mu E_h$ from the SCF limit of Davidson and Chakravorty [47].

The convergence of the correlation energy with extension of the basis is much slower for conventional calculations, while with R12 terms it is nearly as fast as at SCF level. This is seen on Table 3 for HF and on Table 4 for F^- . In both cases the best computed values, namely with the CCSD[T]-R12 or the CCSD(T)-R12 method (and basis ET-C), agree with their experimental counterparts [48–50] within a few tenths of a millihartree (mE_h) with the CCSD(T)-R12 values slightly closer to the experimental counterparts. While for all methods with R12 the results from the aug5-fd basis or better differ by only a few mE_h from the basis limit, a deviation of 20–30 mE_h from the basis limit is observed in the calculations without R12. Even for the best basis sets considered here, without R12 one misses $\approx 10 mE_h$ from the basis set limit. CCSD[T]-R12 and CCSD(T)-R12 differ by $\approx 0.3 mE_h$, CCSD-R12 is off by $\approx 8 mE_h$, while MP2-R12 is closer to CCSD[T], namely in error by only

Table 4. Hartree-Fock energies for F^- for various basis sets (in hartree)

Basis		Basis set description	F^-
Name	N	F	SCF
aug3	29	11s6p	-99.450 858
aug4	34	13s7p	-99.457 464
aug5	42	15s9p	-99.459 250
aug6	50	17s11p	-99.459 425
aug6+SD	54	18s12p	-99.459 431
ET	67	22s15p	-99.459 446
Limit ^a			-99.459 454

^a[46]

$\approx 4 mE_h$. It is well-known that for 10-electron systems like HF MP2 is unusually good.

Two measures of basis completeness are (1) the difference of the energy of the MP2-R12/A and MP2-R12/B approaches, and (2) the so-called diagnostic [51]. For the former we get 0.65 mE_h with basis ET-C, which is quite good, while with ET-A this difference is 2.5 mE_h , which is still not bad. The diagnostic is ideally 0.5 for singlet and 0.25 for triplet pairs. For ET-C we get 0.47 and 0.22; for ET-A 0.44 and 0.20.

We have already argued [23] that the total energies obtained from CCSD(T)-R12 or CCSD[T]-R12 with a good basis are chemically accurate, i.e. in error by something of the order 1 kcal/mol or less. The two methods are also chemically accurate relative to each other. Energy differences are actually more accurate. Unfortunately we could not document this for the dissociation energy of $HF \rightarrow H + F$, since our R12 methods so far only allow the treatment of closed-shell states. We have evaluated the dissociation energy of $HF \rightarrow H^+ + F^-$, i.e. the proton affinity of F^- , which shows a more similar agreement with its experimental counterpart than do the total energies of HF and F^- with the corresponding experimental energies (see also [15]). We have not documented the results because they can easily be obtained from Tables 3–6.

We have further not documented the correlation energy of the valence electrons only. Readers interested in this quantity find some information in [23].

3.2. Equilibrium distance

Let us now have a look at the equilibrium distances in Table 7. First one notes that the variation of r_e depending on basis sets and methods for the treatment of correlation is only ≈ 0.1 pm (except for CCSD which

Table 5. The correlation energy^a of HF at $r = 1.7328 a_0$ (91.70 pm) for various methods and basis^b sets (in millihartree)

Basis	Basis set description				Method							
	N	F	H	H	MP2	MP2-R12	CCSD	CCSD-R12	CCSD[T]	CCSD[T]-R12	CCSD(T)	CCSD(T)-R12
aug3-fd	74	11s6p3d2f		5s2p1d	-333.543	-371.794	-335.292	-373.859	-343.648	-381.962	-343.275	-381.635
aug4-fd	112	13s7p5d4f		6s3p2d	-352.216	-379.505	-352.700	-376.510	-361.650	-385.272	-361.286	-384.944
aug4-gd	139	13s7p5d4f+3g		6s3p2d	-363.022	-380.132	-362.406	-377.638	-371.603	-386.727	-371.265	-386.404
aug4-gf	146	13s7p5d4f+3g		6s3p2d1f	-363.440	-380.228	-362.721	-377.691	-371.934	-386.801	-371.596	-386.477
aug5-fd ^c	132	15s9p6d5f		6s3p2d	-355.824	-382.423	-356.114	-377.226	-365.135	-386.074	-364.778	-385.747
aug5-fd ^c	139	15s9p6d5f		6s3p2d1f	-356.927	-382.467	-357.110	-377.467	-366.168	-386.198	-365.811	-385.869
aug5-gd ^c	168	15s9p6d5f+4g		6s3p2d	-366.427	-382.748	-365.627	-378.228	-374.872	-387.332	-374.537	-387.008
aug5-gf ^c	175	15s9p6d5f+4g		6s3p2d1f	-366.792	-382.809	-365.895	-378.392	-375.157	-387.396	-374.821	-387.072
aug5-hd ^c	201	15s9p6d5f+4g+3h		6s3p2d1f	-369.928	-382.615	-368.344	-378.176	-377.651	-387.410	-377.323	-387.087
aug5-hf ^c	208	15s9p6d5f+4g+3h		6s3p2d1f	-370.203	-382.700	-368.537	-378.688	-377.859	-387.447	-377.530	-387.164
aug5-fd	142	15s9p6d5f		8s4p3d	-356.069	-382.535	-356.310	-377.301	-365.339	-386.160	-364.981	-385.831
aug5-gd	178	15s9p6d5f+4g		8s4p3d	-366.587	-382.858	-365.735	-378.251	-374.986	-387.413	-374.650	-387.089
aug5-hd	211	15s9p6d5f+4g+3h		8s4p3d	-370.076	-382.722	-368.441	-378.258	-377.754	-387.492	-377.426	-387.169
aug5-hg	234	15s9p6d5f+4g+3h		8s4p3d2f1g	-370.752	-382.879	-368.911	-378.379	-378.254	-387.656	-377.925	-387.333
aug6-fd	172	17s11p7d6f		10s5p4d	-357.774	-383.314	-357.835	-377.647	-366.895	-386.540	-366.539	-386.213
aug6-fd+D	188	18s12p8d7f		10s5p4d	-357.786	-383.771	-357.845	-377.669	-366.906	-386.563	-366.550	-386.236
aug6-fd+DS	216	18s12p10d8f		10s7p5d	-360.195	-383.476	-360.109	-377.810	-369.179	-386.715	-368.823	-386.388
aug6-gd+DS	270	18s12p10d8f+6g		10s7p5d	-371.408	-384.165	-	-378.985	-379.331	-388.236	-378.996	-387.914
ET-A ^d	173	22s15p6d4f		7s4p3d2f	-354.084	-382.507	-354.459	-376.982	-363.465	-385.822	-363.102	-385.492
ET-B	285	22s15p13d11f		9s7p5d3f	-361.857	-383.744	-	-378.083	-	-387.008	-	-386.680
ET-C	335	22s15p12d10f+8g		10s5p4d3f	-372.393	-384.389	-	-379.134	-	-388.424	-	-388.102

^a Experimental estimate for the correlation energy: $E = -388.2 E_h$ [47–49]^b The basis sets are described in Sect. 2^c Basis for H is cc-pVQZ instead of cc-pV5Z^d The iterative CCSDT1A yields: $E_{\text{CCSDT1A}} = -363.625 \text{ mE}_h$ and $E_{\text{CCSDT1-R12}} = -386.005 \text{ mE}_h$ for the ET-A basis

Table 6. The correlation energy^a of F⁻ for various methods and basis sets (in millihartree)

Basis	Basis set description		Method		CCSD	CCSD-R12	CCSD[T]	CCSD[T]-R12	CCSD(T)	CCSD(T)-R12
	N ^b	F	MP2 ^c	MP2-R12 ^c						
aug3-f	58	11.s6p3d2f	-349.274	-382.089	-343.167	-376.925	-355.359	-388.826	-354.001	-387.456
aug4-f	87	13.s7p5d4f	-367.479	-392.390	-360.026	-382.377	-372.981	-395.072	-371.694	-393.815
aug4-g	114	13.s7p5d4f + 3g	-379.453	-393.763	-370.632	-383.931	-383.787	-396.995	-382.592	-395.771
aug5-f	107	15.s9p6d5f	-371.208	-396.543	-363.490	-383.798	-376.557	-396.556	-375.273	-395.354
aug5-g	143	15.s9p6d5f + 4g	-382.788	-397.044	-373.776	-385.133	-386.999	-398.224	-385.814	-397.048
aug5-h	176	15.s9p6d5f + 4g + 3h	-386.295	-397.149	-376.424	-385.252	-389.690	-398.429	-388.531	-397.265
aug6-f	127	17.s11p7d6f	-372.740	-398.080	-364.854	-384.577	-377.978	-397.367	-376.682	-396.168
aug6-f + D	143	18.s12p8d7f	-372.784	-400.424	-385.720	-385.720	-378.060	-398.493	-376.740	-397.312
aug6-f + DS	160	18.s12p10d8f	-375.147	-400.503	-364.891	-385.825	-380.295	-398.611	-378.977	-397.430
aug6-g + DS	214	18.s12p10d8f + 6g	-388.010	-401.263	-367.118	-387.321	-391.719	-400.566	-390.496	-399.401
ET-A ^d	125	22.s15p6d4f	-368.344	-399.098	-360.854	-384.708	-373.931	-397.376	-372.591	-396.180
ET-B	209	22.s15p13d11f	-375.333	-400.389	-	-385.867	-380.410	-398.669	-379.099	-397.488
ET-C	269	22.s15p12d10f + 8g	-388.597	-401.051	-	-387.322	-392.157	-400.590	-390.941	-399.425

^a Experimental estimate $E = -399.4$ mE_h [47]^b Number of basis functions^c The numerical MP2 limit obtained through extrapolation of FEM calculations is $E_{\text{MP2}} = -401.7$ mE_h [63]^d The iterative CCSDT1a yields: $E_{\text{CCSDT1a}} = -374.087$ mE_h and $E_{\text{CCSDT1-R12}} = -397.546$ mE_h for the ET-A basis

is off by ≈ 0.3 pm, and for some smaller basis sets like aug3-fd), with a similar dependence on the method and on the basis set. Hartree-Fock calculations are in error by 2 pm. They are not documented in Table 7, but can be found in Table 9.

For a given method, improvement of the basis leads to a slight (but not very systematic) decrease of r_e ; the same is found on going from a method without R12 to one with R12. In the calculations with R12 the basis dependence is extremely small, with variations of the order 0.02 pm. For a more detailed discussion of basis set effects, see Sect. 3.6.

With the largest basis (ET-C) we get for r_e 91.69 pm from CCSD[T]-R12 and 91.66 pm from CCSD(T)-R12. The most sophisticated level of electron correlation used here is CCSDT1-R12. We could afford this only for basis ET-A, for which we get 91.67 pm for CCSD(T)-R12, 91.70 pm for CCSD[T]-R12, and 91.71 pm for CCSDT1-R12. From these data one can extrapolate 91.70 for CCSDT1-R12 and basis ET-C. This is our “best” theoretical prediction of r_e , without considering relativistic and non-Born-Oppenheimer (NBO) corrections. As discussed in Sect. 3.4, these are expected to affect only the fourth digit, and increase it by less than one unit, so the prediction $r_e = 91.70$ pm is hardly changed.

The experimental value recommended by Huber and Herzberg [52] for r_e is 91.681 pm, with respect to which our best value is “in error” by $\approx 0.02\%$. Huber and Herzberg give different r_e values for DF and TF, on which we comment in Sect. 3.4. For a final comparison of theory and experiment for r_e , see Sect. 3.7. There it will also become clear that the CCSDT1-R12 value is more accurate than that (91.66 pm) from CCSD(T).

The calculations documented in Table 7 were done with inclusion of the core correlation. If one limits the calculations to the correlation effects of the valence electrons only, deviations of the order 0.1 pm arise (without core correlation the bond is actually longer; see Table 8), i.e. the inclusion of the core correlation is necessary for an accuracy to three significant figures.

In Table 9 the results for r_e from Hartree-Fock and various density functional treatments are collected. While Hartree-Fock underestimates r_e by 2 pm, most density functional methods overestimate r_e by almost the same amount. The B3P86 and B3PW91 functionals lead to an r_e that is only ≈ 0.4 pm too large.

3.3. Harmonic frequency

As seen from Table 10, the scatter in ω_e from various correlation treatments with different basis sets is of the order of 20 cm^{-1} except for CCSD, which is off by $\approx 50 \text{ cm}^{-1}$, and for some of the smaller basis sets (like aug3-fd). The variation of ω_e with the basis size does not look very systematic, but like for r_e the results from calculations with R12 are more stable with respect to variation of the basis than those without R12. Much larger variations with the basis set were found in [13] and [14], where other basis sets, including smaller and possibly unbalanced ones, were considered. Again we

Table 7. Equilibrium distance r_e of HF for various methods and basis sets (in pm)

Name	N	Basis set description		Method [r_e /pm]		CCSD-R12	CCSD[T]	CCSD[T]-R12	CCSD(T)	CCSD(T)-R12
		F	H	MP2	MP2-R12					
aug5-fd	142	15s9p6d5f	8s4p3d	91.68	91.78	91.36	91.74	91.67	91.61	91.64
aug5-gd	178	15s9p6d5f+4g	8s4p3d	91.78	91.78	91.37	91.71	91.69	91.68	91.65
aug5-hd	211	15s9p6d5f+4g+3h	8s4p3d	91.78	91.76	91.36	91.70	91.68	91.67	91.65
aug5-fd ^a	132	15s9p6d5f	6s3p2d	91.73	91.81	91.36	91.68	91.70	91.64	91.67
aug5-gd ^a	168	15s9p6d5f+4g	6s3p2d	91.82	91.80	91.43	91.75	91.72	91.72	91.69
aug5-hd ^a	201	15s9p6d5f+4g+3h	6s3p2d	91.82	91.80	91.42	91.74	91.72	91.71	91.68
aug5-ff ^a	139	15s9p6d5f	6s3p2d+1f	91.67	91.79	91.30	91.62	91.69	91.58	91.66
aug5-gf ^a	175	15s9p6d5f+4g	6s3p2d+1f	91.80	91.80	91.41	91.78	91.71	91.71	91.68
aug5-hf ^a	208	15s9p6d5f+4g+3h	6s3p2d+1f	91.82	91.79	91.42	91.78	91.71	91.71	91.68
aug3-fd	74	11s6p3d2f	5s2p1d	92.11	91.98	91.74	92.05	91.83	92.02	91.80
aug4-fd	112	13s7p5d4f	6s3p2d	91.76	91.80	91.39	91.71	91.71	91.68	91.65
aug5-fd	168	15s9p6d5f	8s4p3d	91.68	91.78	91.31	91.64	91.67	91.61	91.64
aug6-fd	172	17s11p7d6f	10s5p4d	91.66	91.76	91.35	91.62	91.66	91.58	91.63
aug6-fd+D	188	18s12p8d7f	10s5p4d	91.66	91.77	91.31	91.62	91.66	91.58	91.64
aug6-fd+DS	216	18s12p10d8f	10s7p5d	91.66	91.76	91.29	91.62	91.66	91.58	91.63
ET-A ^b	176	22s15p6d4f	7s4p3d2f	91.71	91.82	91.34	91.66	91.70	91.63	91.67
ET-B	285	22s15p13d11f	9s7p5d3f	91.54	91.78	91.35	—	91.65	—	91.63
aug4-gd	112	13s7p5d4f3g	6s3p2d	91.82	91.79	91.42	91.75	91.70	91.70	91.67
aug5-gd	132	15s9p6d5f4g	8s4p3d	91.78	91.78	91.38	91.71	91.69	91.68	91.65
aug6-gd	172	17s11p7d6f5g	10s5p4d	91.78	91.78	91.38	91.71	91.69	91.68	91.66
aug6-gd+DS	216	18s12p10d8f6g	10s7p5d	91.78	91.78	91.38	91.71	91.70	91.67	91.65
ET-C	335	22s15p12d10f8g	10s5p4d3f	91.73	91.79	91.36	—	91.69	—	91.66

^aBasis for H is cc-pVQZ instead of cc-pV5Z^bThe CCSDT1A and CCSDT1-R12 values with the ET-A basis are: CCSDT1A, $r_e = 91.66$ pm; CCSDT1-R12, $r_e = 91.71$ pm

Table 8. Effect of core (and core-valence) correlation on the equilibrium bond length r_e in HF (in pm). Neglecting these effects, the results in Table 7 are enlarged by the values given in the present table

Basis	Basis set description			Method							
	N	F	H	MP2	MP2-R12	CCSD	CCSD-R12	CCSD[T]	CCSD[T]-R12	CCSD(T)	CCSD(T)-R12
aug3-fd	74	11s6p3d2f	5s2p1d	0.032	0.058	0.037	0.074	0.037	0.069	0.032	0.069
aug4-fd	112	13s7p5d3f	6s3p2d	0.021	0.069	0.021	0.069	0.032	0.064	0.016	0.064
aug5-fd	168	15s9p6d5f	8s4p3d	0.064	0.064	0.064	0.064	0.058	0.069	0.053	0.069
aug6-fd	172	17s11p7d6f	10s5p4d	0.069	0.069	0.064	0.064	0.058	0.064	0.058	0.064

Table 9. Equilibrium distance and harmonic frequency of HF calculated at the Hartree-Fock level and with various density functionals calculated with the aug3-fd basis

Functional	r_e (pm)	ω_e (cm^{-1})
X α	93.420	3951.2
LSDA	93.245	3988.7
BP86	93.284	3956.4
BLYP	93.493	3917.7
B3LYP	92.404	4073.8
B3P86	92.127	4119.0
B3PW91	92.132	4115.8
SCF	89.696	4473.9
Exp. ^a	91.681	4138.3

^a [52]

postpone a detailed discussion of basis effects to Sect. 3.6.

There are rather large differences between the results from different levels of approximation for the electron correlation. We note, in particular, a difference of $\approx 6 \text{ cm}^{-1}$ between the two best approaches, namely CCSD(T)-R12 and CCSD[T]-R12.

For ET-A we have also performed CCSDT1-R12 calculations, which lead, like for r_e , to an ω_e very close to that from CCSD[T]-R12, actually to an ω_e smaller than $\approx 1 \text{ cm}^{-1}$ than the CCSD[T]-R12 value. Martin and Taylor [13] have – for DZP basis sets – compared CCSD(T) with full CI, and found that ω_e of CCSD(T) compared to that from full CI is too large by $\approx 6 \text{ cm}^{-1}$. We conclude indirectly that – in this case – ω_e from CCSD[T] or CCSDT1 should differ from that of full CI by only $\approx 1 \text{ cm}^{-1}$. This agrees with our observation that CCSD[T] appears to be very close to real truth (possibly too large by $\approx 1 \text{ cm}^{-1}$). So our best non-relativistic Born-Oppenheimer value for ω_e is that of CCSD[T] with the ET-C basis, i.e. 4142.0 cm^{-1} , which should correspond to a CCSDT1-R12 value of 4140.8 cm^{-1} . Relativistic effects (see Sect. 3.4) are likely to reduce this by 2.6 cm^{-1} , while adiabatic and non-adiabatic corrections are expected to matter less than 1 cm^{-1} . So we get to within $\approx 1 \text{ cm}^{-1}$ to the experimental ω_e of 4138.3 cm^{-1} [52].

Our tentative conclusion is that (1) quadruple excitations are not important, provided that one treats triple excitations by means of the iterative, non-perturbative CCSDT1-R12 method, and (2) that, for the calculation of r_e and ω_e , CCSD[T]-R12 is nearly as good, while CCSD(T)-R12 is in error for ω_e by $\approx 6 \text{ cm}^{-1}$.

Like for r_e , core-correlation effects are non-negligible for ω_e . Limitation to valence-only calculations (Table 11) would change ω_e by $\approx 5 \text{ cm}^{-1}$. Neglect of core correlation decreases ω_e . If one ignores core-correlation effects, one may, owing to a compensation of errors, be led to the conclusion that either CCSD(T) is better than CCSD[T], or that conventional calculations truncated at g -functions are good enough.

Hartree-Fock and density functional results are collected in Table 9. While SCF overestimates ω_e by $\approx 10\%$, density functional approximations currently underestimate ω_e . The range of DFT values goes from 3917.7 cm^{-1} for BLYP to 4119.0 cm^{-1} for B3P86. The best DFT result (B3P86) is off from experiment by

Table 10. Harmonic frequency ω_e of HF for various methods and basis sets (in cm^{-1})

Basis	Basis set description				Method: ω_e (cm^{-1})							
	N	F	H		MP2	MP2-R12	CCSD	CCSD-R12	CCSD[T]	CCSD[T]-R12	CCSD(T)	CCSD(T)-R12
aug5-fd	142	15s9p6d5f	8d4p3d		4142.9	4137.5	4193.9	4196.4	4138.1	4142.6	4144.6	4148.6
aug5-gd	178	15s9p6d5f + 4g	8d4p3d		4136.9	4138.7	4191.3	4197.1	4135.7	4142.4	4141.8	4148.3
aug5-hd	211	15s9p6d5f + 4g + 3h	8d4p3d		4140.5	4140.4	4195.6	4198.3	4140.1	4143.5	4146.1	4149.5
aug5-fd ^a	132	15s9p6d5f	6s3p2d		4142.7	4138.9	4193.5	4196.0	4137.8	4142.0	4144.2	4147.9
aug5-gd ^a	168	15s9p6d5f + 4g	6s3p2d		4137.5	4140.9	4194.2	4197.0	4136.5	4142.2	4142.6	4148.1
aug5-hd ^a	201	15s9p6d5f + 4g + 3h	6s3p2d		4139.8	4141.8	4195.2	4197.9	4139.8	4143.0	4145.7	4148.9
aug5-ff ^a	139	15s9p6d5f	6s3p2d + 1f		4153.7	4140.0	4204.6	4192.6	4149.3	4143.4	4155.7	4149.4
aug5-gf ^a	175	15s9p6d5f + 4g	6s3p2d + 1f		4138.4	4140.9	4193.1	4196.0	4137.4	4141.8	4143.2	4147.7
aug5-hf ^a	208	15s9p6d5f + 4g + 3h	6s3p2d + 1f		4139.3	4142.5	4195.0	4197.9	4139.6	4142.8	4145.5	4148.6
aug3-fd	74	11s6p3d2f	5s2p1d		4123.7	4141.4	4172.8	4199.8	4119.9	4152.6	4126.5	4158.4
aug4-fd	112	13s7p5d4f	6s3p2d		4142.9	4139.9	4193.1	4198.4	4137.7	4144.9	4144.1	4150.8
aug5-fd	132	15s9p6d5f	8s4p3d		4142.9	4137.5	4193.9	4196.4	4138.1	4142.6	4144.6	4148.6
aug6-fd	172	17s11p7d6f	10s5p4d		4149.3	4141.0	4199.7	4198.2	4144.1	4144.4	4150.6	4150.4
aug6-fd + D	188	18s12p8d7f	10s5p4d		4149.2	4140.4	4199.8	4198.5	4144.0	4144.1	4150.5	4150.1
aug6-fd + DS	216	18s12p10d8f	10s7p5d		4150.0	4142.0	4199.5	4198.1	4144.8	4146.2	4151.3	4152.2
ET-A ^b		22s15p6d4f	7s4p3d2f		4146.8	4136.5	4197.5	4194.9	4142.1	4140.9	4148.1	4146.9
ET-B	285	22s15p13d11f	9s7p5d3f		4160.6	4138.8	—	4197.8	—	4143.8	—	4149.8
aug4-gd	112	13s7p5d4f3g	6s3p2d		4138.1	4142.0	4192.3	4199.9	4136.7	4145.3	4142.8	4151.2
aug5-gd	132	15s9p6d5f4g	8s4p3d		4136.9	4138.7	4193.9	4196.4	4135.7	4142.4	4141.8	4148.3
aug6-gd	172	17s11p7d6f5g	10s5p4d		4138.6	4139.9	4193.4	4199.7	4137.4	4142.4	4143.5	4148.3
aug6-gd + DS	216	18s12p10d8f6g	10s7p5d		4138.3	4140.2	4193.1	4197.9	4137.1	4142.5	4143.2	4148.4
ET-C	335	22s15p12d10f8g	10s5p4d3f		4144.8	4138.3	—	—	—	4142.0	—	4147.9

^a Basis for H is cc-pVQZ instead of cc-pV5Z^b The CCSDT1A and CCSDT1-R12 values with the ET-A basis are: CCSDT1A, $\omega_e = 4141.1 \text{ cm}^{-1}$; CCSDT1-R12, $\omega_e = 4139.7 \text{ cm}^{-1}$

20 cm^{-1} , the worst (BLYP) by more than 200 cm^{-1} . These are hardly candidates for spectroscopically accurate methods.

We have also evaluated $\omega_e x_e$, but only for the ET-A basis sets. The results are in Table 14 for the three isotopomers HF, DF, and TF (see Sect. 3.5).

3.4. Relativistic and beyond-Born-Oppenheimer effects

We have obtained relativistic corrections in the leading order $O(c^{-2})$ by means of direct perturbation theory (DPT) on Hartree-Fock [53] and MP2 levels [40] (Table 12).

To show the reliability of first-order DPT for the evaluation of relativistic corrections of molecules built up from light atoms like HF, we have performed calculations with the same basis set as used in Dirac-Hartree-Fock calculations recently published by Parpia and Mohanty [45]. The error for the total relativistic energy of our first-order DPT calculation on the SCF level is $196\text{ }\mu\text{E}_h$. The present authors are not aware of energy data for HF calculated with four-component

MP2 codes. However, from previous calculations on atoms [40], where a comparison with data from four-component methods was possible, we conclude that the MP2-DPT calculations give more than 95% of the relativistic correction to the MP2 energy.

We find a relativistic lowering of the energy of HF at the SCF level by 91.706 mE_h . The additional lowering on MP2 level is 0.194 mE_h for HF and 0.248 mE_h for F^- .

The relativistic effect (Table 13) on r_e is a decrease of 0.002 pm at SCF level and an increase of 0.004 pm on the MP2 level owing to the so-called cross-terms between relativity and correlation. We expect that on a correlated level of higher sophistication there is an increase of r_e , but probably by somewhat less than on the MP2 level. Anyway, this effect is very small.

For ω_e the relativistic effect is more clear-cut. On the SCF level, ω_e is reduced by 2.1 cm^{-1} , on the MP2 level by 2.6 cm^{-1} . This effect is not very sensitive to variations of the basis ($\approx 0.2\text{ cm}^{-1}$). The cross terms between relativity and correlation have only a small effect (-0.5 cm^{-1}) on ω_e .

On Fig. 1 we have plotted the dependence of the relativistic correction on the internuclear distance. The relativistic correction has a maximum near r_e . This

Table 11. Effect of core (and core-valence) correlation on the harmonic frequency ω_e in HF (in cm^{-1}). Neglecting these effects, the results in Table 10 are reduced by the values given in the present table

Basis		Basis set description		Method							
Name	N	F	H	MP2	MP2-R12	CCSD	CCSD-R12	CCSD[T]	CCSD[T]-R12	CCSD(T)	CCSD(T)-R12
aug3-fd	74	11s6p3d2f	5s2p1d	-2.6	-5.5	-3.5	-7.9	-2.7	-7.5	-2.4	-7.1
aug4-fd	112	13s7p5d3f	6s3p2d	-2.0	-5.1	-3.3	-5.8	-2.3	-4.8	-1.9	-4.5
aug5-fd	168	15s9p6d5f	8s4p3d	-4.7	-4.4	-5.7	-6.1	-4.8	-5.4	-4.5	-5.0
aug6-fd	172	17s11p7d6f	10s5p4d	-5.3	-5.3	-5.9	-5.9	-4.9	-5.2	-4.9	-4.8

Table 12. Comparison of various relativistic and non-relativistic SCF and MP2 results for various basis sets

Basis	HF				F ⁻
	[45]	ET-A	ET-B (<i>spd</i>)	ET-B (<i>spdf</i>)	ET-B (<i>spdf</i>)
F	22s16p4d1f	22s15p6d4f	22s15p13d	22s15p13d11f	22s15p13d11f
H	11s4p1d	7s4p3d2f	9s7p5d	9s7p5d3f	9s7p5d3f
SCF	-100.069744	-100.070653	-100.070389	-100.070778	-99.459446
MP2	-100.398833	-100.424749	-100.401167	-100.432635	-99.834779
SCF-DPT	-100.161452	-100.162359	-100.162095	-100.162484	-99.551077
MP2-DPT(a) ^a	-100.459540	-100.516455	-100.492873	-100.524341	-99.926410
MP2-DPT(b) ^a	-100.490746	-100.516670	-100.493084	-100.524535	-99.926658

^a Variant (a) means that the cross-term of relativity and correlation is neglected. Variant (b) denotes the inclusion of this term. When not indicated otherwise, all references in the text refer to variant (b)

Table 13. SCF and MP2 results for HF, DF, and TF with and without relativistic corrections^{a,b}

	$E(r = 1.7328)$	r_e (pm)	ω_e (cm^{-1})		
			HF	DF	TF
SCF	-100.070778	89.700	4473.9	3241.4	2712.9
SCF-DPT	-100.162484	89.698	4471.8	3241.8	2711.6
MP2	-100.432635	91.544	4160.7	3016.3	2522.9
MP2-DPT(a) ^b	-100.524341	91.543	4158.4	3014.6	2521.2
MP2-DPT(b) ^b	-100.524535	91.547	4157.9	3014.2	2521.2
MP2-R12	-100.454522	91.775	4138.8	3000.4	2509.7

^a The basis set ET-B

^b Variant (a) means that the cross-term of relativity and correlation is neglected. Variant (b) denotes the inclusion of this term. When not indicated otherwise, all references in the text refers to variant (b)

makes understandable why there is little effect on the equilibrium distance, but a significant one (lowering) on the harmonic vibration frequency.

Huber and Herzberg [52] give three different r_e values for the isotopomers HF (91.681 pm), DF (91.694 pm), and TF (91.76 pm). In principle, adiabatic corrections could lead to differences in r_e for isotopomers. Using data from Kolos et al. [2, 4] we have evaluated this effect for H_2 and its isotopomers, where we find an increase of r_e with respect to the Born-Oppenheimer value by a factor 1.00028 for H_2 , 1.00014 for D_2 , and 1.00009 for T_2 , i.e. a decrease of r_e from H_2 towards T_2 . The corresponding ratio for H_2 obtained by Handy and Lee [25] at the Hartree-Fock level is 1.00029. Hence for H_2 the effect of electron correlation on the adiabatic corrections is very small. If this also holds for HF, we can rely on the Hartree-Fock ratio 1.000025 [25] for HF, and corresponding factors closer to 1 for DF and TF. This means we should expect for HF a very small increase with respect to the BO-value by ≈ 0.0025 pm and a corresponding decrease of r_e from HF via DF to TF and not a (relatively large) increase as the data of Huber and Herzberg suggest.

We shall later show that the experimental r_e values for DF and TF used in [52] are rather inaccurate due to an insufficient number of data for the extrapolation from the B_v to B_e , and moreover that the conversion from the B_e to the r_e has been based on “wrong” masses, such that there are no indications for a significant difference of r_e between HF, DF and TF.

According to Handy and Lee [25], the harmonic vibrational frequency is more influenced by non-adiabatic than by adiabatic effects, the former being simulated by replacing the nuclear by the atomic masses. This change amounts to 1.5 cm^{-1} at the Hartree-Fock level, while we find a decrease of ω_e by $\approx 1 \text{ cm}^{-1}$. Note that all our tabulated values for vibrational frequencies were obtained with atomic masses (unless indicated otherwise). The adiabatic effect of [25] is a lowering of ω_e by $\approx 0.3 \text{ cm}^{-1}$.

There was actually an inconsistency in Table 2 of [25]. Correspondence with the authors revealed that entry (f) should be changed from 4357.53 to 4357.91 cm^{-1}

3.5. The isotopomers

The results for ω_e of the various isotopomers HF, DF, and TF are collected in Table 14 for various methods, but for a single basis set, namely ET-A. This is not our very best set, and there is some indication (see Sect. 3.3) that it underestimates ω_e by $\approx 1 \text{ cm}^{-1}$, but it is the only set for which we could afford CCSDT1-R12 calculations. It is also the set with which the quantum mechanical calculations of the IR spectrum (see Sect. 3.7) were performed, such that a direct comparison is possible. The comparison with experiment is puzzling insofar as the difference theory (CCSD[T]-R12 versus experiment) has a maximum for DF.

This puzzle is resolved if one does not take the ω_e values from Huber and Herzberg [52] uncritically, but looks at their sources [54–57]. While there is nothing wrong with the experimental ω_e for HF, that for DF was based on two observed frequencies ν and 2ν only [56]. Recently two more frequencies 3ν and 4ν were reported [58, 59]. If one includes them in the extrapolation, an ω_e is obtained that is in good agreement with our theoretical estimate. The ω_e for TF [57] was based on ν and 2ν as well, but with some additional assumptions.

3.6. Detailed discussion of basis effects

The dependence of ω_e on the basis, which looks rather unsystematic at first glance, deserves some comments. Let us first mention that our calculations were not corrected for basis-set superposition errors (BSSE), since this would require programs that treat open-shell

Fig. 1. First-order relativistic corrections to the SCF and MP2 energy for the HF molecule

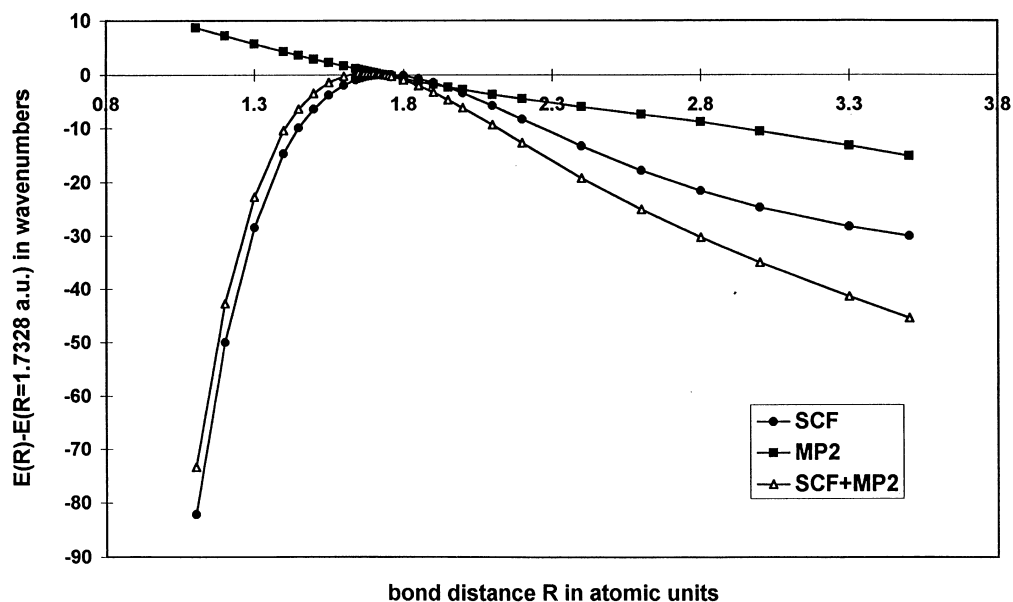


Table 14. Results for ω_e , $\omega_e x_e$, and B_e^a of the three isotopomers HF, DF, and TF as evaluated directly from the potential curve with the ET-A basis with various methods

	HF			DF			TF		
	ω_e	$\omega_e x_e$	B_e	ω_e	$\omega_e x_e$	B_e	ω_e	$\omega_e x_e$	B_e
MP2	4146.8	86.49	20.955	3006.2	45.46	11.010	2514.5	31.80	7.702
MP2-R12	4136.5	86.69	20.901	2998.8	45.56	10.982	2508.3	31.87	7.683
CCSD	4197.5	87.30	21.125	3043.0	45.88	11.099	2545.3	32.10	7.765
CCSD-R12	4194.9	87.60	21.101	3041.1	46.04	11.087	2543.7	32.69	7.756
CCSD[T]	4142.1	88.85	20.977	3002.8	46.69	11.022	2511.0	32.67	7.711
CCSD[T]-R12	4140.9	89.10	20.957	3002.0	46.83	11.011	2511.7	32.76	7.703
CCSD(T)	4148.6	88.59	20.992	3007.5	46.56	11.030	2615.6	32.57	7.716
CCSD(T)-R12	4147.0	88.86	20.971	3006.4	46.70	11.018	2514.7	32.67	7.708
CCSDT1A	4141.1	88.79	20.974	3002.1	46.66	11.020	2511.1	32.65	7.709
CCSDT1-R12	4139.7	89.06	20.953	3001.0	46.80	11.009	2510.2	32.74	7.702
CCSDT1-R12 + MP2-DPT	4136.9	89.99	20.951	2999.4	46.77	11.008	2508.5	32.72	7.701
Exp.	4138.3 ^b	89.88 ^b	20.956 ^b	2998.2 ^c	45.76 ^c	11.010 ^c	2508.5 ^d	32.5 ^d	7.692 ^d
	4138.4 ^e	89.92 ^e	–	3000.3 ^e	47.44 ^e	–	–	–	–

^a All ω_e and $\omega_e x_e$ values were calculated using atomic masses, while nuclear masses were used for the evaluation of B_e (see Sect. 3.7)

^b [52], [54], [55], and [59]

^c [52], [56], based only on 1ν and 2ν

^d [52], [57]

^e Extrapolation from $1\nu, 2\nu, 3\nu$, and 4ν ; for DF, data from [58] and [59] were included

systems, which are not yet available. Of course, for large enough basis sets, BSSE converges to zero. Moreover, they are always much smaller for R12 methods than for their conventional counterparts [18].

Let us first have a look at the dependence of the Hartree-Fock energies on the basis. Actually chemical accuracy is achieved if the F basis is sufficiently saturated in the *spdf* part; *g* or *h* functions only play a marginal role. Beyond the aug5-fd basis there is not much improvement. The aug3-fd basis leads to errors of almost 10mE_h , the basis aug4-fd of only $\approx 2\text{mE}_h$, which looks rather acceptable. This holds both for HF and F^- .

For the calculation of the correlation energy with the R12 methods, again aug3-fd is too small, with errors varying around 10mE_h , while aug4-gf implies only an error $\approx 2\text{mE}_h$ (slightly more for MP2). The effect of *g* functions on F is noticeable (lowering by $\approx 2\text{mE}_h$), but *h* functions on F or *f* functions on H have only a marginal effect. We have not included basis sets without *f* on F; they would not be acceptable [62].

For the conventional calculations (without R12) the situation is quite different: *g* functions have an effect of $\approx 10\text{mE}_h$, *h* functions of $\approx 3\text{mE}_h$. To compete with R12 calculations up to *g*, in conventional calculations up to *i* functions or beyond ought to be included – at least as far total energies are concerned.

For r_e one finds in the calculations with R12 that *g* and *h* functions increase r_e slightly, while saturation of the low angular momenta reduces r_e . Without R12 one finds – on the whole – a decrease for both types of basis improvement. The effects are very small, especially if one leaves out the aug3-fd basis. For the largest basis sets the results with and without R12 have converged to within 0.01 pm.

For ω_e with R12, *g* and *h* functions mostly increase ω_e slightly, while saturation of the low angular momenta

lead, on the whole, to a slight decrease of ω_e . Leaving out the aug3-fd basis, the basis dependence of ω_e is very small. This is different in calculations without R12. Here *g* and *h* functions increase ω_e , while the saturation of the low angular momenta does not look systematic. Even for the largest basis sets – without *h* functions on F – (considered here), the conventional ω_e values have not converged to the R12 counterpart, they are still too small by as much as 5cm^{-1} . The discrepancy is reduced to roughly $1\text{--}2\text{cm}^{-1}$ if *h* functions on F are included. The answer to the question [6] “are *h* functions enough?” can be answered as: this depends on the accuracy that one wants to achieve. Spectroscopic accuracy in a strict sense is certainly not possible without *h* functions (unless one uses R12 methods). However, a higher level of the treatment of correlation is necessary before one would care to extend the basis beyond *h*.

Usually the inclusion of R12 increases ω_e (and decreases r_e). This is, however, not the case for basis sets truncated at *f* (for both F and H), where it is probably due to a BSSE. The basis for F is too poor (but only in the conventional calculations) and picks up functions on H and this more for small than for large distances, which leads to an artificial decrease of r_e and increase of ω_e . This artifact is absent in the R12 calculations.

While, at the basis set limit, CCSD[T] yields a better ω_e than CCSD(T) (where ω_e is too large by $\approx 6\text{cm}^{-1}$), truncating a conventional calculation at *g* functions may lead to the conclusion that CCSD(T) is better (because two errors compensate each other).

Let us finally try to find out basis sets which reduce the computational effort required for the large sets ET-C or aug-6-gd-DS, but are almost as good. Good choices appears to be aug-5-hd (201), aug-6-gd (172), aug-5-gd(132), and ET-A (176), where the number of basis functions are indicated in parentheses. The ET-A basis appears to be a particularly good compromise.

3.7. The theoretical versus the experimental IR spectrum

For the evaluation of the vibrational levels the potential curve for a more extended region, say up to $r = 3.5a_0$ is needed. There is a problem with the CCSD(T) and CCSD[T] methods, insofar as these – in spite of performing well near the equilibrium distance – become unreliable for large distances, e.g. showing a spurious hump in the potential curve [60]. The iterative CCSDT1A-method, although only slightly better than CCSD[T] near the minimum, does not show such artifacts and approaches the asymptotic limit rather smoothly. We have therefore based the calculation of the IR spectra mainly on CCSDT1-R12 calculations, and have included CCSD(T)-R12 and CCSD[T]-R12 as well as their conventional counterparts without R12 only for the sake of comparison.

We could not afford a CCSDT1-R12 calculation with our best basis set, and we decided to choose the basis ET-A as a compromise. The results for the vibrational frequencies are in Tables 15–17. We have also displayed the error of various calculations graphically on Figs. 2 and 3.

Since we have shown that relativistic effects are non-negligible, but since we are not able to perform relativistic calculations at the CCSDT1-R12 level, we have taken the relativistic corrections from a MP2-DPT calculation and added these corrections to the CCSDT1-R12 curve. We offer this “combined” curve as our best theoretical potential curve. It is documented in Table 18.

For small v the error of the computed frequencies ν_{v-0} , also called νv , with experiment is essentially linear in v (and ν) for all considered approaches. For these small v -values the error is roughly three times larger for CCSD(T) than for CCSD[T] or CCSDT1A. The difference between the latter two methods is relatively small. Inclusion of R12 terms leads generally to an improvement. This is not so significant for small v , but spectacular for large v (v between 10 and 15). The inclusion of relativistic corrections leads CCSDT1-R12 very close to experiment for all observed frequencies, with a relative error of $\approx 5 \times 10^{-5}$ for all isotopomers.

It is in view of the good agreement of the computed with the experimental vibrational frequencies up to $v = 19$ that we have decided to document the potential energy surface based on CCSDT1-R12 with relativistic corrections (Table 18). The zero-point energies obtained quantum mechanically with this basis are 9.323 mE_h for HF, 6.779 mE_h for DF, and 5.677 mE_h for TF.

We have also used our theoretical ν_{v-0} values to extrapolate ω_e in the way spectroscopists do this. Differences to the directly computed ω_e of $\approx 0.3 \text{ cm}^{-1}$ were found.

Since there is some inconsistency in the experimental r_e values for the isotopomers DF and TF, we have decided to compare directly the data from which r_e was extracted, i.e. the rotational structure of the vibrational bands.

The B_v, D_v, B_e and D_e values are compared in Table 19. These are still not directly measured quantities, but at least the extrapolation to the B_v from rotational-

Table 15. Results for the vibrational frequencies of HF from the quantum mechanical calculation of the IR spectrum for various methods with the ET-A basis

Method	ν_{1-0}	ν_{2-0}	ν_{3-0}	ν_{4-0}	ν_{5-0}	ν_{6-0}	ν_{7-0}	ν_{8-0}	ν_{9-0}	ν_{10-0}
CCSD[T]	3966.57	7761.01	11387.63	14850.02	18150.90	21292.12	24274.44	27097.46	29759.67	32258.11
CCSD[T]-R12	3965.26	7759.01	11385.67	14849.12	18152.55	21298.35	24287.90	27121.50	29798.38	32316.34
CCSD(T)	3973.66	7775.86	11410.96	14882.59	18193.66	21346.22	24341.44	27179.08	29858.50	32377.33
CCSD(T)-R12	3971.83	7772.78	11407.29	14879.32	18192.18	21348.46	24349.83	27196.97	29889.61	32426.19
CCSDT1A	3965.71	7759.63	11386.07	14848.67	18150.41	21293.50	24279.34	27108.38	29780.31	32293.74
CCSDT1-R12	3964.04	7756.84	11382.28	14845.96	18149.58	21296.44	24288.44	27126.61	29811.19	32341.32
CCSDT1-R12 + MP2-DPT	3961.35	7751.55	11375.03	14835.73	18137.01	21281.59	24271.36	27107.35	29789.75	32317.62
Experiment	3961.42 ^a	7750.79 ^a	11372.78 ^a	14831.63 ^a	18130.97 ^b	21273.69 ^b	24262.18 ^b	27097.87 ^b	29781.33 ^b	32311.79 ^b

^a [59]

^b [54]

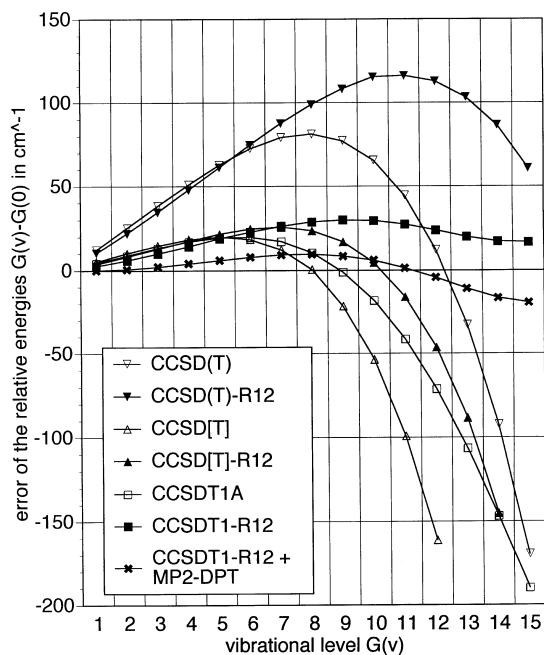
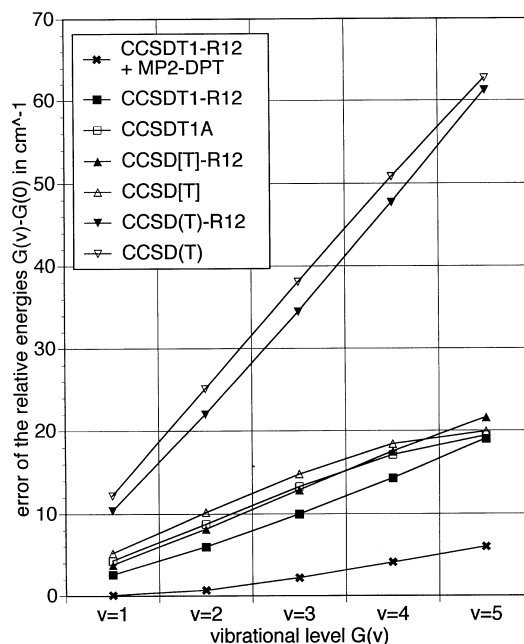
Table 16. Results for the vibrational frequencies of DF from the quantum mechanical calculation of the IR-spectrum for various methods with the ET-A basis

Method	ν_{1-0}	ν_{2-0}	ν_{3-0}	ν_{4-0}	ν_{5-0}	ν_{6-0}	ν_{7-0}	ν_{8-0}	ν_{9-0}	ν_{10-0}
CCSD[T]	2909.42	5727.68	8456.58	11097.74	13652.75	16122.91	18509.23	20812.78	23034.06	25173.50
CCSD[T]	2909.42	5727.68	8456.58	11097.74	13652.75	16122.91	18509.23	20812.79	23034.06	25173.50
CCSD(T)	2915.51	5739.89	8474.94	11122.25	13683.29	16159.28	18551.11	20859.72	23085.47	25228.72
CCSD(T)-R12	2914.06	5737.29	8471.48	11118.29	13679.31	16155.89	18549.09	20860.07	23089.40	25237.69
CCSDT1A	2909.81	5728.34	8457.33	11098.39	13652.98	16122.33	18507.37	20809.12	23028.02	25164.58
CCSDT1-R12	2908.48	5725.95	8454.20	11094.86	13649.51	16119.54	18506.02	20810.18	23032.66	25174.18
CCSDT1-R12 + MP2-DPT	2906.51	5722.06	8448.43	11087.27	13640.14	16108.43	18493.22	20795.71	23016.57	25156.48
Experiment ^a	2906.66	5721.66	8447.38	11085.01	–	–	–	–	–	–

^a [59]

Table 17. Results for the vibrational frequencies of TF from the quantum mechanical calculation of the IR spectrum for various methods with the ET-A basis

Method	$\nu_{1\leftarrow 0}$	$\nu_{2\leftarrow 0}$	$\nu_{3\leftarrow 0}$	$\nu_{4\leftarrow 0}$	$\nu_{5\leftarrow 0}$	$\nu_{6\leftarrow 0}$	$\nu_{7\leftarrow 0}$	$\nu_{8\leftarrow 0}$	$\nu_{9\leftarrow 0}$	$\nu_{10\leftarrow 0}$
CCSD[T]	2447.14	4829.96	7149.54	9406.85	11602.90	13738.37	15814.04	17830.47	19788.18	21687.40
CCSD[T]-R12	2446.18	4828.27	7147.35	9404.39	11600.46	13736.30	15812.80	17830.60	19790.35	21692.42
CCSD(T)	2451.28	4838.48	71627.03	9424.90	11626.09	13766.99	15848.40	17870.91	19835.08	21741.22
CCSD(T)-R12	2450.02	4836.18	7159.55	9421.12	11621.96	13762.84	15844.65	17868.08	19833.82	21742.29
CCSDT1A	2446.54	4828.89	7148.12	9405.20	11601.13	13766.63	15812.50	17829.36	19787.81	21688.20
CCSDT1-R12	2445.38	4826.77	7145.25	9401.78	11597.44	13733.00	15809.35	17827.20	19787.25	21690.00
CCSDT1-R12 + MP2-DPT	2443.72	4823.49	7140.38	9395.37	11589.51	13723.58	15798.67	17814.89	19773.54	21674.89
Experiment ^a	2443.86	4823.8	—	—	—	—	—	—	—	—

^a [52]**Fig. 2.** Error of the calculated vibrational frequencies $\nu_{v\leftarrow 0}$ in cm^{-1} as obtained with the ET-A basis with various CC methods**Fig. 3.** Error of the calculated vibrational frequencies $\nu_{v\leftarrow 0}$ in cm^{-1} as obtained with the ET-A basis with various CC methods

vibrational spectra should not be problematic since usually a sufficient number of rotational lines is available. The difference between theory and experiment for the B_v and B_e is generally smaller than $\approx \pm 0.02\%$ both for HF and DF (with the theoretical B_e smaller than the experimental one), while for TF there is a larger and apparently systematic deviation of $\approx 0.1\%$ in the B_v , and with the opposite sign for the difference between theory and experiment for B_e .

To understand this inconsistency we have gone one step further and compared directly the rotational-vibrational spectra, which are displayed in Table 20. Now we find systematic errors of $\approx 0.05\%$ for all isotopomers (with the theoretical values greater than the experimental ones – except for the P-band of TF), but a substantial noise superimposed on the experimental values of TF. Since the experiments on TF are rather old [57], it is not surprising that their accuracy was limited (as also admitted by the authors).

In Table 21 one sees the comparison between theory and experiment for the pure rotational spectrum of HF [59] and DF [61]. The better agreement with the recent data for HF [59] (deviations of $\approx 0.01\%$) than with the old ones [61] for DF (deviations of $\approx 0.1\%$) is certainly due to the higher accuracy of the recent values.

To get an idea of the error that we expect for B_e , we note that the r_e obtained from the CCSDT1-R12 (basis ET-A) curve with relativistic corrections is 91.71 pm while our best prediction of r_e is 91.70 pm. Hence we should underestimate B_e by $\approx 0.02\%$, as we actually do. So the comparison with the experimental B_e confirms our best $r_e = 91.70$ pm. This is in slight disagreement with the spectroscopic value [52] of 91.68 pm. This difference can be explained if one notes that the spectroscopic r_e is based on identifying

$$B_e = \frac{\hbar^2}{2\mu r_e^2} \quad (2)$$

Table 18. Total energies of all points of the CCSDT1A and CCSDT1-R12 potential energy curves of HF and values of the relativistic correction at the MP2-DPT level (in hartree) with the basis ET-A

r (a_0)	CCSDT1A	CCSDT1-R12	Relativistic correction from MP2-DPT
1.1000	-100.105089828	-100.127116613	-0.0920802864
1.2000	-100.239049133	-100.261127302	-0.0919338712
1.3000	-100.325436385	-100.347549512	-0.0918359136
1.4000	-100.379424306	-100.401578049	-0.0917729684
1.5000	-100.411220256	-100.433438350	-0.0917350631
1.5500	-100.421069636	-100.443325349	-0.0917231134
1.6000	-100.427795880	-100.450089295	-0.0917148218
1.6500	-100.431937365	-100.454266392	-0.0917095648
1.7000	-100.433941749	-100.456302910	-0.0917068083
1.7328	-100.434277824	-100.456657849	-0.0917061360
1.7500	-100.434181943	-100.456571134	-0.0917060962
1.8000	-100.432969241	-100.455382311	-0.0917070399
1.8500	-100.430564101	-100.452997203	-0.0917093096
1.9000	-100.427184971	-100.449634712	-0.0917126247
1.9500	-100.423015484	-100.445478904	-0.0917167509
2.0000	-100.418210321	-100.440684804	-0.0917214882
2.2000	-100.394957983	-100.417453452	-0.0917436408
2.4000	-100.369001323	-100.391478570	-0.0917665058
2.6000	-100.343303695	-100.365712923	-0.0917871170
2.8000	-100.319368109	-100.341648877	-0.0918045455
3.5000	-100.257089869	-100.278366079	-0.0918432893
10.0000	-100.23101 ^a	-100.23101 ^a	-0.091906 ^a

^a Extrapolated

(in energy units). The relation between r_e and B_e depends on the value inserted for the reduced mass. If one constructs μ from atomic masses, as is customary in spectroscopy, one gets for HF a r_e value smaller by $\approx 0.02\%$ than that evaluated using nuclear masses. We believe [25–28] that the nuclear masses are the right choice for the rotational (not the vibrational) problem, and we have made this choice in our quantum computation of the rotational frequencies. One cannot tell with sufficient accuracy what the experimental r_e is, as long as one has not understood which masses should be taken in order to simulate non-adiabatic effects. If there were no non-adiabatic effects, the nuclear masses had to be taken anyway. The reason behind this problem is that in an exact theory – and in experiment – a potential surface, and hence an equilibrium distance, is not defined. Only the IR frequencies are observables.

Taking the experimental B_e values for HF and DF, and using the nuclear rather than the atomic masses for the construction of r_e , we get $r_e = 91.705$ pm for HF and practically the identical value $r_e = 91.706$ pm for DF, in agreement with our best prediction, and confirming again the superiority of CCSDT1-R12 or CCSD[T]-R12 over CCSD(T)-R12. The larger experimental r_e value for DF than for HF [52] is obviously an artifact due to the use of atomic rather than nuclear masses. This statement is perfectly confirmed by our analysis of H₂ and its isotopomers to be published elsewhere.

4. Conclusions

The present study has revealed that for such a simple molecule as HF it is not easy to obtain vibrational frequencies with an error of less than ≈ 1 cm⁻¹. This is in contrast with the observation [16] that standard CCSD(T) calculations with moderate basis sets are able to predict vibrational frequencies for larger, even polyatomic, molecules with an accuracy of ≈ 8 cm⁻¹. This average error has the magnitude of the difference between CCSD(T)-R12 and CCSD[T]-R12 for our example.

The main message of the present paper is that with the R12 method one is able to get sufficiently close to the basis limit even for not too large basis sets, such that basis saturation is possible; however, it is more delicate to reach the limit of the level of the treatment of electron correlation. The relatively poor performance of CCSD is an indication that triple excitations are important. The difference between CCSD(T) and CCSD[T] indicates that the approximation of the triple excitation matters and that possibly even quadrupole excitations may play a role.

The good performance of CCSDT1A as far as agreement with experiment is concerned, as well as the indirectly confirmed closeness of CCSD[T] with full CI, appears to indicate that CCSDT1A is the best choice among the methods which are feasible, with CCSD[T] nearly as good, at least near the equilibrium distance.

This is a challenge to consider, in forthcoming studies CCSD[T] calculations more seriously and to compare them with CCSD(T). From our present experience it appears that CCSD(T) overestimates ω_e by ≈ 6 cm⁻¹, but that truncation of the basis at g functions in a conventional CCSD(T) calculation leads to an underestimation of ω_e of the order of 5 cm⁻¹, and so does neglect of core-correlation effects, while neglect of relativistic effects causes an overestimation of 2–3 cm⁻¹. So using CCSD(T), but truncating the basis at g and neglecting both core correlation and relativistic effects, one may arrive at a spurious “spectroscopic” accuracy due to a fortunate error compensation.

More studies are needed to see whether this is a special feature of HF, or whether it is more general.

The only molecule that we have treated so far at a comparable level is LiH [11]. There we obtained ω_e too large by ≈ 1 cm⁻¹, but there was practically no difference between CCSD(T)-R12, CCSD[T]-R12, and CCSDT1-R12, indicating that triple excitations do not play a decisive role. The remaining discrepancy is possibly due to neglect of NBO effects, which are expected to be larger in LiH than in HF, while relativistic effects are probably smaller. Like in the present case, conventional calculations (without R12) tend to underestimate ω_e by a few cm⁻¹ unless a very large basis is used. Note that, long ago, Meyer and Rosmus [12] obtained ω_e of LiH with an error of only ≈ 4 cm⁻¹.

The wealth of basis sets included in the present study may look excessive. It does, however, allow conclusions how basis sets should be chosen in future calculations of larger molecules. The question of how large the basis must be in order to approach the limit can be answered,

Table 19. Results for B_v , B_e , D_v , D_e , and α (in cm^{-1}) calculated with the ET-A basis at the CCSDT1-R12+MP2-DPT level of theory

v	HF				DF				TF			
	B_v		$D_v \times 10^4$		B_v		$D_v \times 10^4$		B_v		$D_v \times 10^4$	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
0	20.557	20.560 ^f	20.87	21.12 ^f	10.858	10.860 ^f	5.873	5.87 ^f	7.613	7.603 ^h	2.874	2.6 ^h
1	19.788	19.787 ^f	20.62	20.64 ^f	10.563	10.564 ^f	5.752	5.76 ^f	7.440	7.431 ^h	2.818	2.7 ^h
2	19.037	19.035 ^f	20.07	20.15 ^f	10.273	10.273 ^f	5.644	5.67 ^f	7.269	7.266 ^h	2.764	2.9 ^h
3	18.304	18.301 ^f	19.57	19.61 ^f	9.988	9.988 ^f	5.511	5.52 ^f	7.101	–	2.720	–
4	17.587	17.582 ^f	19.09	19.12 ^f	9.708	9.707 ^f	5.439	5.14 ^f	6.936	–	2.704	–
5	16.883	16.879 ^g	18.68	18.64 ^g	9.433	–	5.343	–	6.772	–	2.653	–
6	16.190	16.190 ^g	18.29	18.38 ^g	9.162	–	5.275	–	6.611	–	2.607	–
7	15.506	15.503 ^g	18.01	17.96 ^g	8.894	–	5.158	–	6.452	–	2.550	–
8	14.825	14.827 ^g	17.73	17.76 ^g	8.629	–	5.119	–	6.295	–	2.541	–
9	14.144	14.150 ^g	17.57	17.56 ^g	8.367	–	5.037	–	6.139	–	2.490	–
	B_e		$D_e \times 10^4$		B_e		$D_e \times 10^4$		B_e		$D_e \times 10^4$	
	20.9487 ^a	20.9557 ⁱ	2.098 ^a	2.151 ⁱ	11.0077 ^a	11.0102 ⁱ	5.796 ^a	5.94 ⁱ	7.7009 ^a	7.692 ⁱ	2.9146 ^a	2.6 ⁱ
	20.9510 ^b				11.0080 ^b				7.7010 ^b			
	20.9399 ^c				11.0050 ^c				7.6995 ^c			
	r_e (pm)		r_e (pm)		r_e (pm)		r_e (pm)		r_e (pm)		r_e (pm)	
	Calc.	Exp. ⁱ	Calc.	Exp. ⁱ	Calc.	Exp. ⁱ	Calc.	Exp. ⁱ	Calc.	Exp. ⁱ	Calc.	Exp. ⁱ
	91.720	91.705 ^d			91.717	91.706 ^d			91.716	91.769 ^d		
		91.680 ^e				91.694 ^e				91.760 ^e		

Values for α_e : HF: calc. 0.788, exp.^k 0.798; DF: calc. 0.301, exp. 0.302; TF: calc. 0.176, exp. 0.176

^a Extrapolated from B_v and D_v , respectively (nuclear masses were used for the evaluation of B_v and D_v)

^b From r_e as minimum of the potential curve, calculated with nuclear masses

^c From r_e as minimum of the potential curve, calculated with atomic masses

^d Obtained from B_e using nuclear masses

^e Obtained from B_e using atomic masses

^f [59] ^g [55] ^h [56] ⁱ [57] ^k [52]

but the answer is different for methods without and with R12. While in conventional calculations a sufficient number of basis functions with high angular momentum is necessary, this is not the case for calculations with the R12 methods. There f on F and d on H is practically sufficient, but the basis sets must be near-saturated for the low angular momenta. A strategy for choosing basis sets for R12 calculations has previously been suggested [18, 62], but has only partially been followed in more recent calculations. One can conclude from the present study that the ET-A basis is a good compromise with a minimum size for acceptable accuracy. One sees from our study also that convergence of ω_e within say 0.1 cm^{-1} is not even reached for very large basis sets, such that it is probably unrealistic to expect results of sub- cm^{-1} accuracy with methods of the type used here.

Repeating again the importance of the sufficiently high level of electron correlation, core correlation, and relativistic effects, we must also point out that NBO effects are smaller by roughly an order of magnitude, such that their inclusion is not required, as long as one does not control the treatment of electron correlation with sufficient accuracy. The situation is very different from the well understood cases of H_2 or H_3^+ .

The comparison of theoretical and experimental r_e or ω_e values can be dangerous. While the theoretical values

directly document properties of the potential curve at the minimum, the experimental counterparts are obtained by extrapolations based on certain assumptions. Often (like for DF or TF), lack of data makes these extrapolation uncertain. It is much more meaningful to compare directly theoretical and experimental IR frequencies.

As to r_e , it does not only depend on the extrapolation by which B_e is obtained, but also on the not finally answered question whether nuclear or atomic masses should be used. This makes a difference of $\approx 0.02\%$, which is small compared to other errors that are not yet under control, but it matters if one wants to approach real spectroscopic accuracy. In fact this mass problem makes the experimental r_e more uncertain than the theoretical one. The observed increase of r_e from HF to DF is probably an artifact due to the use of the wrong (atomic) masses for the evaluation of r_e from B_e .

Anyway, if one can afford this, one should not depend on the uncertainties of experimental r_e and ω_e values and compare directly computed observables, i.e. IR absorption frequencies and differences between these, with their theoretical counterparts.

The most challenging open question from the present study is to find out why CCSDT1-R12 performs so well and whether this is generalizable to other systems, provided that one pushes the effort as much as is done here.

Table 20. Comparison of the calculated and observed vibrational rotational spectra (in cm^{-1}) for $v_{1\leftarrow 0}$ and $v_{2\leftarrow 0}$. Rotational lines of the P- and R-branches are given relative to the Q-branch

(J)	HF				DF				TF			
	$v_{1\leftarrow 0}$		$v_{2\leftarrow 0}$		$v_{1\leftarrow 0}$		$v_{2\leftarrow 0}$		$v_{1\leftarrow 0}$		$v_{2\leftarrow 0}$	
	Calc.	Exp. ^a	Calc.	Exp. ^a	Calc.	Exp. ^b	Calc.	Exp. ^b	Calc.	Exp. ^c	Calc.	Exp. ^c
R(9)	+318.76	+318.54	+236.92	–	+182.47	+182.43	+150.72	+150.58	+132.10	131.99	+113.38	+113.2
R(8)	+295.08	+294.91	+227.94	+227.43	+167.25	+167.18	+141.25	+141.14	+120.64	+120.46	+105.31	+105.4
R(7)	+269.47	+269.33	+215.69	+215.42	+151.32	+151.18	+130.51	+130.41	+108.76	+108.72	+96.50	+96.7
R(6)	+241.98	+241.88	+200.10	+199.90	+134.70	+134.71	+118.50	+118.45	+96.50	+96.32	+86.95	+87.1
R(5)	+212.62	+212.56	+181.19	+181.03	+117.40	+117.39	+105.25	+105.21	+83.84	+83.81	+76.68	+77.0
R(4)	+181.47	+181.41	+159.00	+158.90	+99.44	+99.42	+90.75	+90.72	+70.79	+70.71	+65.67	+65.7
R(3)	+148.54	+148.53	+133.55	+133.48	+80.81	+80.81	+75.02	+74.99	+57.37	+57.24	+53.95	+54.0
R(2)	+113.89	+113.88	+104.89	+104.84	+61.54	+61.54	+58.06	+58.06	+43.57	+43.54	+41.52	+41.2
R(1)	+77.55	+77.55	+73.04	+73.01	+41.64	+41.64	+39.90	+39.92	+29.40	+29.32	+28.38	+28.3
R(0)	+39.57	+39.57	+38.07	+38.05	+21.12	+21.13	+20.54	+20.54	+14.88	+14.94	+14.54	+14.2
Q	3961.35	3961.42	7751.56	7750.81	2906.50	2906.67	5722.06	5721.82	2443.72	2443.87	4823.49	4823.7
P(1)	–41.11	–41.13	–41.11	–41.11	–21.71	–21.74	–21.71	–21.73	–15.23	–15.24	–15.23	–15.2
P(2)	–83.70	–83.72	–85.20	–85.22	–44.00	–44.02	–44.58	–44.60	–30.79	–30.79	–31.13	–31.1
P(3)	–127.74	–127.76	–132.24	–132.30	–66.86	–66.89	–68.60	–68.62	–46.69	–46.67	–47.71	–47.7
P(4)	–173.15	–173.19	–182.16	–	–90.26	–90.31	–93.74	–93.76	–62.91	–62.80	–64.96	–65.0
P(5)	–219.90	–219.94	–234.89	–235.00	–114.19	–114.23	–119.99	–120.04	–79.46	–79.18	–82.87	–82.0
P(6)	–267.92	–268.01	–290.40	–290.54	–138.64	–138.76	–147.72	–147.42	–96.31	–96.15	–101.43	–101.4
P(7)	–317.16	–317.26	–348.60	–348.80	–163.60	–163.64	–175.75	–175.86	–113.47	–113.35	–120.63	–120.3
P(8)	–367.56	–367.71	–409.44	–	–189.04	–189.13	–205.23	–205.37	–130.92	–130.75	–140.46	–140.3
P(9)	–419.07	–	–472.85	–473.18	–214.95	–215.26	–235.77	–	–148.66	–148.51	–159.93	–159.9
P(10)	–471.62	–471.86	–538.76	–	–241.32	–241.42	–267.32	–	–166.69	–166.58	–182.01	–182.0

^a [55]^b [56]^c [57]**Table 21.** Comparison of the calculated and observed pure rotational spectrum of HF and DF (in cm^{-1}). The theoretical results were obtained with the ET-A basis at the CCSDT1-R12+MP2-DPT level

J	HF		DF		
	CCSDT-1A-R12 + MP2-DPT	Exp. ^a	CCSDT-1A-R12 + MP2-DPT	Exp. ^b	Exp. ^c
1 → 2	82.16	82.17	43.41	43.56	43.42
2 → 3	123.12	123.12	65.09	65.07	65.10
3 → 4	163.92	163.94	86.72	86.75	86.73
4 → 5	204.52	204.54	108.29	108.33	108.31
5 → 6	244.87	244.90	129.79	130.06	–
6 → 7	284.92	284.95	151.21	151.57	151.24
7 → 8	324.62	324.65	172.53	172.74	172.57
8 → 9	363.92	363.95	193.75	193.82	193.78
9 → 10	402.78	402.79	214.83	214.87	214.87

^a [59]^b [61]^c [64]

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It is a pleasure to dedicate this paper to Wilfried Meyer, the great pioneer of spectroscopically accurate quantum chemical calculations. With respect to his landmark paper from 1975, the present state-of-the art study appears as hardly more than a slight improvement, noting that – depending on the property – only one or two orders of magnitude in the accuracy were gained.

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