

DREAM OR REALITY: COMPLETE BASIS SET FULL CONFIGURATION INTERACTION POTENTIAL ENERGY HYPERSURFACES

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1. OVERVIEW

All knowledge about molecules outside of our solar system comes from study of their spectra. Although laboratory measurements are usually the prime source for the data needed to interpret astronomical observations, there are a number of reasons why theory has played, and will continue to play, a central role in the study of molecules in space.

Astronomical environments, such as those found in the interstellar medium, are very different from those on earth. This dissimilarity leads to fundamentally different chemistry and to the production of species that can be hard to create in the laboratory. Theory can play an impor-

tant role in both predicting main features of spectra of such species or in looking for possible spectral matches.

Even where laboratory spectra have been recorded for a particular species, this data may only be partial. One such situation, which is particularly common for unstable or reactive species, is that wavelengths can be measured to high accuracy but there is no information on transition probabilities or line strengths. Line strength data are essential for obtaining useful information from astronomical spectra. Without them observation of a spectrum simply indicates that a particular species is present. Use of the line strengths gives column densities as well as the local temperature if thermodynamic equilibrium prevails, or other environmental information if a non-equilibrium environment is being probed. The H_3^+ molecule provides a good example of this situation. The laboratory infrared spectrum of H_3^+ is well known. Its original measurement [1], and indeed subsequent experiments, relied heavily on *ab initio* theory. H_3^+ has now been observed in giant planets, diffuse and dense clouds in the interstellar medium [2], and the remnants of a supernova [3]. The infrared spectrum of H_3^+ has provided a particularly powerful handle on ionospheric activity in giant planets [4], giving detailed information on a whole variety of effects including, for example, the electrojets which power the auroral activity on Jupiter. Yet while the characteristic wavelengths used for observations of H_3^+ all come from experiment, all line strengths used to model the spectra are theoretical and are the result of *ab initio* calculations [5].

Some astronomical applications, stellar models being a classic example, are particularly demanding on spectroscopic data. The stellar opacity problem for stars hotter than our own Sun was only solved by the systematic calculation of large quantities of spectral data for atoms and atomic ions by the international Opacity Project Team [6]. The spectroscopic properties of cooler stars are dominated by molecular absorptions [7]. However, to model the role of a triatomic molecule such as H_2O or HCN , which are important components of oxygen- and carbon-rich cool stars respectively, it may be necessary to consider up to a billion vibration-rotation transitions. The laboratory measurement and analysis of a dataset of transitions of this size is completely impractical. Recently this task has been addressed by theory, where large linelists of rotation-vibration transitions have been produced for HCN [8] and H_2O [9, 10]. It has been found that including these transitions can fundamentally alter conclusions about the structure of the stellar atmosphere [8]. Despite the use of very high level theory and large datasets, recent stellar models have shown, for example, that the best water linelists are still not adequate for reproducing the observed spectra [11]. Large datasets of

energy levels produced by theory can also be used to model other astronomically important properties such as temperature-dependent partition functions [12] or equilibrium constants [13].

The vibration-rotation spectrum of water is perhaps the most important and intensely studied of all molecular spectra. For instance, water vapour is thought to be responsible for absorbing 70% of the sunlight lost in a cloudless atmosphere [14]. Many decades of work have focused on measuring, analysing, and modeling the spectrum of water. In something of a theoretical triumph, Polyansky *et al.* [15, 16] have used the combination of high level *ab initio* electronic structure and variational nuclear motion calculations to assign 1687 transitions to water in the sunspot spectra recorded in the 10 – 20 μm region. Yet these transitions represent only about 15% of the clearly resolved features observed in sunspots in this spectral region. It is likely that nearly all the unassigned features are also due to water. Further significant progress in assigning these features will require corresponding theoretical developments. It is therefore important to consider all possible factors which influence the *ab initio* calculation of transition frequencies. The major factor determining the accuracy of a computed rotation-vibration spectrum is the potential energy hypersurface (PES) employed. State-of-the-art *ab initio* electronic structure calculations have become able to predict vibrational band origins (VBOs) of triatomics, like water, to within a few wavenumbers, and other spectroscopic properties with similar ($\sim 0.1\%$) accuracy [10, 15–21]. Standard treatments of molecular electronic structure theory tacitly neglect several physically significant factors which become important in high-accuracy theoretical work: core-valence electron correlation, coupling between electronic and nuclear motion, part of which is considered in the so-called diagonal Born–Oppenheimer correction (DBOC), and relativistic corrections. A number of groups have recently started exploring the validity of the Born–Oppenheimer approximation when calculating vibration-rotation spectra, using water as the test molecule [10, 22]. Electronic relativistic effects [23] are also receiving considerable interest, although attention is only starting to be paid to the possible spectroscopic consequences of the relativistic correction for light molecules [24–30].

2. INTRODUCTION

Ever since the Egyptians invented them, maps (*pinax* for Greeks, *orbis pictus* or *tabula* for Romans) have helped mankind to find directions in the known world and, at the same time, to make explorations

of the unknown world. In fact, the history of maps is intertwined with the history of mankind.

The concept of potential energy hypersurfaces [31, 32] is as fundamental to the understanding of most modern branches of chemistry and physics including almost the whole of spectroscopy and kinetics, as maps are for our everyday life. Nevertheless, PESs exist only within the so-called Born–Oppenheimer (BO) separation of electronic and nuclear motion [33, 34]. Following this separation, potential energy hypersurfaces for nuclear motion arise describing the variation in the total electronic energy of a chemical system as a function of its geometry (internal coordinates of the N constituent nuclei). Usually, attention is focused on cases where a single BO–PES is sufficiently uncoupled from other surfaces (electronic states) that their interaction may be ignored.

Despite their great importance, production of detailed and accurate maps took quite a long time to achieve. In a similar manner, due to methodological problems and insufficient computational power, *ab initio* quantum mechanical study of PESs remained unrealistic until about 1970.

Recent developments in electronic structure theory and computer technology have facilitated the computations necessary for the theoretical determination of high accuracy potential energy hypersurfaces. Theory is now capable, over a rather large range of geometries, of obtaining near chemical accuracy (± 1 kcal/mol) for the relative energies of small and medium-sized molecular systems. In favorable cases this translates into an accuracy of a few cm^{-1} for rovibrational eigenstates computed from these PESs, as shown below.

The computational errors in today’s approximate solutions to the time-independent non-relativistic electronic Schrödinger equation result from the truncation of the atomic orbital one-electron basis and the truncation of the n -electron basis of all Slater determinants that constitute the full configuration interaction (FCI) wave function. Techniques which aim to achieve chemical accuracy for energetic quantities include the Gaussian- n [35–38], the complete basis set (CBS) [39, 40], and the W - n [41] model chemistries. These approaches may rely on empirical parameters which are optimized to minimize the errors for a given test set of molecules. An alternative parameter-free method is the focal-point [42, 43] approach (see Section 4 below), which seeks to achieve the complete one-electron basis set (CBS) and n -electron (FCI) limit by performing a series of electronic structure computations employing convergent basis sets and correlation methods. The previously mentioned model chemistries may be considered as approximations to the focal-point approach, and are therefore more computationally efficient but

may be less accurate for certain troublesome cases. Furthermore, the focal-point approach allows efficient estimation of the remaining computational error [43–45] for the given problem, while in the case of model chemistries one needs to rely on average error estimates.

The determination of the complete one-electron basis set limit has received considerable attention in recent years [41,43–51]. Formulas have been advanced providing an estimate of the CBS energy limit from calculations employing systematically constructed families of basis sets (e.g., the correlation-consistent (cc) basis sets of Dunning and co-workers [52–54]). These studies show that different levels of electronic structure theory follow distinct basis set extrapolation patterns; most notably, Hartree–Fock (HF) energies converge almost exponentially toward the CBS limit [49], while correlation energies seem to follow an X^{-3} dependence [43, 46], where X is the cardinal number of the cc basis sets [52]. Therefore, the expressions $E^X = E_{\text{CBS}} + a \exp(-bX)$ and $E^X = E_{\text{CBS}} + cX^{-3}$, where E_{CBS} is the extrapolated energy, E^X denotes energies obtained from correlation-consistent basis sets with cardinal number X , while a , b , and c are fitting constants, are now commonly employed for estimating the complete basis set (E_{CBS}) Hartree–Fock and correlation energies, respectively. Accordingly, the above formulas are employed throughout this study for CBS extrapolations. Note that certain correlation contributions may behave differently, such as the relativistic 2-electron Darwin correction [50], which scales as slowly as X^{-1} .

Of equal importance is the determination of the FCI limit in a given one-particle basis from approximate n -electron methods. Numerous studies have shown the diminishing energy contribution of higher excitation levels. Coupled-cluster (CC) methods [55] including triple excitations [56–58] or configuration interaction with up to quadruple substitutions [59] typically provide accurate and reliable approximations to the FCI energy, in contrast to Møller–Plesset perturbation methods [60]. In particular, the CCSD(T) [56] approach represents a good compromise between cost and accuracy for predicting high-quality energies and properties [61]. Nevertheless, to compute energies to better than chemical accuracy it is necessary to consider the energy contributions from higher-order excitations. For the estimation of higher-order correlation effects neglected in the CCSD(T) and CCSDT approaches, we present here a technique called scaled higher-order correlation energy (SHOC) ([62]; see Section 5). It is important to note that if SHOC is carried out at the extrapolated CBS limit, the penultimate (CBS FCI) solution of the non-relativistic electronic Schrödinger equation may be closely approximated.

Reproduction of spectroscopic observations provides the most stringent test for checking the intrinsic accuracy of any *ab initio* PES. Therefore, in this paper we primarily focus on the *ab initio* generation of PESs and on the accuracy of the subsequent prediction of the rovibrational spectra of two molecules of recent interest for us and to astronomers: H₂O and H₂S.

3. COMPUTATIONAL DETAILS

Detailed documentation of the computational methods described in the text can be found in the original papers [27–29, 43–45]. When excerpts from previous work are presented, the notation utilized in the source is not modified. A brief summary of computational details and programs is provided to aid readers already familiar with most of the notation.

3.1. ELECTRONIC STRUCTURE CALCULATIONS

The configuration interaction (CI) calculations, including full CI (FCI), utilized the DETCI code [59] interfaced with the PSI3 program system [63], while the ACESII code [64] has been employed for the coupled-cluster (CC) calculations. Kinetic relativistic effects have been gauged by first-order perturbation theory applied to the one-electron mass-velocity and the one- and two-electron Darwin terms [23], as implemented via the recipe of Klopper [65] within the DALTON program system [66]. Calculation of the Gaunt correction surface utilized the program package MOLFDIR [67, 68].

The correlation-consistent (cc-pVXZ) basis sets of Dunning and co-workers [52–54], as well as their augmented (aug-cc-pVXZ), core-valence (cc-pCVXZ), and uncontracted variants, have been employed almost exclusively in our studies.

3.2. NUCLEAR MOTION CALCULATIONS

The rovibrational energy states have been determined using an exact kinetic energy (EKE) operator expressed in Radau coordinates augmented with the fitted *ab initio* PESs. The nuclear motion calculations utilized the DVR3D program suite [69] and optimized basis sets [70, 71]. Rovibrational calculations are only reported here for the H₂¹⁶O and H₂³²S isotopomers. All calculations presented used a hydrogen mass midway between the atomic and nuclear value, as recommended by Zobov *et al.* [22].

4. THE FOCAL-POINT APPROACH (FPA)

Characteristics of the focal-point approach [42, 43], comprising the dual extrapolation to the one- and n -particle *ab initio* limits, are as follows: (a) use of a family of basis sets which systematically approaches completeness (e.g., the cc-pVXZ, aug-cc-pVXZ, and cc-pCVXZ sets of Dunning and co-workers [52–54]); (b) application of low levels of electronic structure theory with basis sets as large as possible (typically direct Hartree–Fock (HF) and MP2 computations with hundreds of basis functions); (c) higher-order valence correlation treatments [CCSD(T), CCSDT, BD(TQ), MP4, MP5, and preferably FCI] with the largest possible basis sets; (d) construction of a two-dimensional extrapolation grid based on the assumed additivity of correlation *increments* to energy differences; and (e) avoidance of empirical corrections. Focal-point investigations [42–45, 72–74] and numerous other theoretical studies have shown that even in systems without particularly heavy elements, account may also be needed for core correlation and relativistic phenomena, as well as the diagonal Born–Oppenheimer correction (DBOC). Auxiliary shifts for these effects are appended to valence-only focal-point analyses not only to ensure the highest possible accuracy but also to enhance our understanding of the manifestation of these effects for different chemical applications (e.g., conformational energy and dissociation energy calculations).

The focal-point scheme assumes that the correlation energy increments have rather different convergence characteristics, with the higher-order correlation increments showing diminishing basis set dependence. This assumption has allowed efficacious estimation of molecular barriers at the CBS FCI limit for H₂O, H₂S, NH₃, SiH₃[−], C₂H₆, HCOOH, HNCO, and SiC₂ [43–45, 72, 73]. These calculations, employing two reference structures on the same PES, represent the simplest way to judge the performance of *ab initio* techniques for the calculation of semiglobal PESs. Indeed, they provide plentiful instruction in the pursuit of the *ab initio* limit. Following Table VII of Ref. [43], the diverse (basis set, correlation) convergence may be characterized as follows: NH₃ and SiH₃[−] inversion barriers and H₂O barrier to linearity (poor, good); HNCO inversion barrier (good, poor); C₂H₆ and HCOOH torsional energetics (good, good); and SiC₂ barrier to linearity (poor, poor).

In Table 1 we extend our previous valence-only focal-point studies [43–45, 72–74] with a problem in the (good, good) category, and report results for the rotational barrier of CH₃SiH₃, representing the difference between the energies of the eclipsed and staggered conformations. RHF theory recovers most of the rotational barrier; specifically, the RHF bar-

Table 1. Valence focal-point analysis of the torsional barrier of methyl silane^a

Series CC	$\Delta E_e(\text{RHF})$	$\delta[\text{MP2}]$	$\delta[\text{CCSD}]$	$\delta[\text{CCSD(T)}]$	$\delta[\text{CCSDT}]$	$\delta[\text{BD(TQ)}]$	$\Delta E_e(\text{CC})$
cc-pVDZ(62)	588	+10	-33	+3	-1	-1	566
aug-cc-pVDZ(104)	554	-44	-22	-6	-1	[-1]	[480]
cc-pVTZ(148)	568	-2	-23	0	[-1]	[-1]	[541]
cc-pVTZ+d(153)	577	-3	-22	-1	[-1]	[-1]	[549]
CVTZ(210)	577	-10	-22	-1	[-1]	[-1]	[542]
aug-cc-pVTZ(234)	576	-28	-23	-4	[-1]	[-1]	[519]
aug-cc-pVTZ+d(239)	583	-27	-23	-4	[-1]	[-1]	[527]
cc-pVQZ(294)	574	-19	-21	-3	[-1]	[-1]	[529]
aug-cc-pVQZ(440)	575	-25	[-21]	[-3]	[-1]	[-1]	[524]
cc-pV5Z(516)	579	-22	[-21]	[-3]	[-1]	[-1]	[531]
aug-cc-pV5Z(738)	579	-26	[-21]	[-3]	[-1]	[-1]	[527]
CBS	583	-27	-21	-3	-1	-1	530
Series MP	$\Delta E_e(\text{RHF})$	$\delta[\text{MP2}]$	$\delta[\text{MP3}]$	$\delta[\text{MP4}]$	$\delta[\text{MP5}]$	$\delta[\text{MP}\infty]$	$\Delta E_e(\text{MP})$
cc-pVDZ(62)	588	+10	-23	0	-5	-1	568
aug-cc-pVDZ(104)	554	-44	-18	-4	[-5]	[-1]	[482]
cc-pVTZ(148)	568	-2	-18	-2	[-5]	[-1]	[540]
cc-pVTZ+d(153)	577	-3	-17	-2	[-5]	[-1]	[549]
aug-cc-pVTZ(234)	576	-28	-19	-4	[-5]	[-1]	[519]
aug-cc-pVQZ(440)	575	-25	-17	-4	[-5]	[-1]	[523]

^a For each basis set the total number of contracted Gaussian functions is given in parentheses. For correlated-level calculations the symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory as given by the hierarchy RHF \rightarrow MP2 \rightarrow CCSD \rightarrow CCSD(T) \rightarrow CCSDT \rightarrow BD(TQ) and RHF \rightarrow MP2 \rightarrow MP3 \rightarrow MP4 \rightarrow MP5 \rightarrow MP ∞ for Series CC and Series MP, respectively. Brackets signify assumed increments from smaller basis set results. All values are given in cm^{-1} . Extrapolations to the CBS limit were performed according to the formulas given in the text.

Table 2. A comparison of predicted barriers to linearity for water (H_2^{16}O when adiabatic effects are considered)

Reference	Barrier Height	Comments
Carter and Handy [78]	11493 cm^{-1}	Spectroscopic Empirical
Jensen [79]	11246 cm^{-1}	Spectroscopic Empirical
Polyansky <i>et al.</i> [80]	10966 cm^{-1}	Spectroscopic Empirical
Lanquetin <i>et al.</i> [81]	11154 cm^{-1}	Effective Hamiltonian
Partridge and Schwenke (PS) [10]	11155 cm^{-1}	<i>Ab initio</i>
Partridge and Schwenke [10]	11128 cm^{-1}	Spectroscopic Empirical
PS + adiabatic + relativistic corr.	11192 cm^{-1}	<i>Ab initio</i>
Császár <i>et al.</i> [43]	11046 \pm 70 cm^{-1}	Extrapolated <i>ab initio</i>
Tarczay <i>et al.</i> [44]	11127 \pm 35 cm^{-1}	High accuracy <i>ab initio</i>
Kain <i>et al.</i> [82]	11105 \pm 5 cm^{-1}	Semitheoretical
Valeev <i>et al.</i> [83]	11119 \pm 12 cm^{-1}	<i>Ab initio</i> (MP2-R12)

rier is less than 55 cm^{-1} from the true valence-only electronic barrier. Since there are no stereochemically active lone pairs in CH_3SiH_3 , diffuse functions are only moderately important. The valence-only CBS FCI barrier is 530 cm^{-1} (note the excellent agreement between extrapolated Series CC and Series MP results), as compared with the best experimental value of 603 cm^{-1} [75–77]. We estimate, at the CVTZ CCSD(T) level, the core-valence and the relativistic corrections as +6 and +1 cm^{-1} , respectively. These small values are indicative of the lack of re-hybridization during the rotational motion. These auxiliary corrections bring the calculated barrier to somewhat closer agreement with experiment; nevertheless, the remaining discrepancy deserves further studies.

In the various focal-point studies we looked critically at the auxiliary corrections to standard valence-only *ab initio* electronic structure calculations. For water, for example, inclusion of the kinetic relativistic correction raises the all-electron extrapolated barrier height by 50 cm^{-1} or about 0.5%. After this correction the extrapolated *ab initio* result for the barrier to linearity of water [43] was in good but not perfect agreement with the best empirical value available in 1998 [80]. In Table 2 we give a compilation of older and recent theoretical and empirical estimates of the barrier to linearity on the ground-state PES of water. Using the focal-point approach Császár *et al.* [43] deduced a converged estimate of 11046 \pm 70 cm^{-1} for the barrier, while later research [44], extending the previous work, determined 11127 \pm 35 cm^{-1} . In an attempt to reproduce available empirical rovibrational levels supported by the ground electronic state of water, Kain *et al.* [82] modified existing high-quality PESs [10, 22, 27] and arrived at a value of 11105 \pm 5 cm^{-1} for the

barrier, which is bracketed by the previous, nearly-converged *ab initio* estimates. Important conclusions of the first *ab initio* investigations were that, as usual, it was easiest to estimate the Hartree–Fock (HF) limit, the well-established HF value being $11247 \pm 2 \text{ cm}^{-1}$; it proved hardest to arrive at the MP2 limit; and corrections beyond MP2 were much less dependent on the quality of the basis set. Using the MP2-R12/A level and very large basis sets, Valeev *et al.* [83] have most recently obtained a converged MP2 estimate of $-357 \pm 5 \text{ cm}^{-1}$, significantly different from the best previous *ab initio* estimate of -348 cm^{-1} [44]. The improved estimate of the MP2 limit yielded an improved (lower) estimate for the uncertainty of the *ab initio* barrier. Relativistic corrections beyond the kinetic term also influence the barrier. For example, the Gaunt correction increases the barrier by 6 cm^{-1} , while consideration of the Lamb-shift effect [29] lowers the barrier by almost 4 cm^{-1} . These and some other high-quality *ab initio* results led Valeev *et al.* [83] to surmise that the best present *ab initio* estimate of the barrier to linearity of H_2O is $11119 \pm 12 \text{ cm}^{-1}$. In summary, consideration of all possible computational effects on the barrier has finally resulted in excellent accord between theory and experiment.

5. SCALED HIGHER-ORDER CORRELATION ENERGIES (SHOC)

Since FCI computations are very expensive, even with small basis sets, there is little hope that larger basis set FCI calculations will become routine in the near future. Even with the explosive growth in computing power, FCI benchmarks are typically limited to small basis sets and molecules with up to two heavy atoms [60, 85–96]. However, large basis set coupled-cluster (CC) computations, which include through triple excitations (CCSD(T) [56] and CCSDT [57, 58]), are viable for a large number of molecular systems where small basis set FCI computations are feasible.

Therefore, in a recent study Császár and Leininger [62] explored a simple multiplicative approach, termed scaled higher-order correlation (SHOC), for approximating the full configuration interaction (FCI) limit at the complete basis set (CBS) limit from small basis set FCI and coupled cluster (most notably CCSD(T) and CCSDT) calculations. In the SHOC approach an attempt is made to scale correlation energies obtained at lower levels of theory to correct for neglected excitations and arrive at the FCI limit within a particular one-particle basis set. Note that linear scalings, though with different goals in mind, have been employed before, see, e.g., the PCI-X method of Siegbahn and co-workers

Table 3. Hartree–Fock and correlation energies (in E_h) of the $N(^4S)$ atom and the N_2 molecule (at $r = 1.0996$ Å) calculated at different levels of theory, and the resulting valence-only total atomization energy (TAE, in kcal/mol) of N_2^a

	(U)HF	$\Delta E_{\text{corr}}[(\text{U})\text{CCSD}]$	$\Delta E_{\text{corr}}[(\text{U})\text{CCSDT}]$	$\Delta E_{\text{corr}}[\text{FCI}]$
N atom				
cc-pVDZ	-54.391115	-0.086760	-0.087517	-0.087436
cc-pVTZ	-54.400686	-0.111746	-0.114341	-0.114183
cc-pVQZ	-54.403718	-0.118297	-0.121440	-0.121294
CBS	-54.405124	-0.123077	-0.126620	-0.126483
N ₂				
cc-pVDZ	-108.953856	-0.309691	-0.321684	-0.323350
cc-pVTZ	-108.983089	-0.372249	-0.390516	-0.392539
cc-pVQZ	-108.990687	-0.393463	-0.413286	-0.415426
CBS	-108.993355	-0.408943	-0.429902	-0.432127
TAE	HF	CCSD	CCSDT	FCI
cc-pVDZ	107.7	193.1	200.3	200.9
cc-pVTZ	114.0	207.4	215.6	217.0
cc-pVQZ	115.0	213.4	221.9	223.4
CBS	114.9	217.1	225.8	227.3

^a Finite-basis HF, CCSD, CCSDT, and FCI results are taken from Refs. [101, 102]. The FCI results reported for N_2 utilize CCSDT results and the SHOC scheme (see text). Basis set extrapolations were performed with formulas given in the text.

[97], the G3S method of Pople and co-workers [38], as well as the scaled external correlation (SEC) scheme [98], and the scaling all correlation (SAC) method [99] of Truhlar and co-workers. The utility of the HOC scaling approach is best understood by examples. In this review two examples are given. The first concerns the total atomization energy of N_2 . The second example concerns the PES of H_2O .

5.1. HOC EFFECTS ON THE TOTAL ATOMIZATION ENERGY OF N_2

The scaled higher-order correlation (SHOC) correction scheme has been demonstrated [62] to extrapolate CCSD(T) correlation energies for the global minima of the ground electronic states of BH and AlH, as well as \tilde{X}^3B_1 and \tilde{a}^1A_1 CH_2 [100], to the FCI limit with almost μE_h accuracy. The SHOC approach is used here to investigate the HOC correction on the total atomization energy of N_2 , employing data computed at the CCSD, CCSDT, and FCI levels by Feller and Sordo [101–103]. As it is clear from Table 5.1, containing Hartree–Fock and correlation energies for the $N(^4S)$ atom and the N_2 molecule, the SHOC correction

for the total atomization energy of N_2 , with a SHOC factor of 1.005182 obtained from our own cc-pVDZ CCSDT and FCI computations, is +1.5 kcal/mol. The resulting extrapolated CBS FCI value is 227.3 kcal/mol. Core-valence correlation and relativistic effects, not considered during calculation of the valence-only CBS FCI value, have been estimated by Feller and Sordo [102] to be +0.8 kcal/mol. This last correction brings our computed value very close to the best experimental value, 228.5 ± 0.4 kcal/mol [104].

5.2. HOC EFFECTS ON POTENTIAL ENERGY SURFACES

The proposed SHOC scheme is multiplicative, and it can readily be applied to the study of PESs. The effectiveness of using SHOC has been tested on the ground-state PES of H_2S in Refs. [62, 71]. The HOC energy corrections resulted in an order of magnitude *uniform* reduction of the valence-only correlation energy error of the CCSD(T) calculation. Here the analysis is extended to H_2O . Four geometries [105] have been selected, covering an energy range of 0–23000 cm^{-1} . Valence-only cc-pVDZ FCI and CCSD(T) computations have been performed at these geometries, resulting in estimates of valence-only correlation energies. The FCI – CCSD(T) energy differences before and after the HOC scaling, using the arithmetical average of the scale factors determined, 1.002811, are as follows: [-636, -625, -706, -419] and [-34, -26, -97, +147] μE_h , respectively. It is clear from these numbers that the SHOC scale factors change relatively little over the PES and that the SHOC correction results again in an order of magnitude reduction in the valence-only correlation energy error of the CCSD(T) calculation.

6. THE VIBRATIONAL SPECTRUM OF H_2S

Several valence-only potential energy hypersurfaces have been determined at the CCSD(T) level for H_2S in Ref. [71], with aug-cc-pVTZ+d, aug-cc-pVQZ+d, and aug-cc-pV5Z basis sets. As discussed in some detail in Refs. [45, 106], augmentation of the original aug-cc-pVXZ basis sets of Dunning [52, 53] for S with tight polarization functions (+d) is necessary in order to obtain reliable RHF energies. This so-called core polarization effect has been dealt with through extension of the d -space (+d) of the aug-cc-pVXZ ($X = T$ and Q) basis sets with an additional function whose exponent is the same as the largest d exponent in the aug-cc-pV5Z basis. Another surface, denoted CBS CCSD(T), results when the electronic energies obtained with the finite basis sets are extrapolated, using the equations given in Section 2, to the complete basis

Table 4. Differences between observed (obs.) vibrational band origins of H_2^{32}S and those computed at the CCSD(T) level^a

Label	Obs.	TZ+d	QZ+d	5Z	CBS	CBS FCI
010/00 1	1182.57	-0.3	-1.7	-2.1	-2.5	-3.0
020/00 2	2353.96	+5.4	+2.2	+0.9	+0.3	-0.7
100/10 ⁺ 0	2614.14	-5.0	+0.9	+1.8	+3.1	+2.3
001/10 ⁻ 0	2628.46	-6.1	+0.2	+1.3	+2.5	+1.8
030/00 3	3513.79	+11.3	+6.3	+4.1	+3.5	+1.9
040/00 4	4661.68	+14.3	+7.6	+5.1	+4.2	+2.2
120/10 ⁺ 2	4932.70	+2.1	+5.0	+4.2	+5.0	+3.2
021/10 ⁻ 2	4939.10	-0.2	+3.4	+3.6	+4.4	+2.6
200/20 ⁺ 0	5144.99	-10.2	+2.9	+4.6	+6.9	+5.4
101/20 ⁻ 0	5147.22	-10.8	+2.5	+4.0	+6.5	+5.0
002/11 0	5243.10	-10.7	+1.6	+3.6	+5.8	+4.4
050/00 5	5797.24	+12.8	+4.7	+2.8	+1.5	-1.1
210/20 ⁺ 1	6288.15	-9.4	+2.7	+3.9	+5.8	+3.7
111/20 ⁻ 1	6289.17	-10.0	+2.2	+3.4	+5.5	+3.5
300/30 ⁺ 0	7576.38	-16.4	+5.3	+7.8	+11.4	+9.0
102/21 ⁺ 0	7752.26	-16.2	+5.4	+8.0	+11.5	+9.0
003/21 ⁻ 0	7779.32	-16.2	+3.4	+6.3	+9.5	+7.2

^a All values are given in cm^{-1} . All differences are reported as calculated - observed. TZ+d = aug-cc-pVTZ+d CCSD(T) PES; QZ+d = aug-cc-pVQZ+d CCSD(T) PES; 5Z = aug-cc-pV5Z CCSD(T) PES; CBS = complete basis set CCSD(T) PES; CBS FCI = CBS full configuration interaction PES. Normal mode ($v_1 v_2 v_3$)/local mode($v_{r_1} v_{r_2} v_\theta$) labeling. Observed VBOs from Ref. [107]. Average absolute errors, in cm^{-1} , for the entries of this table are as follows: TZ+d = 9.3, QZ+d = 3.4, 5Z = 4.0, CBS = 5.3, and CBS FCI = 3.9.

set (CBS) limit. The most accurate valence-only PES, at least within the present approach, is denoted as CBS FCI and is obtained when the CBS CCSD(T) correlation energies are scaled, as described in Section 5, to the FCI limit. All these surfaces have been employed to calculate VBOs for H_2^{32}S . The results obtained are presented in Table 4.

It is clear from Table 4 that extension of the basis set ($X = 3, 4, 5$, and ∞) shifts the calculated VBOs more or less systematically. The least accurate results are obtained with $X = 3$; however, the CBS CCSD(T) results, though substantially different from the $X = 3$ results, deviate about as much from experiment. The $X = 4$ results [aug-cc-pVQZ+d CCSD(T)] have the smallest mean deviation. This observation is not surprising, in fact it is a result of fortuitous error cancellation which is often utilized in quantum chemical calculations. Much better agreement between theory and experiment is achieved when core-valence correlation, relativistic, and DBOC effects are included in the *ab initio* treatment [71].

7. THE ROVIBRATIONAL SPECTRUM OF H₂O

There is a very high quality *ab initio* ground-state PES available for H₂O, determined by Partridge and Schwenke [10]. Nevertheless, neither basis set extrapolations nor HOC energy corrections have been performed to reach the CBS FCI limit. For this reason and due to remaining computational errors, small empirical adjustment [10] of the *ab initio* PES resulted in a much better quality semitheoretical PES, which reproduces a large number of rovibrational levels up to about 10000 cm⁻¹ with an average accuracy of about 0.2 cm⁻¹, and levels up to 18000 cm⁻¹ with an average accuracy of about 1.2 cm⁻¹. From the detailed *ab initio* studies [43, 44] of the barrier to linearity of water, it became clear that relativistic corrections should influence substantially the calculated VBOs. Over the last two years we calculated several relativistic correction surfaces for the ground-state PES of H₂O, including a one-electron mass-velocity and Darwin (MVD1) surface [27], a two-electron Darwin (D2) surface, a Gaunt correction surface, and correction surfaces due to the Lamb-shift effect [29].

Our results, presented in Tables 5 and 6, clearly show that the relativistic corrections have a significant influence on the calculated behavior of both the vibrational and rotational states of water. This should be compared with inclusion of the DBOC, which only has a minor influence [22]. As expected from the changes in the barrier to linearity found upon inclusion of relativistic effects [43, 44, 29], the relativistic corrections to the PES can either raise or lower the rovibrational bands. For example, the kinetic relativistic effect (MVD1) raises both the barrier and the band origins of the bending states. Empirical test calculations [82] which augmented the BO potential with a simple term proportional to the bending coordinate alone resulted in a decrease in the barrier height and a simultaneous decrease in bending band origins. These observations are particularly interesting because of difficulties encountered in representing bending excitations both in water [80] and in H₂S [107] by fitting to spectroscopic data. While the average discrepancy between *ab initio* theory and observation for the VBOs of water is not significantly changed by inclusion of the relativistic corrections in the calculation, there is a marked shift in the error. The error in all band origins using the nonrelativistic BO potential surface of Partridge and Schwenke [10] is approximately constant at 0.1 – 0.2%. Inclusion of the relativistic correction in the PES greatly improves predictions for the stretching states at the expense of worsening (doubling) the error for the pure bending modes. It is also clear from the calculated VBOs that, in accord with

Table 5. Independent contributions of selected relativistic correction surfaces to the vibrational ($J = 0$) band origins of $\text{H}_2^{16}\text{O}^a$

(v_1, v_2, v_3)	Observed	+MVD1	+D2	+Gaunt	+L1	+L2
(010)	1594.75	+1.29	+0.09	-0.09	-0.09	+0.00
(020)	3151.63	+2.73	+0.18	-0.15	-0.18	+0.01
(030)	4666.79	+4.38	+0.28	-0.17	-0.29	+0.02
(040)	6134.01	+6.40	+0.40	-0.13	-0.43	+0.02
(050)	7542.44	+8.96	+0.54	-0.01	-0.60	+0.03
(060)	8869.95	+12.72	+0.73	+0.27	-0.86	+0.04
(100)	3657.05	-2.80	-0.05	-0.79	+0.18	+0.00
(200)	7201.54	-5.60	-0.09	-1.57	+0.36	-0.01
(300)	10599.69	-8.38	-0.14	-2.34	+0.54	-0.01
(400)	13828.28	-11.06	-0.18	-3.09	+0.71	-0.01
(500)	16898.40	-13.0	-0.20	-3.73	+0.83	-0.01
(600)	19782.00		-0.26	-4.47	+1.01	-0.01
(700)	22529.30		-0.34		+1.19	-0.02
(101)	7249.82	-5.68	-0.09	-1.69	+0.37	-0.01
(201)	10613.35	-8.43	-0.14	-2.31	+0.54	-0.01
(301)	13830.94	-11.05	-0.18	-1.83	+0.71	-0.01
(401)	16898.84	-12.98	-0.20	-4.66	+0.83	-0.01
(501)	19781.10	-15.80	-0.26		+1.01	-0.01
(601)	22529.44	-19.31	-0.34		+1.19	-0.02
(701)	25120.28		-0.39		+1.29	-0.02

^a All VBOs and corrections are given in cm^{-1} . Observed VBOs, provided only for guidance, are taken from Refs. [108, 109, 110]. The one-electron mass-velocity and Darwin (MVD1) results are taken from Ref. [27]. L1 = one-electron Lamb-shift correction surface. L2 = two-electron Lamb-shift correction surface. The Lamb-shift correction surfaces were obtained using the procedure of Ref. [29].

expectation, the kinetic relativistic correction has the largest effect followed by the Gaunt correction and the Lamb shift. Note that the full Breit correction [28] is somewhat smaller than the Gaunt correction. It is also notable how small the influence of the 2-electron correction terms (2-electron Darwin, D2, and 2-electron Lamb, L2) is on the VBOs, though for some VBOs, especially for the bends, the D2 correction, increasing with increasing excitation, is not negligible.

Table 6 shows the $J = 20$ rotational term values calculated using the same models analysed above for the VBOs. Results are only presented for the vibrational ground state [109]. The effect of the inclusion of relativistic corrections on the rotational term values is strongly dependent on K_a . For high values of K_a , the relativistic correction lowers the rotational term values leading to significant disagreement with the observed

Table 6. Independent contributions of selected relativistic correction surfaces to the $J = 20$ rotational $[(v_1 v_2 v_3)=(000)]$ energy levels of $\text{H}_2^{16}\text{O}^a$

J_{K_a, K_c}	Observed	+MVD1	+D2	+Gaunt	+L1	+L2
20 _{0,20}	4048.250	-0.455	+0.067	-1.051	+0.079	+0.003
20 _{1,19}	4412.316	-0.481	+0.073	-1.144	+0.085	+0.004
20 _{2,18}	4738.622	-0.426	+0.083	-1.214	+0.085	+0.004
20 _{3,17}	5031.794	-0.297	+0.094	-1.268	+0.078	+0.006
20 _{4,16}	5292.103	-0.045	+0.111	-1.297	+0.064	+0.006
20 _{5,15}	5513.236	+0.526	+0.141	-1.282	+0.027	+0.007
20 _{6,14}	5680.788	+1.400	+0.183	-1.218	-0.032	+0.009
20 _{7,13}	5812.074	+1.397	+0.186	-1.247	-0.032	+0.010
20 _{8,12}	5966.823	+0.206	+0.137	-1.421	+0.052	+0.007
20 _{9,11}	6170.832	-1.023	+0.087	-1.609	+0.140	+0.004
20 _{10,10}	6407.443	-1.968	+0.051	-1.771	+0.207	+0.002
20 _{11,9}	6664.173	-2.820	+0.018	-1.924	+0.268	+0.001
20 _{12,8}	6935.428	-3.646	-0.013	-2.075	+0.328	-0.001
20 _{13,7}	7217.562	-4.463	-0.043	-2.226	+0.386	-0.002
20 _{14,6}	7507.545	-5.274	-0.072	-2.375	+0.445	-0.005
20 _{15,5}	7802.709	-6.084	-0.103	-2.523	+0.502	-0.005
20 _{16,4}	8100.291	-6.895	-0.132	-2.669	+0.560	-0.007
20 _{17,3}	8397.648	-7.712	-0.162	-2.814	+0.617	-0.009
20 _{18,2}	8691.927	-8.538	-0.193	-2.956	+0.676	-0.011
20 _{19,1}	8979.881	-9.382	-0.225	-3.095	+0.735	-0.012
20 _{20,0}	9257.459	-10.260	-0.258	-3.230	+0.797	-0.015

^a All rotational data are given in cm^{-1} . The observed rotational term values, provided only for guidance, are taken from Refs. [108, 109, 111, 112]. Many rotational transitions come in quasi-degenerate pairs (cf. Ref. [27]). To save space, only one member in each pair is reported in this table. The one-electron mass-velocity and Darwin (MVD1) results are taken from Ref. [27]. L1 = one-electron Lamb-shift correction surface. L2 = two-electron Lamb-shift correction surface. The Lamb-shift correction surfaces were obtained using the procedure of Ref. [29].

levels [27]. This is consistent with the large increase observed in the VBOs of the bending overtones. Similarly to the VBOs, the order of the magnitude of the different corrections to the rotational term values is kinetic > Gaunt > Lamb. The two-electron relativistic corrections (D2 and L2) are again rather small, the two-electron Lamb-shift correction can safely be ignored. This is not true, however, for the one-electron Lamb shift, L1. For example, the 20_{20,0} rotational level is shifted, due to L1, by more than 0.7 cm^{-1} , some 500 times more than the present experimental accuracy [108], which in this case could be improved by up to three orders of magnitude using current technology. The Lamb-shift effect increases with increasing excitation both for the vibrations and for the rotations.

8. SUMMARY

High-resolution rovibrational spectra provide a wealth of information on molecular properties and vibration-rotation dynamics provided that the "inverse eigenvalue problem" of molecular spectroscopy can be unravelled to some degree. First-principles techniques do not suffer from the inverse eigenvalue dilemma and thus provide both complementary and competitive approaches to the understanding of chemical phenomena. A big step in this direction is the *ab initio* determination of potential energy hypersurfaces of "spectroscopic" accuracy. In this review a snapshot of some aspects of the state of evolution of *ab initio* methodologies in the determination of accurate PESs has been presented. The focus of the attention has been on the focal-point approach involving a dual extrapolation to the complete basis set (CBS) and full configuration interaction (FCI) asymptotes. The numerical results presented show again the intrinsic accuracy and utility of *ab initio* techniques in general and the focal-point approach in particular. It is shown that scaling the higher-order correlation energy (SHOC) increases the dissociation energy, D_e , of N_2 , and reduces the error with respect to experiment, and it also results in an order of magnitude error reduction in the FCI – CCSD(T) correlation energy of H_2O . A pragmatic and sophisticated *ab initio* approach, based on the focal-point and SHOC schemes, has been utilized for the construction of valence-only PESs for the ground electronic state of H_2S . Convergence analysis of the VBOs computed using these PESs reveals the usefulness of the approach. Small corrections, not considered in the valence-only treatment, including core-valence correlation, relativistic effects, and the diagonal Born–Oppenheimer correction (DBOC), are known to be important for the accurate prediction of rovibrational levels. In this review the relativistic effects are quantified for the rovibrational spectrum of H_2O . It is shown that among the relativistic effects the dominant one is the kinetic relativistic effect, while, in general, the Gaunt correction and quantum electrodynamics (QED) corrections make smaller and smaller contributions to the rovibrational levels. Nevertheless, at about 10000 cm^{-1} and above the QED effect may result in changes as large as 1 cm^{-1} for some rovibrational states.

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