A Comparison of One-Particle Basis Set Completeness, Higher-Order Electron Correlation, Relativistic Effects, and Adiabatic Corrections for Spectroscopic Constants of BH, CH^+, and NH[†]

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To investigate the relative importance of various small sources of error in theoretical predictions of molecular properties, we report spectroscopic constants for the ground electronic states of BH, CH^+, and NH, which are nearly converged to the adiabatic ab initio limit. Computations are performed using full configuration interaction and coupled-cluster singles, doubles, and perturbative triples methods with correlation-consistent basis sets of double- to sextuple-ζ quality. The equilibrium bond lengths, r_e, harmonic vibrational frequencies, ω_e, anharmonicity constants, $\omega_e x_e$, centrifugal distortion constants, $\bar{D}_e$, and other quantities are compared with experiment for each species. The systematic dependence of spectroscopic constants on the one-particle basis is used to estimate the complete basis set limit values by using a two-point linear extrapolation scheme. The importance of core correlation, scalar relativistic corrections, higher-order electron correlation, and basis set completeness are carefully investigated. Moreover, deviations from the Born−Oppenheimer (BO) approximation are studied by computing the diagonal BO correction. The remaining error is attributed primarily to nonadiabatic effects. Our ab initio limit, adiabatic results for r_e are within 0.0007 Å of experiment when nonadiabatic effects are insignificant or have been removed. Adiabatic predictions of ω_e are within 0.5 cm^{-1} of experiment.

1. Introduction

As state-of-the-art ab initio electronic structure computations become more accurate, it is important to ask how the remaining errors, such as basis set completeness, nonfactorizable four-body and higher electron correlation, and relativistic, adiabatic, and nonadiabatic corrections, compare to each other. Within the scope of the nonrelativistic Born−Oppenheimer (BO) approximation, the quality of a quantum-chemical calculation depends only on the completeness of the one- and *n*-particle model spaces, *n* being the number of electrons in the system. The choice of a basis set dictates the truncation of the one-particle expansion, while the wave-function model determines the completeness of the *n*-particle space. The ultimate goal within this scheme is to achieve the complete basis set full configuration interaction (CBS FCI) values, which represent the exact solution of the time-independent Schrödinger equation under the framework of the BO approximation. However, the restriction to the nonrelativistic BO approximation itself may lead to errors which are significant in some applications, such as matching the high rovibrational levels of the water molecule as required to prove the presence of water on the sun or to model the greenhouse effect on earth.[1,2]

In gauging the maximum accuracy that can be achieved by ab initio electronic structure theory, the study of diatomics has been valuable because of their small size and the availability of spectroscopic data. Extensive work on spectroscopic-quality ab initio molecular properties of small diatomic hydrides has been done by Martin,[3,4] who observed that nonadiabatic effects, which are considered to be smaller or comparable to errors in the best ab initio methods, could actually be much more significant corrections, as in the case of BeH and BH. He performed a convergence study of spectroscopic constants of diatomic hydrides with respect to contracted and uncontracted basis sets. By accounting for the one- and *n*-particle incompleteness, he computed benchmark-quality spectroscopic constants and compared his best results with true BO results that are derived from experimental data, thereby showing the level of accuracy that can be expected from high-level electronic structure theory methods. Another paper by Martin[5] studied the spectroscopic constants of the hydroxyl anion, OH^-, by converging the one- and *n*-particle basis and indicating the importance of connected quadruples of the coupled-cluster expansion and scalar relativistic effects in predicting constants accurately. Feller and Sordo[6] studied first-row diatomic hydrides using coupled-cluster theory with full inclusion of triple excitations (CCSDT) and concluded that the improvement of CCSDT over coupled-cluster singles, doubles, and perturbative triples methods (CCSD(T)) is minimal compared to the significant computational cost of the former, even though some of the differences between CCSDT and CCSD(T) remain significant on a spectroscopic scale. Nevertheless, this does not mean that inclusion of connected quadruple and even pentuple excitations in the coupled-cluster wave function produce similarly unimportant corrections. Recent benchmarking studies on the reliability of computed spectroscopic constants have been done with less correlated methods such as coupled-cluster with singles and doubles (CCSD),[7] second-order perturbation theory (MP2),[7] and density-functional theory (DFT).[8]

Significant work has been devoted to analyzing the systematic convergence of different properties with respect to increasing basis set size. As a result, various extrapolation schemes exist

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for determining the CBS values for self-consistent field (SCF) and correlation energies, particularly for Dunning's correlation-consistent basis sets,[9−13] which are known to give a systematic convergence of energies and properties toward the CBS limit. Feller[14] showed that SCF energies approach the CBS limit exponentially, while Helgaker et al.[15] derived an inverse-cubic form (eq 1) for extrapolating correlation energies.

In addition to accounting for basis set and correlation incompleteness, some of the more significant corrections to standard ab initio techniques include relativistic,[16−18] adiabatic,[19−21] and nonadiabatic[22,23] contributions. In this work, we quantify the importance of these effects in achieving benchmark quality spectroscopic constants for three diatomic hydrides.

2. Computational and Theoretical Methods

All FCI computations were carried out using the DETCI[24] module in the PSI 3.2[25] program package, while ACES II[26] was used to obtain CCSD(T) results. Computations were performed on a 72-processor IBM SP as well as dual-processor Linux workstations.

For Dunning's[9−13] correlation-consistent polarized valence N-ζ (cc-pVNZ) basis sets, only valence−valence correlation is considered (using the frozen-core approximation), while the cc-pCVNZ basis sets enable the addition of core−core and core−valence correlation due to the presence of high-exponent inner-shell basis functions. Both sets of correlation-consistent basis sets use pure angular momentum Gaussian functions. Our largest basis, cc-pCV5Z, is of (18s12p7d5f3g1h/10s9p7d5f3g1h) quality for first-row atoms, while the cc-pV5Z basis for hydrogen has a (8s4p3d2f1g/5s4p3d2f1g) contraction scheme.

The one-particle calibration was done at the CCSD(T) level by taking the most accurate SCF energies and adding extrapolated correlation energies. It has been observed that SCF energies nearly converge to their CBS limit with cc-pV5Z or cc-pV6Z basis sets.[3,15] The correlation energies asymptotically approach their basis set limit as

$$E_{\mathrm{corr}}^{X} = d + fX^{-3} \tag{1}$$

The CBS limit may be estimated by the two-point linear extrapolation scheme of Helgaker et al.[15] For basis sets of consecutive cardinal numbers X and $Y = X - 1$, the extrapolated correlation energies would have the form

$$E_{\mathrm{corr}}^{XY} = \frac{E_{\mathrm{corr}}^{X}X^{3} - E_{\mathrm{corr}}^{Y}Y^{3}}{X^{3} - Y^{3}} \tag{2}$$

The estimated CBS CCSD(T) potential-energy curve is the sum of the cc-pVXZ SCF energy and the extrapolated correlation energy, E_{corr}^{XY}. This two-point linear extrapolation accelerates the convergence of energies and spectroscopic constants, which are computed as derivatives of the potential-energy curve.[7] The n-particle calibration was performed by comparing CCSD(T) and FCI energies. For a given basis set, full configuration interaction gives the exact solution within the BO approximation, thus capturing all the correlation energy in a complete n-particle Hilbert space.

When nuclei and electrons move in time scales that are not greatly different, deviations from the BO approximation become significant and adiabatic and nonadiabatic effects deserve consideration. The diagonal BO correction (DBOC)[19] is a first-order adiabatic correction to the BO approximation, and instead of assuming that nuclei are infinitely heavy, it takes into account the finite mass of the nuclei. The DBOC correction involves the expectation value of the nuclear kinetic energy operator, $\hat{T}_n$

$$E_{\mathrm{DBOC}} = \langle \Psi_{\mathrm{e}}(r;R) | \hat{T}_n | \Psi_{\mathrm{e}}(r;R) \rangle \tag{3}$$

Valeev and Sherrill have recently reported on the convergence behavior of this correction with respect to basis set and correlation treatment using configuration interaction wave functions.[21]

The importance of relativistic effects was estimated by first-order perturbation theory. The relativistic corrections were computed as expectation values of the one-electron mass−velocity and Darwin terms[27] using unrelaxed CCSD densities in PSI 3.2.[25]

Spectroscopic constants were generated from a sixth-order polynomial, $U(r)$, determined from seven energy points evenly spaced about r_{e} (step size of 0.005 Å). Each energy calculation was converged to 10^{-12} Hartrees. The rotational (J) and vibrational (ν) energy levels of a diatomic are generally given by Dunham's[28] expansion

$$E_{\nu J} = h \sum_{ln} Y_{ln} \left(\nu + \frac{1}{2} \right)^{l} J^{n} (J+1)^{n} \tag{4}$$

Expanding the first few terms, we get

$$E \approx U(r_{\mathrm{e}}) + h\omega_{\mathrm{e}}\left(\nu + \frac{1}{2}\right) + hB_{\mathrm{e}}J(J+1) - h\omega_{\mathrm{e}}x_{\mathrm{e}}\left(\nu + \frac{1}{2}\right)^{2} \tag{5}$$

$$-h\alpha_{\mathrm{e}}\left(\nu + \frac{1}{2}\right)J(J+1) - h\bar{D}_{\mathrm{e}}J^{2}(J+1)^{2} + \ldots \tag{6}$$

where we have substituted the Dunham expansion coefficients with the more familiar spectroscopic constants: $Y_{01} \cong B_{\mathrm{e}}$, $Y_{10} \cong \omega_{\mathrm{e}}$, $Y_{02} \cong \bar{D}_{\mathrm{e}}$, $Y_{20} \cong -\omega_{\mathrm{e}}x_{\mathrm{e}}$, and $Y_{11} \cong -\alpha_{\mathrm{e}}$. In our polynomial expansion in r, spectroscopic constants are given in terms of derivatives of $U(r)$ in the usual way[29]

$$I_{\mathrm{e}} \equiv \mu r_{\mathrm{e}}^{2} \quad B_{\mathrm{e}} \equiv \frac{h}{8\pi^{2} I_{\mathrm{e}}} \quad \omega_{\mathrm{e}} \equiv \frac{1}{2\pi}\left[\frac{U''(r_{\mathrm{e}})}{\mu}\right]^{1/2} \tag{7}$$

$$\omega_{\mathrm{e}}x_{\mathrm{e}} \equiv \frac{B_{\mathrm{e}}^{2} r_{\mathrm{e}}^{4}}{4h\omega_{\mathrm{e}}^{2}}\left[\frac{10B_{\mathrm{e}}r_{\mathrm{e}}^{2}[U'''(r_{\mathrm{e}})]^{2}}{3h\omega_{\mathrm{e}}^{2}} - U^{\mathrm{iv}}(r_{\mathrm{e}})\right] \tag{8}$$

$$\alpha_{\mathrm{e}} \equiv -\frac{2B_{\mathrm{e}}^{2}}{\omega_{\mathrm{e}}}\left[\frac{2B_{\mathrm{e}}r_{\mathrm{e}}^{3}U'''(r_{\mathrm{e}})}{h\omega_{\mathrm{e}}^{2}} + 3\right] \quad \bar{D}_{\mathrm{e}} \equiv \frac{4B_{\mathrm{e}}^{3}}{\omega_{\mathrm{e}}^{2}} \tag{9}$$

where μ is the reduced mass, I_{e} is the moment of inertia, B_{e} is the rotational constant, ω_{e} is the harmonic vibrational frequency, $\omega_{\mathrm{e}}x_{\mathrm{e}}$ is the anharmonicity constant, α_{e} is the vibration−rotation coupling constant, and $\bar{D}_{\mathrm{e}}$ is the centrifugal distortion constant. As suggested by Handy and Lee,[30] we have computed the reduced mass, μ, and the DBOC using atomic masses instead of nuclear masses.

3. Results and Discussion

The spectroscopic constants are presented in Tables 1 (BH), 2 (CH^{+}), and 3 (NH). The CBS extrapolation, FCI calibration, scalar relativistic correction, and DBOC are included in the lower sections of Tables 1−3. These calculated values are compared with experimental numbers[31−34] as well as adiabatic[35−37] and BO values when available. Spectroscopists normally determine experimental spectroscopic constants by fitting their rovibrational spectra directly to a simple Dunham-type expan-

TABLE 1: Spectroscopic Constants of the $\tilde{X}^1\Sigma^+$ State of BH

level of theory	r_e	ω_e	$\omega_e x_e$	B_e	$\bar{D}_e$	α_e
FCI/cc-pVDZ	1.25597	2340.72	48.8	11.574	0.00113	0.397
FCI/cc-pVTZ	1.23560	2348.71	49.1	11.959	0.00124	0.422
FCI/cc-pVQZ	1.23349	2356.78	48.8	12.001	0.00124	0.420
FCI/cc-pV5Z	1.23285	2358.21	49.2	12.013	0.00125	0.421
FCI/cc-pCVDZ	1.25434	2340.12	48.8	11.604	0.00114	0.392
FCI/cc-pCVTZ	1.23339	2355.26	49.0	12.002	0.00125	0.421
CCSD(T)/cc-pVDZ	1.25578	2342.65	48.6	11.578	0.00113	0.395
CCSD(T)/cc-pVTZ	1.23540	2350.84	49.0	11.963	0.00124	0.421
CCSD(T)/cc-pVQZ	1.23329	2358.91	48.7	12.004	0.00124	0.419
CCSD(T)/cc-pV5Z	1.23266	2360.27	49.0	12.016	0.00125	0.420
CCSD(T)/cc-pV6Z	1.23254	2360.25	49.3	12.019	0.00125	0.419
CCSD(T)/cc-pCVDZ	1.25415	2342.10	48.7	11.608	0.00114	0.392
CCSD(T)/cc-pCVTZ	1.23321	2357.37	48.9	12.005	0.00125	0.420
CCSD(T)/cc-pCVQZ	1.23017	2368.23	49.1	12.065	0.00125	0.421
CCSD(T)/cc-pCV5Z	1.22946	2370.30	49.3	12.079	0.00125	0.422
Extrapolation						
CCSD(T)/cc-pCV(Q5)Z[a]	1.22899	2371.25	49.5	12.088	0.00128	0.423
Δ_{FCI}[b]	+0.00018	−2.07	+0.2	−0.003	0.00000	+0.001
$\Delta_{relativistic}$[c]	+0.00001	−0.59	0.0	0.000	0.00000	0.000
best BO	1.22917	2368.59	49.6	12.085	0.00126	0.424
Δ_{DBOC}[d]	+0.00066	−2.25		−0.013	0.00000	
best adiabatic	1.22983	2366.34		12.072	0.00126	
$\Delta_{nonadiabatic}$[e]	+0.0025					
best nonadiabatic	1.2323					
error (BO vs exp(BO))[f]	−0.0003					
error (BO vs expt)[g]	−0.00300	1.86	0.3	0.059	0.00003	0.001
error (adiabatic vs exp(adiabatic))[h]	0.0001					
error (adiabatic vs exp)[g]	−0.00234	−0.39		0.046	0.00003	
error (nonadiabatic vs exp)[h]	−0.0001					
exp (BO)[e]	1.2295					
exp (adiab)[e]	1.2297					
exp[i]	1.23217	2366.73	49.3	12.026	0.00123	0.422

[a] $E = E^5_{SCF} + E^{Q5}_{corr}$, where E^{Q5}_{corr} is given by eq 2. [b] FCI/cc-pCVTZ − CCSD(T)/cc-pCVTZ. [c] CCSD/ccpCV5Z level with unrelaxed densities. [d] CISD/cc-pVTZ DBOC values are not sufficiently converged to give reliable higher order derivatives; $\omega_e x_e$ and α_e are not reported. [e] Computed by Martin.[3] [f] Compared with BO values derived from experiment (exp(BO)) by Martin.[3] [g] Compared with raw experimental values including effective adiabatic and nonadiabatic effects (exp). [h] Compared with adiabatic result derived from experiment (exp(adiab)) by Martin.[3] [i] Fernando et al.[31]

TABLE 2: Spectroscopic Constants of the $\tilde{X}\ ^1\Sigma^+$ State of CH^+

level of theory	r_e	ω_e	$\omega_e x_e$	B_e	$\bar{D}_e$	α_e
FCI/cc-pVDZ	1.14598	2892.15	64.6	13.807	0.00126	0.492
FCI/cc-pVTZ	1.13132	2846.66	57.4	14.167	0.00140	0.491
FCI/cc-pVQZ	1.12999	2853.02	58.8	14.200	0.00141	0.494
FCI/cc-pV5Z	1.12953	2855.30	59.9	14.211	0.00141	0.496
FCI/cc-pCVDZ	1.14540	2892.91	64.5	13.820	0.00126	0.490
FCI/cc-pCVTZ	1.13047	2853.11	57.0	14.188	0.00140	0.489
CCSD(T)/cc-pVDZ	1.14580	2894.61	64.4	13.811	0.00126	0.490
CCSD(T)/cc-pVTZ	1.13109	2849.66	57.2	14.172	0.00140	0.490
CCSD(T)/cc-pVQZ	1.12977	2855.91	58.4	14.206	0.00141	0.493
CCSD(T)/cc-pV5Z	1.12932	2858.07	59.5	14.217	0.00141	0.493
CCSD(T)/cc-pV6Z	1.12933	2857.59	59.3	14.217	0.00141	0.493
CCSD(T)/cc-pCVDZ	1.14524	2895.35	64.5	13.824	0.00126	0.489
CCSD(T)/cc-pCVTZ	1.13025	2856.05	57.8	14.193	0.00140	0.488
CCSD(T)/cc-pCVQZ	1.12824	2861.29	58.8	14.244	0.00141	0.495
CCSD(T)/cc-pCV5Z	1.12770	2863.70	59.3	14.258	0.00141	0.496
Extrapolation						
CCSD(T)/cc-pCV(Q5)Z[a]	1.12732	2864.56	59.4	14.267	0.00142	0.497
Δ_{FCI}[b]	+0.00021	−2.92	+0.2	−0.005	0.00000	+0.001
$\Delta_{relativistic}$[c]	−0.00002	−0.74	0.0	0.000	0.00000	0.000
best BO	1.12751	2860.90	59.6	14.262	0.00142	0.498
Δ_{DBOC}[d]	+0.00063	−2.81		−0.016	0.00000	
best adiabatic	1.12815	2858.09		14.246	0.00142	
error (BO vs exp)[e]	−0.00339	2.90	0.3	0.086	0.00005	0.005
error (adiabatic vs exp)[e]	−0.00275	0.09		0.070	0.00005	
exp[f]	1.1309	2858	59.300	14.176	0.00137	0.493

[a] $E = E^5_{SCF} + E^{Q5}_{corr}$, where E^{Q5}_{corr} is given by eq 2. [b] FCI/cc-pCVTZ − CCSD(T)/cc-pCVTZ. [c] CCSD/cc-pCV5Z level with unrelaxed densities. [d] CISD/cc-pVTZ DBOC values are not sufficiently converged to give reliable higher order derivatives; $\omega_e x_e$ and α_e are not reported. [e] Compared with raw experimental values including effective adiabatic and nonadiabatic effects (exp). [f] Carrington et al.[32]

sion (eq 4). However, this expansion is derived assuming a single BO potential-energy surface, whereas the experimental data are influenced by adiabatic and nonadiabatic effects. Hence the spectroscopic constants thus derived will incorporate some effective adiabatic and nonadiabatic contributions. Watson has shown[36] that a more complete mathematical treatment of the Dunham expansion (eq 4) allows for an approximate separation of these effects. Spectroscopists typically deduce an “equilibrium

TABLE 3: Spectroscopic Constants of the $\tilde{X}\ ^3\Sigma^-$ State of NH

level of theory	r_e	ω_e	$\omega_e x_e$	B_e	$\bar{D}_e$	α_e
FCI-cc-pVDZ	1.05647	3188.20	81.7	16.065	0.00163	0.656
FCI-cc-pVTZ	1.03970	3259.19	79.3	16.587	0.00172	0.656
FCI/cc-pCVDZ	1.05547	3191.49	81.8	16.096	0.00164	0.657
CCSD(T)/cc-pVDZ	1.05588	3196.93	80.9	16.083	0.00163	0.652
CCSD(T)/cc-pVTZ	1.03921	3267.77	78.4	16.603	0.00172	0.653
CCSD(T)/cc-pVQZ	1.03716	3282.12	78.4	16.669	0.00172	0.650
CCSD(T)/cc-pV5Z	1.03685	3285.58	78.8	16.679	0.00172	0.648
CCSD(T)/cc-pCVDZ	1.05488	3200.33	80.9	16.113	0.00163	0.652
CCSD(T)/cc-pCVTZ	1.03788	3268.24	78.5	16.646	0.00173	0.657
CCSD(T)/cc-pCVQZ	1.03607	3288.74	78.2	16.704	0.00172	0.650
CCSD(T)/cc-pCV5Z	1.03558	3292.67	78.6	16.720	0.00172	0.649
		Extrapolation				
CCSD(T)/cc-pCV(Q5)Z[a]	1.03527	3294.23	78.2	16.730	0.00173	0.649
Δ_{FCI}[b]	+0.00052	−8.05	+0.6	−0.017	0.00000	+0.004
$\Delta_{\mathrm{relativistic}}$[c]	+0.00003	−1.75	0.0	−0.001	0.00000	0.000
best BO	1.03582	3284.43	78.9	16.712	0.00173	0.653
Δ_{DBOC}[d]	+0.00027	−1.38		−0.009	0.00000	
best adiabatic	1.03609	3283.05		16.703	0.00173	
error (BO vs exp(BO))[e]	−0.00073					
error (BO vs exp(adiabatic))[f]	−0.00093					
error (BO vs exp)[f]	−0.00093	1.85	0.0	0.013	0.00002	0.004
error (adiabatic vs exp(adiabatic))[f]	−0.00066					
error (adiabatic vs exp)[f]	−0.00066	0.47		0.004	0.00002	
exp (BO)[g]	1.03655					
exp (adiabatic)[h]	1.03675					
exp[i]	1.03675	3282.583	78.915	16.700	0.00171	0.649

[a] $E = E^5_{\mathrm{SCF}} + E^{\mathrm{Q5}}_{\mathrm{corr}}$, where $E^{\mathrm{Q5}}_{\mathrm{corr}}$ is given by eq 2. [b] FCI/cc-pCVTZ − CCSD(T)/cc-pCVTZ. [c] CCSD/cc-pCV5Z level with unrelaxed densities. [d] CISD/cc-pVTZ DBOC values are not sufficiently converged to give reliable higher order derivatives; $\omega_e x_e$ and α_e are not reported. [e] Compared with BO values derived from experiment (exp (BO)). See ref 3. [f] Compared with raw experimental nonadiabatic (≈adiabatic) values (exp). [g] Martin.[4] [h] According to Martin,[4] nonadiabatic effects in the $\tilde{X}\ ^3\Sigma^-$ state of NH are very small, so $r_e^{\mathrm{ad}} \approx r_e^{\mathrm{nonad}}$. [i] Bernath et al.[33,34]

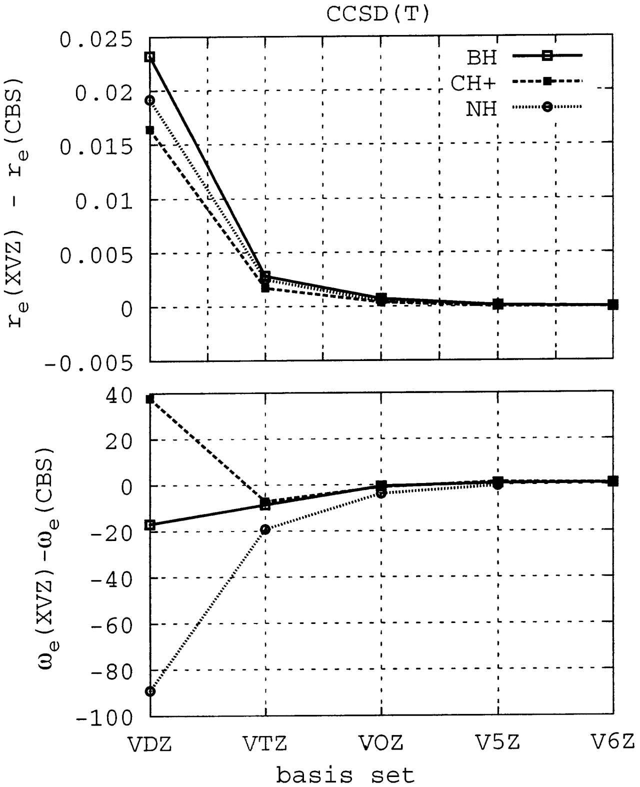

Figure 1. Convergence of CCSD(T) r_e and ω_e toward the CBS limit derived for valence-only (cc-pVNZ) basis sets.

bond length" as that which satisfies $Y_{01} = \hbar/\mu r_e^2$ for a fitted Dunham coefficient Y_{01}. However, a more detailed treatment[36] shows that

$$Y_{01} = \frac{\hbar}{2\mu (r_e^{\mathrm{ad}})^2}\left[1 + \frac{\Delta Y_{01}^{\mathrm{D}}}{B_e} + \frac{m_e}{m_p} g_J\right] \qquad (10)$$

where r_e^{ad} is an adiabatic bond length, $\Delta Y_{01}^{\mathrm{D}}$ is a Dunham correction (involving up to the fifth derivative of the potential), and g_J is the Zeeman effect rotational factor incorporating nonadiabatic contributions. Following Watson, one may correct the experimental bond length (r_e^{exp}) to obtain adiabatic (r_e^{ad}) and BO (r_e^{BO}) values as

$$r_e^{\mathrm{ad}} = r_e^{\mathrm{exp}}(1 + \Delta Y_{01}^{\mathrm{D}}/B_e + m_e g_J/m_p)^{1/2} \qquad (11)$$

$$r_e^{\mathrm{BO}} = r_e^{\mathrm{ad}}/(1 + m_e d_1^{\mathrm{ad}}/M_1 + m_e d_2^{\mathrm{ad}}/M_2) \qquad (12)$$

where d_1^{ad} and d_2^{ad} are constants, m_e is mass of an electron, and M_1 and M_2 are nuclear masses. These allow for a more direct comparison to the equilibrium bond lengths (r_e^{BO}) and the DBOC-corrected bond lengths (r_e^{ad}) computed theoretically in this work. This approach has been used by Martin[3,4] to derive BO bond lengths from experimental values for BH and NH. Rigorous discussion of adiabatic and nonadiabatic effects in rovibrational spectra of diatomics is given by Watson[36] and Tiemann and Ogilvie[35] and a more qualitative discussion is given in refs 3, 4, and 37.

3.1. Convergence of the One-Particle Space. Figure 1 illustrates how the CCSD(T) predictions of r_e and ω_e monotonically converge toward the cc-pVNZ-derived CBS limit as the size of the cc-pVNZ (valence-only) basis increases. On the scale of these graphs, the errors for the cc-pVDZ basis are much larger than those for other basis sets, suggesting that this basis set is too small to be used reliably in extrapolation schemes for molecular properties.[38] The cc-pVQZ basis appears sufficient to converge r_e to 0.001 Å, but a cc-pV5Z basis is required to converge ω_e to 1 cm^{-1}.

Similarly, Figures 2 and 3 show the convergence of r_e and ω_e toward the CBS limit derived using cc-pCVNZ basis sets. Errors in r_e go from approximately 0.02 Å for the cc-pCVDZ basis to under 0.005 Å for cc-pCVTZ and under 0.001 Å for cc-pCVQZ. Again, however, cc-pCVQZ does not appear

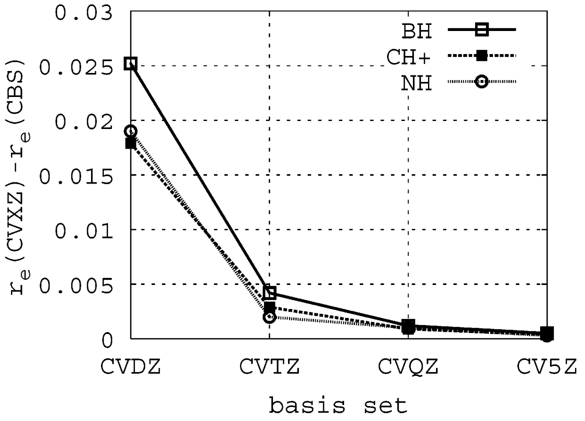

Figure 2. Convergence of CCSD(T) r_e toward the CBS limit derived for core-valence (cc-pCVNZ) basis sets.

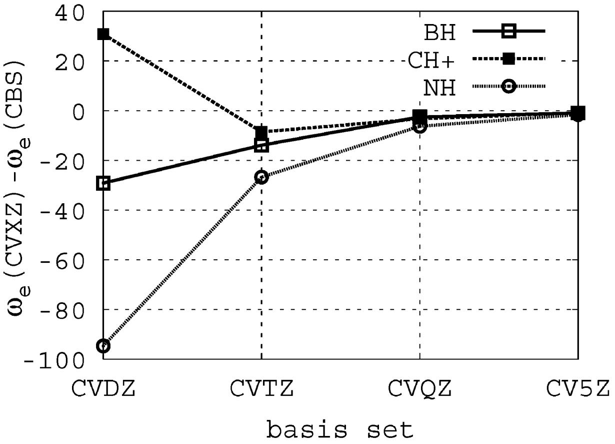

Figure 3. Convergence of CCSD(T) ω_e toward the CBS limit derived for core-valence (cc-pCVNZ) basis sets.

sufficient to converge ω_e within 1 cm^{-1}. When the cc-pV5Z basis is increased to cc-pCV5Z and core electrons are correlated, bond lengths are shortened by 0.001−0.003 Å and vibrational frequencies are increased by 6−10 cm^{-1}. These changes demonstrate that direct comparison of valence-only results with experiment is not justified if spectroscopic accuracy is desired. We note that the difference between all-electron cc-pCVNZ and frozen-core cc-pVNZ values for r_e and ω_e grows with basis set size.

Similarly to r_e and ω_e, the other spectroscopic constants tend to change significantly on going from a double-ζ to a triple-ζ basis set, but the changes become smaller with subsequent expansion of the basis. However, the convergence is more erratic and not monotonic for α_e and $\omega_e x_e$, which depend on the third and fourth derivatives, respectively, of the potential. These two terms appear to be rather insensitive to core correlation. The centrifugal distortion constant $\bar{D}_e$ converges for triple-ζ basis sets and beyond and is not sensitive to core correlation.

As mentioned earlier, significant effort[6,7,14,15] has gone into understanding the systematic convergence of different properties toward the CBS limit. In this study, we use the two-point linear extrapolation scheme of Helgaker et al. for correlation energies[15] to estimate the CBS limit. Results of this extrapolation using the cc-pCVQZ and cc-pCV5Z basis sets are denoted cc-pCV(Q5)Z, as indicated in the lower half of Tables 1−3. As expected, both increasing the size of the basis and the CBS extrapolation result in smaller predicted bond lengths.

Compared to the experimentally derived BO values for BH,[3] the cc-pCV(Q5)Z-estimated CBS limit for CCSD(T) differs by −0.0005 Å for r_e. For NH, the extrapolated CCSD(T)/cc-pCV(Q5)Z value for r_e deviates by −0.00128 Å from the experimentally deduced BO value.[4] This error demonstrates that even estimates of the CBS CCSD(T) limit are not always able to come within 0.001 Å of experimentally deduced BO bond lengths without additional correction for small effects.

TABLE 4: Difference between FCI and CCSD(T) Spectroscopic Constants for BH, CH$^+$, and NH

basis set	r_e	ω_e	$\omega_e x_e$	B_e	$\bar{D}_e$	α_e
			BH			
cc-pVDZ	0.00019	−1.93	0.2	−0.0035	0.00000	0.0012
cc-pVTZ	0.00020	−2.13	0.1	−0.0038	0.00000	0.0011
cc-pVQZ	0.00019	−2.13	0.2	−0.0030	0.00000	0.0011
cc-pV5Z	0.00019	−2.06	0.2	−0.0036	0.00000	0.0011
cc-pCVDZ	0.00019	−1.98	0.2	−0.0035	0.00000	0.0013
cc-pCVTZ	0.00018	−2.10	0.2	−0.0036	0.00000	0.0011
			CH$^+$			
cc-pVDZ	0.00018	−2.46	0.2	−0.0047	0.00000	0.0012
cc-pVTZ	0.00023	−3.00	0.2	−0.0059	0.00000	0.0013
cc-pVQZ	0.00022	−2.89	0.4	−0.0055	0.00000	0.0013
cc-pV5Z	0.00018	−2.77	0.5	−0.0052	0.00000	0.0016
cc-pCVDZ	0.00016	−2.44	0.0	−0.0046	0.00000	0.0010
cc-pCVTZ	0.00022	−2.94	−0.8	−0.0054	0.00000	0.0012
			NH			
cc-pVDZ	0.00058	−8.73	0.9	−0.0177	0.00000	0.0043
cc-pVTZ	0.00049	−7.59	0.9	−0.0156	0.00000	0.0038
cc-pCVDZ	0.00059	−8.84	0.9	−0.0178	0.00000	0.0044

3.2. Importance of Higher-Order Excitations: *n*-Particle Convergence. The *n*-particle calibration has been done to determine the remaining error in spectroscopic constants due to the incomplete treatment of electron correlation in the popular CCSD(T) model. Full CI provides a complete treatment of electron correlation within the given one-particle basis set, and Table 4 shows that the error in the CCSD(T) spectroscopic constants due to the incomplete treatment of electron correlation is around 0.0002−0.0006 Å for r_e, 2−9 cm^{-1} for ω_e, 0−1 cm^{-1} for $\omega_e x_e$, 0.003−0.018 cm^{-1} for B_e, and 0.001−0.004 cm^{-1} for α_e. The correction to the centrifugal distortion constant $\bar{D}_e$ is zero to the digits reported. The FCI corrections to CCSD(T) are very similar for the isoelectronic BH and CH$^+$ molecules, but they are around 2−4 times as large for NH.

It is immediately clear from Table 4 that the difference between CCSD(T) and FCI spectroscopic constants is almost insensitive to changes in the one-particle basis set. This weak coupling between the one-particle and *n*-particle spaces is advantageous because it allows one to approximate large-basis FCI potential-energy curves by computing much less expensive CCSD(T) energies using a large basis and adjusting these values with a FCI correction computed using a smaller basis. Thus, the large-basis FCI energies are estimated by

$$E_{\mathrm{FCI/VXZ}} \approx E_{\mathrm{CCSD(T)/VXZ}} + [E_{\mathrm{FCI/VYZ}} - E_{\mathrm{CCSD(T)/VYZ}}] \quad (13)$$

where cardinal number $Y < X$. According to Table 4, even a polarized double-ζ basis is sufficient to obtain a reliable estimate of the higher-order correlation correction.

Tables 1−3 give the Δ_{FCI} correction to the spectroscopic constants for BH, CH$^+$, and NH obtained in this fashion when the extrapolated CBS CCSD(T) energies at each point are adjusted according to the FCI correction in the above equation. For BH and CH$^+$, the FCI correction was obtained using the cc-pCVTZ basis, while for NH, we could only afford a FCI calculation with the cc-pCVDZ basis. Generally, CCSD(T) tends to overestimate ω_e and shrink r_e. Δ_{FCI} for our best computed values of r_e and ω_e are 0.00018 Å and −2.07 cm^{-1} for BH,

TABLE 5: Effect of Different Corrections to r_e and ω_e of BH, CH^+, and NH

	r_e			ω_e		
	BH	CH^+	NH	BH	CH^+	NH
Δextrapolation[a]	−0.00047	−0.00038	−0.00031	0.95	0.86	1.56
ΔFCI[b]	0.00018	0.00021	0.00052	−2.07	−2.92	−8.05
ΔREL[c]	−0.00001	−0.00002	0.00003	−0.59	−0.74	−1.75
ΔDBOC[d]	0.00066	0.00063	0.00027	−2.25	−2.81	−1.38
total	0.00036	0.00045	0.00051	−3.95	−5.61	−9.62

[a] CCSD(T)/cc-pCV(Q5)Z CBS extrapolation − CCSD(T)/cc-pCV5Z. [b] FCI/cc-pCVTZ − CCSD(T)/cc-pCVTZ for BH and CH^+ and FCI/cc-pCVDZ − CCSD(T)/cc-pCVDZ for NH. [c] At the CCSD/cc-pCV5Z level with unrelaxed densities. [d] At the CISD/cc-pVTZ level.

0.00021 Å and −2.92 cm^{-1} for CH^+, and 0.00052 Å and −8.05 cm^{-1} for NH. A recent study by Hirata et al.[39] indicates that the full treatment of triple excitations in coupled-cluster theory via the CCSDT model is nearly converged with respect to electron correlation because spectroscopic constants hardly change upon going to coupled-cluster theory with full quadruples, CCSDTQ. Comparing our CCSD(T) values to the CCSDT results of Feller and Sordo,[6] we find that much of the error in CCSD(T) is indeed recovered by CCSDT, but the effect of higher-order excitations is not completely negligible. For example, the changes in spectroscopic constants going from CCSD(T) to CCSDT for NH in a cc-pVTZ basis are 0.0003 Å (r_e) and −6.6 cm^{-1} (ω_e) compared to the complete FCI corrections of 0.0006 Å (r_e) and −7.6 cm^{-1}. As indicated by Table 5, the corrections for correlation effects beyond CCSD(T) are of roughly the same order as the corrections due to basis set extrapolation considered above. They are somewhat smaller for r_e and larger for ω_e compared to CBS extrapolation.

3.3. Importance of Relativistic Corrections. Even though relativistic effects are usually considered insignificant for first-row diatomics, they are indispensable for the level of spectroscopic accuracy we are trying to achieve. The importance of scalar relativistic effects to achieving high accuracy has been evident in recent literature.[16−18] There exist rigorous relativistic treatments such as the full four-component Dirac−Hartree−Fock theory, but it has been shown that a simple one-component scalar relativisitic Hamiltonian gives excellent results for systems consisting of light atoms.[40] Furthermore, Bauschlicher's work[41] indicated that scalar relativistic corrections computed via first-order perturbation theory using correlated wave functions give nearly identical results to those calculated using the Douglas−Kroll[42] formalism for small molecules. However, it should also be pointed out that, for very high rovibrational levels of water, Quiney et al.[43] found that more complete treatments of relativistic effects could be significant.

Scalar relativistic effects are considerably smaller in light diatomics than in molecules containing heavy atoms. Nevertheless, for BH, CH^+, and NH, these corrections are not necessarily negligible compared to the intrinsic errors in our methods. We find that the relativistic corrections to r_e are very small indeed (no more than 0.00003 Å), but for ω_e they are −0.59 cm^{-1} (BH), −0.74 cm^{-1} (CH^+), and −1.75 cm^{-1} (NH). However, relativistic effects seem to have a very minimal impact on other spectroscopic constants such as $\omega_e x_e$, α_e, B_e, and $\bar{D}_e$.

3.4. Importance of Adiabatic and Nonadiabatic Effects. Relative corrections to spectroscopic constants due to deviations from the BO approximation are assumed to be on the order of the electron/nuclear mass ratio (∼1/2000 for H atom). However, our test cases indicate that both adiabatic and nonadiabatic effects could be more significant. After computing our best results within the framework of the BO approximation and determining adiabatic effects using the DBOC,[21] we assume the majority of the remaining deviation from experimental values is attributable to nonadiabatic effects.[35]

We calculated first-order adiabatic corrections using the DBOC scheme and a correlated wave function, namely, configuration interaction with single and double excitations (CISD) with a cc-pVTZ basis. Our previous study of the DBOC indicates that it converges relatively quickly with respect to the one- and *n*-particle expansions.[21] CISD/cc-pVTZ results were very close to the CISD CBS limit for the cases considered, and electron correlation beyond CISD did not have a significant effect on the DBOC correction to the barrier to linearity in H_2O. In an earlier work, Handy and Lee[30] showed that the RHF/6-31G* DBOC corrections to bond lengths of diatomics decrease with mass in the order $H_2 > HF > N_2 > F_2$. The largest effect was seen for H_2, for which the DBOC correction to r_e was about 0.0002 Å.

The effect of the DBOC on the BH molecule is surprisingly large, 0.00066 Å for r_e and −2.25 cm^{-1} for ω_e. This change is greater than that due to basis set incompleteness (0.00047 Å and −0.95 cm^{-1}) or to correlation effects beyond CCSD(T) (0.00018 Å and −2.07 cm^{-1}). Despite the trend that the DBOC should decrease with increasing mass,[30] the effect on r_e of BH is more than three times larger than that of H_2 (0.0002 Å).[21] The adiabatic contribution to CH^+ is similar to that in BH: 0.00063 Å for r_e and −2.81 cm^{-1} for ω_e. Table 5 indicates that adiabatic corrections become disproportionately smaller in the heavier NH molecule, changing r_e and ω_e by 0.00027 Å and −1.38 cm^{-1}, respectively.

Only small errors remain in the present adiabatic theoretical treatment: residual basis set incompleteness in CCSD(T) energies, the use of finite basis sets in the FCI corrections, the truncation of the one- and *n*-particle spaces in the DBOC correction, and the use of only one-electron terms in the computation of relativistic effects. The preceding discussion indicates the very small size of these remaining uncertainties, and our final spectroscopic constants should be nearly exact in the adiabatic limit. Hence, we attribute most of the remaining difference from experiment to nonadiabatic effects. For BH, then, r_e changes by 0.00234 Å due to nonadiabatic effects. This change is larger than any of the small corrections considered in the present work, but it is consistent with Martin's estimate[3] of 0.0025 Å computed according to eq 11; the rotational g_J factor is found to be unusually large in BH.[3] If we add Martin's nonadiabatic correction of 0.0025 Å to our best adiabatic bond length of 1.22983 Å, the resulting theoretical nonadiabatic r_e of 1.2323 Å is nearly identical to the experimental r_e of 1.2322 Å.

The difference between our best calculated adiabatic results and experiment for CH^+ indicate that the nonadiabatic contribution to r_e should be 0.00275 Å, similar to the isoelectronic BH molecule. Unfortunately, adiabatic or BO-corrected experimental data are not available for CH^+ for comparison. Finally, our results for NH indicate that nonadiabatic effects are much smaller in that case (less than 0.0007 Å for r_e). This agrees qualitatively with the very small difference in experimental measurements of r_e for NH and ND (difference of 0.0001 Å).[33,34] Nevertheless, nonadiabatic effects in NH may still be comparable to some of the small effects presently studied.

3.5. Comparison of Small Effects on Spectroscopic Constants. Table 5 summarizes the effects on r_e and ω_e of the small contributions considered in the present adiabatic theoretical treatment, and these effects are displayed graphically in Figures 4 (r_e) and 5 (ω_e). As pointed out previously, all of these

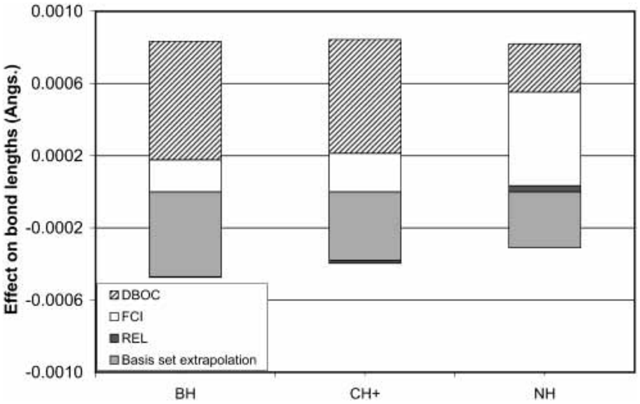

Figure 4. Effect of basis set extrapolation, FCI, relativistic, and adiabatic corrections on r_e.

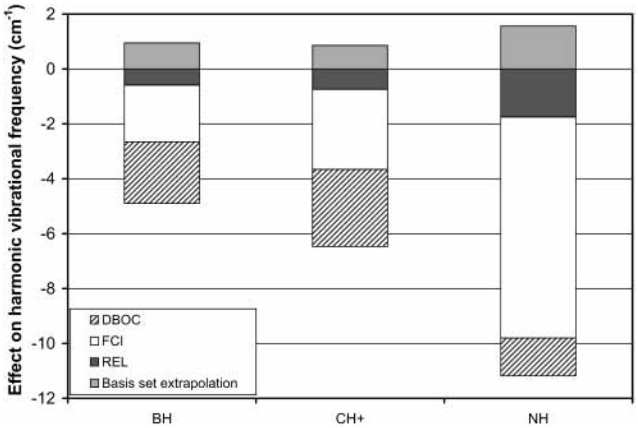

Figure 5. Effect of basis set extrapolation, FCI, relativistic, and adiabatic corrections on ω_e.

contributions are less important than going to core-valence basis sets and correlating the core electrons. For BH and CH^+, the most significant of the small effects on r_e is due to the adiabatic correction (DBOC), lengthening bonds by 0.0006−0.0007 Å. As discussed previously, this effect is unusually large in these molecules, and for NH we find that it becomes much smaller (0.0003 Å) and less important than basis set extrapolation or higher-order correlation effects (FCI correction). Basis set extrapolation beyond cc-pCV5Z is usually more important than the FCI correction for r_e, although the two effects are of a similar size (magnitude of 0.0002−0.0005 Å). The relativistic correction to r_e is negligible. Core correlation and basis set extrapolation consistently decrease bond lengths, while the full CI and adiabatic corrections consistently increase them. Because of these different signs, the net effect of all these contributions is only 0.0004−0.0005 Å. These results thus demonstrate that, as long as core correlation is included, the error in very large basis (e.g., cc-pCV5Z) CCSD(T) computations is probably under 0.001 Å compared to the relativity-corrected adiabatic limit for first-row hydrides.

For BH and CH^+, the adiabatic and FCI corrections to ω_e are similar in magnitude (2−3 cm^{-1}), while for NH, the FCI correction (8 cm^{-1}) is much larger than the adiabatic correction (1 cm^{-1}). For ω_e, the basis set extrapolation correction is similar to but consistently smaller than the FCI correction. Although-relativistic corrections to r_e were negligible, ω_e is changed by 1−2 cm^{-1}, which is relevant on the scale of spectroscopic accuracy. The relativistic correction to ω_e is larger than the adiabatic correction for NH. The net effect of all the small corrections to ω_e is 4−6 cm^{-1}, suggesting that the inherent errors of large-basis CCSD(T) computations of harmonic vibrational frequencies are of this order.

3.6. What is the Limit of ab initio Methods? Previous sections have focused primarily on the relative contributions of the small effects considered in this work. In this section, we will consider how our best computed spectroscopic constants compare to experiment. By accounting for one-particle space convergence by extrapolation of the correlation energy with cc-pCVQZ and cc-pCV5Z basis sets,[15] ensuring completeness of the *n*-particle space by correcting the CCSD(T) energies with full CI corrections, and adding one-electron relativistic terms, our theoretical spectroscopic constants should be near the exact relativity-corrected BO limit. After adding adiabatic corrections via the CISD/cc-pVTZ DBOC, our theoretical results should approach experiment very closely when nonadiabatic effects are small.

Perhaps the most direct comparison to experimentally deduced values can be made for the BH molecule, where Martin[3] used a theoretical value of g_J along with eqs 11 and 12 to estimate adiabatic and BO results for r_e. Our best adiabatic result for r_e is 1.2298 Å, which is nearly identical to Martin's value of 1.2297 Å. The difference between our best BO r_e (1.2292 Å) and Martin's experimentally deduced estimate (1.2295 Å) is slightly larger, but we note that Martin's estimate of the adiabatic effect used to obtain r_e^{BO}, 0.0002 Å, is significantly smaller than our computed adiabatic shift of 0.00066 Å. As noted previously, if we add Martin's computed nonadiabatic correction (0.0025 Å) to our best adiabatic estimate, we obtain 1.2323 Å for r_e, in excellent agreement with the experimental value of 1.2322 Å. By comparison of our adiabatic results directly to the unmodified experimental values, we find that the theoretical ω_e, 2366.34 cm^{-1}, matches very well with the experimental value of 2366.73 cm^{-1}.

Pure BO constants have not been estimated from the experimental data for CH^+, so we compare to the experimental effective constants which include nonadiabatic effects. Our adiabatic-corrected results are $r_e = 1.12815$ Å and $\omega_e = 2858.09$ cm^{-1}. By comparison of these values with effective nonadiabatic experimental values of $r_e = 1.1309$ Å and $\omega_e = 2858$ cm^{-1}, we find an error of −0.0027 Å for the bond length and agreement for the harmonic frequency. We can once again attribute most of this error to the large nonadiabatic effects in CH^+ (which is isoelectronic with BH).

As discussed above and pointed out by Martin,[4] nonadiabatic effects are expected to be small in NH. To the extent that this is true, our adiabatic-corrected constants may be compared directly to the experimental results. Our adiabatic results of $r_e = 1.03609$ Å and $\omega_e = 3283.05$ cm^{-1} match the effective experimental values of 1.03675 Å and 3282.58 cm^{-1} rather well, although the agreement is not quite as good as that seen for adiabatic results for the BH molecule (perhaps because the nonadiabatic terms are not completely negligible in NH).

For BH and CH^+, adiabatic or BO-corrected experimental results are not available for the higher-order spectroscopic constants, but for NH, the unadjusted experimental results are comparable to our BO results to the extent that adiabatic and nonadiabatic effects might be neglected.

4. Conclusions

Small effects usually neglected in quantum chemistry may become significant as higher accuracy is desired. The importance of the completeness of one- and *n*-particle basis sets, as well as that of relativistic and adiabatic corrections, has been quantified for three first-row hydrides, BH, CH^+, and NH. Full CI potential energies have been estimated at the CBS limit and corrected via scalar relativistic terms and the BO diagonal correction. One-particle basis set extrapolation, corrections for electron correlation beyond the CCSD(T) model, and adiabatic corrections are of roughly similar importance for the species studied. Scalar relativistic effects are negligible for bond lengths but are significant for predicting harmonic vibrational frequencies to spectroscopic accuracy. When compared to experimentally deduced adiabatic values, our best results for r_e are accurate within 0.0007 Å. Harmonic vibrational frequencies are accurate to 0.5 cm^{-1} or less, even when compared to experimental values which have not been adjusted to remove nonadiabatic contributions.

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