Benchmark calculations with correlated molecular wave functions. X. Comparison with ''exact'' MP2 calculations on Ne, HF, H_2O, and N_2

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The convergence of the MP2 valence correlation energy and pair energies for the correlation consistent basis sets has been investigated. Ne, HF, H_2O, and N_2 were studied. For all of these molecules, accurate MP2 correlation and pair energies are available from the recent MP2-R12 calculations of W. Klopper [J. Chem. Phys. **102**, 6168 (1995)]. The magnitudes of the calculated MP2 valence correlation and pair energies are found to increase systematically with increasing basis set size, with the cc-pV6Z basis set yielding 97.4%–98.3% of the MP2 valence correlation energy. A detailed analysis of the results for Ne reveals that the error due to truncation of the radial functions in the cc-pV6Z set is comparable to that due to neglect of higher angular momentum functions. Procedures for extrapolating the results to the complete basis set limit have also been investigated. © *1997 American Institute of Physics.* [S0021-9606(97)00721-6]

I. INTRODUCTION

The treatment of electron correlation in atomic and molecular calculations requires careful consideration of the various factors which influence the accuracy of the many-electron wave function. Attention must be given to both problems encountered in accurate *ab initio* calculations. The first of these is the error due to the truncation of the one-electron basis set used to expand the atomic or molecular orbitals. The second is the error due to the use of approximations to the full configuration interaction calculation by employing methods such as Møller–Plesset perturbation theory (MP2, MP3, MP4,...), coupled cluster methods (CCSD, CCSDT,...), or single- and multireference approaches (SDCI, MRCI).

Because the accuracy of the electronic wave function is dependent on both the form chosen for the electronic wave function and the quality of the one-particle basis set, it is important to understand the basis set dependence of the various correlation methods. Too often a more accurate correlated electronic structure method is used with a less accurate one-particle basis set. This can lead to erratic results that limit our understanding of the errors associated with the various correlated methods.[1] Only by approaching the complete basis set limit can the *intrinsic* accuracy of the theoretical model be determined.

Unfortunately, it is difficult to approach the complete basis set (CBS) limit for any particular correlation method. This is due to the slow convergence to the CBS limit as the basis set is systematically expanded which, in turn, is primarily due to the difficulty of satisfying the interelectronic cusp condition with a finite basis set. An acceptable approach might be to obtain an estimate of the CBS limit by extrapolating the results from a series of basis sets that exhibit systematic convergence properties. However, regular convergence is not observed with the majority of the basis sets in use today. As a result, it has proven to be very difficult to obtain estimates of the intrinsic errors in correlated atomic and molecular wave functions.

The family of correlation consistent basis sets[2–4] has been found to be quite unique among the basis sets available today. These sets have been found to exhibit systematic convergence to an apparent CBS limit. As a result, the correlation consistent sets have become quite useful in estimating CBS limits and in understanding the intrinsic errors associated with specific correlated molecular wave functions.[5–11] In this work, we study the behavior of the MP2 valence correlation energy and pair energies upon increasing the size of the correlation-consistent basis sets for H_2O, N_2, HF, and Ne.

For reference, we use the recent MP2-R12 results of Klopper[12] which provide reliable ''exact'' limits for these four systems. In the MP2-R12 method of Kutzelnigg and Klopper,[13–15] terms are included in the wave function which depend linearly on the interelectronic coordinate r_{ij}. These terms provide a far better description of the correlation cusp than can be provided by one-electron basis sets alone. By including such terms, Kutzelnigg, Klopper, and Noga,[12–17] have shown that the exact limit can be reached for a number of correlation methods.

Using the exact limits of the Klopper as reference points, we have also examined various methods for extrapolating the correlation-consistent basis set results to the CBS limit.

II. METHODOLOGY

The correlation consistent basis sets of Dunning and co-workers[2–4,18,19] have been used in the present work, along with three new high-accuracy correlation-consistent sets (cc-pV6Z,[20] aug-cc-pV6Z,[21] and cc-pCV6Z[22]) to further examine issues of convergence and accuracy. These sets which are denoted as cc-pVnZ, where n = D(2), T(3), Q(4), 5, and 6, are constructed by systematically adding *shells* of correlating functions to the atomic Hartree–Fock orbitals. The functions included in each shell contribute a comparable

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TABLE I. Valence pair energies and correlation energies from MP2 calculations on H_2O with the cc-pVnZ basis sets.

	$\epsilon(2a_1^2)$	$\epsilon(2a_1 1b_1)$	$\epsilon(2a_1 3a_1)$	$\epsilon(2a_1 1b_2)$	$\epsilon(1b_1^2)$	$\epsilon(1b_1 3a_1)$	$\epsilon(1b_1 1b_2)$	$\epsilon(3a_1^2)$	$\epsilon(3a_1 1b_2)$	$\epsilon(1b_2^2)$	E(MP2)
cc-pVDZ	−8.98	−18.23	−14.98	−14.92	−19.71	−31.78	−28.88	−17.42	−29.81	−16.91	−201.62
cc-pVTZ	−11.20	−24.91	−21.72	−22.87	−23.10	−38.29	−36.24	−22.28	−38.62	−22.23	−261.46
cc-pVQZ	−12.29	−27.41	−24.16	−25.82	−24.47	−40.24	−38.58	−24.09	−41.45	−24.28	−282.79
cc-pV5Z	−12.75	−28.40	−25.14	−27.05	−25.03	−40.97	−39.49	−24.87	−42.60	−25.20	−291.50
cc-pV6Z	−12.97	−28.83	−25.57	−27.60	−25.29	−41.26	−39.87	−25.25	−43.07	−25.66	−295.37
MP2-R12[a]	−13.31	−29.41	−26.16	−28.33	−25.65	−41.62	−40.30	−25.81	−43.64	−26.31	−300.54
Δ	0.34	0.58	0.59	0.73	0.36	0.36	0.43	0.56	0.57	0.65	5.17

[a]W. Klopper, J. Chem. Phys. **102**, 6168 (1995).

amount to the correlation energy. Because of this aufbau scheme, these basis sets are as compact as possible for a given level of accuracy. For the first row atoms, the valence sets are

	Primitive Sets	Contracted Sets
cc-pVDZ	$(9s4p1d)$	$[3s2p1d]$
cc-pVTZ	$(10s5p2d1f)$	$[4s3p2d1f]$
cc-pVQZ	$(12s6p3d2f1g)$	$[5s4p3d2f1g]$
cc-pV5Z	$(14s8p4d3f2g1h)$	$[6s5p4d3f2g1h]$
cc-pV6Z	$(16s10p5d4f3g2h1i)$	$[7s6p5d4f3g2h1i]$

In addition to the valence (cc-pVnZ) sets, Dunning and co-workers have also developed augmented valence sets (aug-cc-pVnZ) and core-valence sets (cc-pCVnZ). The augmented sets[3,21] include diffuse functions which are important in the description of the long-range behavior of the wave function (critical for describing anions, long-range dispersion forces, etc.). These sets are based on the standard correlation consistent valence sets, but with an additional diffuse function for each angular momentum symmetry. The core–valence sets[4,22] include high exponent functions which are important in the description of core–core and core–valence correlation effects. In this work, all three types of correlation consistent basis sets are used, though calculations using the valence sets have been the primary focus. Only pure spherical harmonic components of the polarization functions are used.

We report the values for the valence MP2 pair energies and correlation energies of several molecules at specific geometries: N_2 ($R_{NN}=2.070\ a_0$), H_2O ($R_{OH}=1.808\,85\ a_0$; $\theta_{HOH}=104.52°$), and HF ($R_{HF}=1.7328\ a_0$). The codes that were used include MOLPRO[23] and SUPERMOLECULE.[24]

III. RESULTS AND DISCUSSION

A. MP2 total and pair energies for H_2O, Ne, N_2, and HF

Tables I–IV summarize the valence MP2 pair energies and correlation energies computed for H_2O, Ne, N_2, and HF using the double zeta through sextuple zeta valence basis sets (cc-pVnZ, $n=$D−6). Tables V and Tables VI list the pair energies and valence correlation energies for calculations on H_2O and Ne using the augmented basis sets through the sextuple zeta level (aug-cc-pV6Z), while Tables VII–IX give all of the pair energies and the core–valence and valence correlation energies for H_2O and Ne using the core–valence sets through the quintuple zeta level for H_2O and through the sextuple zeta level for Ne. In all of these tables, the complete basis set (CBS) limits obtained by Klopper[12] are also listed.

Consider first the MP2 valence correlation energies of H_2O and Ne. As can be seen in Fig. 1, the MP2 valence correlation energies systematically increase in magnitude as the basis set is expanded from cc-pVDZ to cc-pV6Z. With the cc-pV6Z sets, the MP2 valence correlation energy for H_2O (-295.37 mE_h) is 5.17 mE_h higher than the limiting value of -300.54 mE_h, while for Ne the MP2 valence correlation energy (-311.78 mE_h) is 8.22 mE_h higher than the limit of -320.00 mE_h. If the aug-cc-pV6Z sets are used instead, the differences are reduced slightly—to 4.56 mE_h (H_2O) and 7.12 mE_h (Ne); see Fig. 2. Finally, if the cc-pCV6Z set is used for Ne, the error in the total MP2 valence correlation energy is reduced to 7.09 mE_h. From these results it is clear that, as far as the MP2 *valence* correlation energy is concerned, the augmented and core–valence sets add little to the standard cc-pVnZ sets for these systems.

In Fig. 3, the valence correlation energy calculated using

TABLE II. Valence pair energies and correlation energies from MP2 calculations on the neon atom with the cc-pVnZ basis sets.

	$\epsilon(2s2s)$	$\epsilon(2s2p)$	$\epsilon(2p_x^2)$	$\epsilon(2p_x 2p_y)$	E(MP2)
cc-pVDZ	−7.27	−38.11	−48.54	−91.61	−185.53
cc-pVTZ	−9.56	−65.56	−66.48	−122.72	−264.32
cc-pVQZ	−10.75	−76.82	−73.55	−132.46	−293.58
cc-pV5Z	−11.31	−81.80	−76.77	−136.29	−306.17
cc-pV6Z	−11.57	−83.95	−78.32	−137.94	−311.78
MP2-R12[a]	−12.02	−87.09	−80.74	−140.15	−320.00
Δ	0.45	3.14	2.42	2.21	8.22

[a]W. Klopper, J. Chem. Phys. **102**, 6168 (1995).

TABLE III. Valence pair energies and total correlation energies from MP2 calculations on N_2 with the cc-pVnZ basis sets.

	$\epsilon(2\sigma_g^2)$	$\epsilon(2\sigma_g 2\sigma_u)$	$\epsilon(2\sigma_u^2)$	$\epsilon(2\sigma_g 3\sigma_g)$	$\epsilon(2\sigma_u 3\sigma_g)$	$\epsilon(3\sigma_g^2)$	$\epsilon(2\sigma_g 1\pi_u)$	$\epsilon(2\sigma_u 1\pi_u)$	$\epsilon(3\sigma_g 1\pi_u)$	$\epsilon(1\pi_u^2)$	E(MP2)
cc-pVDZ	−8.75	−6.73	−12.89	−8.88	−19.90	−12.46	−39.07	−39.07	−53.11	−104.78	−305.64
cc-pVTZ	−12.76	−8.98	−15.59	−13.47	−26.37	−15.59	−51.34	−50.25	−62.41	−116.28	−373.04
cc-pVQZ	−14.71	−9.87	−16.62	−15.38	−28.55	−16.76	−56.47	−53.63	−65.30	−120.84	−398.13
cc-pV5Z	−15.53	−10.21	−17.07	−16.12	−29.50	−17.27	−58.59	−54.98	−66.41	−122.85	−408.53
cc-pV6Z	−15.92	−10.34	−17.28	−16.43	−29.94	−17.51	−59.54	−55.59	−66.87	−123.81	−413.23
MP2-R12[a]	−16.57	−10.54	−17.64	−16.91	−30.66	−17.93	−60.94	−56.38	−67.55	−125.25	−420.37
Δ	0.65	0.20	0.36	0.48	0.72	0.42	1.40	0.79	0.68	1.44	7.14

[a]W. Klopper, J. Chem. Phys. **102**, 6168 (1995).

each level of basis set is represented as a percentage of the limiting values. At the cc-pVDZ level from 58.0% to 72.7% of the correlation energy is recovered. The largest percentage is recovered for N_2 with a steady decrease from H_2O to HF to Ne. This same trend holds for all of the cc-pVnZ sets, although the magnitude of the spread decreases dramatically: The cc-pVTZ set recovers 82.6%–88.7% of the MP2-R12 limit, cc-pVQZ recovers 91.7%–94.7%, and cc-pV5Z recovers 95.7%–97.2%. The best calculations, which utilize the cc-pV6Z basis set, obtain 97.4%–98.3% of the limit. Although there is a steady increase in the percentage of the correlation energy recovered with basis set, the observed, very gradual improvement at the higher zeta levels illustrates the expected slow convergence of basis set expansions.

The MP2 valence pair energies of N_2 and H_2O are plotted in Figs. 4 and 5, while the percentages recovered are plotted in Fig. 6. For H_2O the pair energies computed with the cc-pV6Z set range in value from 0.34 to 0.73 mE_h higher that the limiting pair energies calculated by Klopper.[12] The range in errors is from nearly 1% to slightly more than 2.5% for the cc-pV6Z set. As can be seen in Fig. 5, the range in errors can be quite large for the smaller basis sets. For example, with the cc-pVDZ set the fraction of the pair energy recovered ranges from 52.7% for $\epsilon(2a_1 1b_2)$ to 76.8% for $\epsilon(1b_1^2)$, while for the cc-pVTZ set the variation is from 80.7% for $\epsilon(2a_1 1b_2)$ to 92.0% for $\epsilon(1b_1 3a_1)$. As expected, the augmented and core–valence sets improve the results only slightly. Note that the errors are distributed over a wide range of electron pairs, i.e., the error in the MP2 valence correlation energy is not due to errors in just a few pair energies.

With the core–valence sets, all-electron calculations were also performed; see Tables VIII–IX. The cc-pCV5Z basis set provides an MP2 core plus core–valence correlation energy for H_2O that is 1.52 mE_h higher than the limiting value of −61.47 mE_h. This is 97.5% of the core and core–valence correlation energy. For Ne, the calculated core plus core–valence correlation energies are −66.04 mE_h (cc-pCV5Z) and −66.87 mE_h (cc-pCV6Z), corresponding to 97.4% and 98.6%, respectively, of the limiting value (−66.80 mE_h) reported by Klopper.[12]

B. Analysis of MP2 calculations on Ne with cc-pV6Z basis set

To better understand the cause of the errors in the current calculations, we determined the contribution of each set of angular momentum functions ($s,p,d,\ldots$) in the cc-pV6Z basis set to the MP2 pair correlation energies in Ne. These contributions are compared with results from accurate atomic calculations by Jankowski and Malinowski[25] in Table X. Except for the last two rows, the columns labeled Δ in the table are simply the errors in $\epsilon(ij)$ for the given angular momentum set. These are a measure of the incompleteness of the *radial* expansions for each angular momentum included in the cc-pV6Z set. In the penultimate row, the Δ columns are a sum of all of the previous rows, i.e., a measure of the total incompleteness in the radial expansions of the angular momenta included in the cc-pV6Z set. In the last row, the Δ columns give the remaining errors in the pair energies as determined by comparison to Jankowski and Malinowski.[25] These differzences are a measure of the incompleteness in the *angular momentum* expansions included in the cc-pV6Z set.

The first point to note is that the residual errors in the radial expansions are comparable to the residual errors in the

TABLE IV. Valence pair energies and total correlation energies from MP2 calculations on HF with the cc-pVnZ basis sets.

	$\epsilon(2\sigma^2)$	$\epsilon(2\sigma 3\sigma)$	$\epsilon(3\sigma^2)$	$\epsilon(2\sigma 1\pi)$	$\epsilon(3\sigma 1\pi)$	$\epsilon(1\pi^2)$	E(MP2)
cc-pVDZ	−8.45	−16.02	−21.84	−28.71	−62.54	−64.07	−201.63
cc-pVTZ	−10.71	−23.69	−26.03	−46.03	−79.97	−85.34	−271.77
cc-pVQZ	−11.89	−26.56	−27.73	−52.80	−85.49	−93.05	−297.52
cc-pV5Z	−12.42	−27.76	−28.44	−55.71	−87.63	−96.34	−308.30
cc-pV6Z	−12.66	−28.26	−28.78	−56.96	−88.51	−97.84	−313.00
MP2-R12[a]	−13.06	−28.98	−29.30	−58.76	−89.64	−100.04	−319.78
Δ	0.40	0.72	0.52	1.80	1.13	2.20	6.78

[a]W. Klopper, J. Chem. Phys. **102**, 6168 (1995).

TABLE V. Valence pair energies and total correlation energies from MP2 calculations on H_2O with the aug-cc-pVnZ basis sets.

	$\epsilon(2a_1^2)$	$\epsilon(2a_11b_1)$	$\epsilon(2a_13a_1)$	$\epsilon(2a_11b_2)$	$\epsilon(1b_1^2)$	$\epsilon(1b_13a_1)$	$\epsilon(1b_11b_2)$	$\epsilon(3a_1^2)$	$\epsilon(3a_11b_2)$	$\epsilon(1b_2^2)$	E(MP2)
aug-cc-pVDZ	−9.13	−19.16	−16.17	−16.53	−20.26	−34.17	−32.15	−18.99	−33.90	−18.89	−219.35
aug-cc-pVTZ	−11.35	−25.37	−22.32	−23.76	−23.30	−38.98	−37.37	−22.83	−40.05	−23.02	−268.35
aug-cc-pVQZ	−12.37	−27.61	−24.42	−26.32	−24.57	−40.51	−39.06	−24.37	−42.09	−24.68	−285.91
aug-cc-pV5Z	−12.79	−28.50	−25.26	−27.23	−25.09	−41.07	−39.68	−25.02	−42.85	−25.41	−292.90
aug-cc-pV6Z	−12.98	−28.87	−25.62	−27.68	−25.31	−41.30	−39.94	−25.32	−43.19	−25.77	−295.98
MP2-R12[a]	−13.31	−29.41	−26.16	−28.33	−25.65	−41.62	−40.30	−25.81	−43.64	−26.31	−300.54
Δ	0.33	0.54	0.54	0.65	0.34	0.32	0.36	0.49	0.45	0.54	4.56

[a]W. Klopper, J. Chem. Phys. **102**, 6168 (1995).

TABLE VI. Valence pair energies and total energies from MP2 calculations on the neon atom with the aug-cc-pVnZ basis sets.

	$\epsilon(2s2s)$	$\epsilon(2s2p)$	$\epsilon(2p_x^2)$	$\epsilon(2p_x2p_y)$	E(MP2)
aug-cc-pVDZ	−7.61	−41.25	−54.50	−103.51	−206.87
aug-cc-pVTZ	−9.72	−68.19	−68.48	−126.14	−272.52
aug-cc-pVQZ	−10.81	−77.98	−74.55	−133.90	−297.24
aug-cc-pV5Z	−11.35	−82.35	−77.32	−136.96	−307.98
aug-cc-pV6Z	−11.60	−84.29	−78.67	−138.32	−312.88
MP2-R12[a]	−12.02	−87.09	−80.74	−140.15	−320.00
Δ	0.42	2.80	2.07	1.83	7.12

[a]W. Klopper, J. Chem. Phys. **102**, 6168 (1995).

TABLE VII. Valence pair energies and total correlation energies from MP2 calculations on H_2O with the cc-pCVnZ basis sets.

	$\epsilon(2a_1^2)$	$\epsilon(2a_11b_1)$	$\epsilon(2a_13a_1)$	$\epsilon(2a_11b_2)$	$\epsilon(1b_1^2)$	$\epsilon(1b_13a_1)$	$\epsilon(1b_11b_2)$	$\epsilon(3a_1^2)$	$\epsilon(3a_11b_2)$	$\epsilon(1b_2^2)$	E(MP2)
cc-pCVDZ	−9.30	−18.76	−15.64	−15.62	−19.73	−31.92	−28.98	−17.56	−30.02	−17.00	−204.53
cc-pCVTZ	−11.46	−25.37	−22.31	−23.59	−23.20	−38.53	−36.49	−22.51	−38.99	−22.49	−264.94
cc-pCVQZ	−12.41	−27.61	−24.42	−26.15	−24.53	−40.35	−38.69	−24.22	−41.63	−24.43	−284.44
cc-pCV5Z	−12.81	−28.49	−25.26	−27.20	−25.06	−41.02	−39.56	−24.95	−42.69	−25.29	−292.33
MP2-R12[a]	−13.31	−29.41	−26.16	−28.33	−25.65	−41.62	−40.30	−25.81	−43.64	−26.31	−300.54
Δ	0.50	0.92	0.90	1.13	0.59	0.60	0.74	0.86	0.95	1.02	8.21

[a]W. Klopper, J. Chem. Phys. **102**, 6168 (1995).

TABLE VIII. Core and core–valence pair energies and total core correlation energies (including core–valence energies) from MP2 calculations on H_2O with the cc-pCVnZ basis sets.

	$\epsilon(1a_1^2)$	$\epsilon(1a_12a_1)$	$\epsilon(1a_11b_1)$	$\epsilon(1a_13a_1)$	$\epsilon(1a_11b_2)$	E(MP2)
cc-pCVDZ	−29.11	−2.71	−1.28	−1.80	−1.87	−36.80
cc-pCVTZ	−35.54	−4.02	−3.43	−4.48	−5.09	−52.56
cc-pCVQZ	−38.85	−4.49	−3.94	−5.10	−5.80	−57.83
cc-pCV5Z	−39.89	−4.65	−4.10	−5.30	−6.02	−59.95
MP2-R12[a]	−40.86	−4.75	−4.22	−5.46	−6.19	−61.47
Δ	0.97	0.10	0.12	0.16	0.17	1.52

[a]W. Klopper, J. Chem. Phys. **102**, 6168 (1995).

TABLE IX. Pair energies and correlation energies from MP2 calculations on the neon atom with the cc-pCVnZ basis sets.

	$\epsilon(1s^2)$	$\epsilon(1s2s)$	$\epsilon(2s^2)$	$\epsilon(1s2p)$	$\epsilon(2s2p)$	$\epsilon(2p_x^2)$	$\epsilon(2p_x2p_y)$	E(MP2)
cc-pCVDZ	−28.38	−3.06	−7.72	−6.55	−41.44	−48.88	−92.27	−228.30
cc-pCVTZ	−34.65	−4.65	−10.00	−18.16	−69.36	−67.71	−124.58	−329.10
cc-pCVQZ	−38.03	−5.23	−10.98	−20.75	−78.78	−74.34	−133.40	−361.51
cc-pCV5Z	−39.18	−5.40	−11.42	−21.46	−82.66	−77.23	−136.79	−374.14
cc-pCV6Z	−39.66	−5.47	−11.65	−21.74	−84.42	−78.60	−138.22	−379.78
MP2-R12[a]	−40.24	−5.53	−12.02	−22.03	−87.09	−80.74	−140.15	−387.80
Δ	0.58	0.06	0.37	0.29	2.67	2.14	1.93	8.02

[a]W. Klopper, J. Chem. Phys. **102**, 6168 (1995).

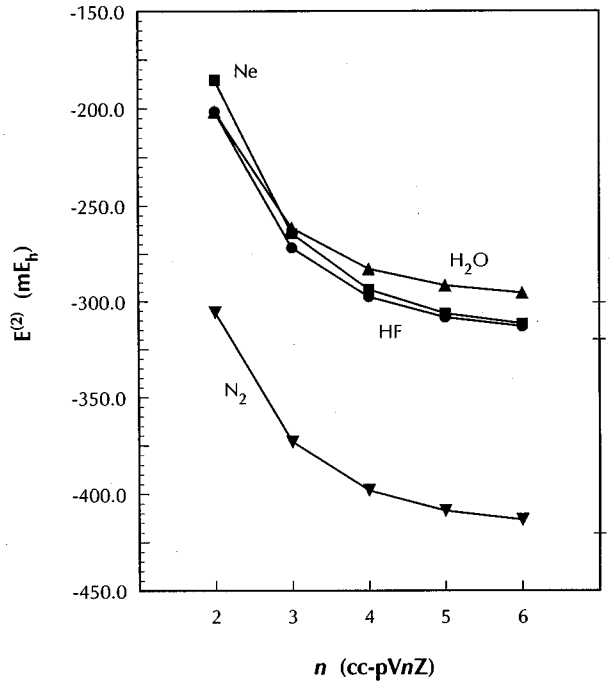

FIG. 1. Valence correlation energies from MP2 calculations on H_2O, N_2, HF, and Ne with the cc-pVnZ basis sets.

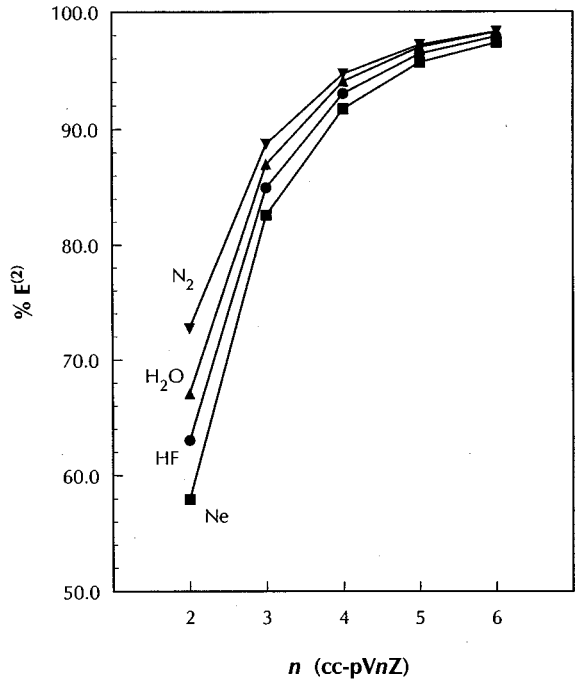

FIG. 3. Percentage of valence MP2 correlation energies of H_2O, N_2, HF, and Ne obtained with the cc-pVnZ basis sets. CBS limits are from Klopper (Ref. 12).

angular momentum expansions: 0.24 vs 0.25 mE_h for $\epsilon(2s2s)$, 1.63 vs 1.57 mE_h for $\epsilon(2s2p)$, and 2.45 vs. 2.09 mE_h for $\epsilon(2p2p)$. This means that any scheme used to extrapolate the MP2 correlation and pair energies to the CBS limit must account for the incompleteness in both the radial and angular expansions. This is very different than in many other studies of the convergence behavior of correlation energies[26] since any extrapolation scheme must simultaneously account for incompleteness in both the expansions, not just in the angular expansion.

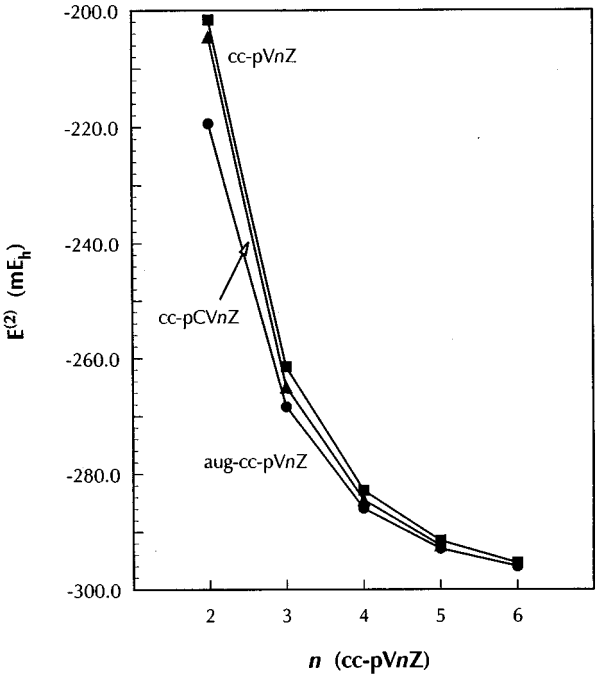

FIG. 2. Valence correlation energies from MP2 calculations on H_2O with the cc-pVnZ, aug-cc-pVnZ, and cc-pCVnZ basis sets.

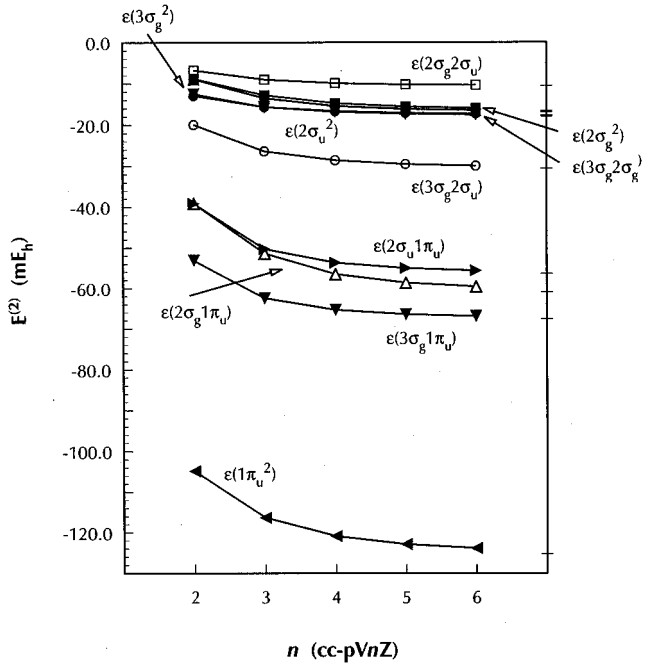

FIG. 4. Valence MP2 pair energies for N_2 from calculations with the cc-pVnZ basis sets.

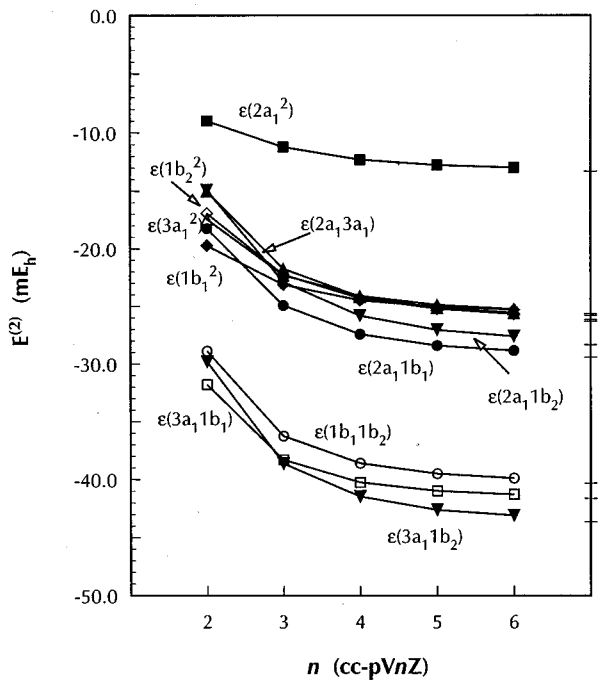

FIG. 5. Valence MP2 pair energies for H_2O from calculations with the cc-pVnZ basis sets.

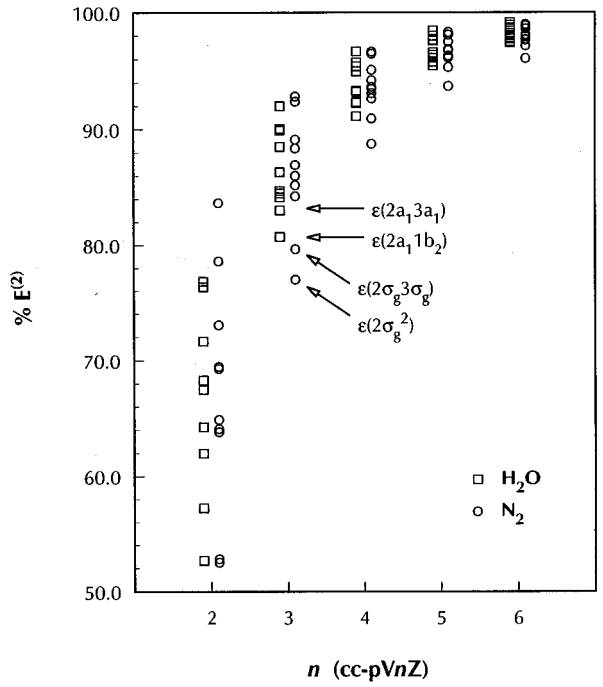

FIG. 6. Percentage of valence MP2 pair energies of H_2O and N_2 obtained with the cc-pVnZ basis sets. CBS limits are from Klopper (Ref. 12).

The calculated pair energies are changed significantly if we use the cc-pCV6Z set, the total errors in the radial expansions being reduced by factors of 1.3–1.5 (see Table XI). More importantly, the tight functions included in this set eliminate the irregularities observed in the p radial expansions in $\epsilon(2s2s)$, the p, d, and f radial expansions in $\epsilon(2s2p)$, and the p, d, f, and g radial expansions in $\epsilon(2p2p)$. However, the total errors in the radial expansions are still greater than 70% of the total errors in the angular expansions.

IV. EXTRAPOLATION TO THE COMPLETE BASIS SET LIMIT

As has been shown above, the large cc-pV6Z basis sets provide valence correlation and pair energies that are within 2% to 3% of the CBS limits. Because of the regular convergence pattern observed with the correlation consistent basis sets, it is of interest to determine if the valence correlation and pair energies can be extrapolated to the CBS limit. In the past, it has been observed,[7,27–29] that various molecular properties, including energetics and spectroscopic properties, converge nearly exponentially with respect to increases in the size of the correlation–consistent basis set. The following functional form has proven useful in extrapolating to the CBS limit.

$$A(n)=A(\infty)+Be^{-Cn}, \tag{1}$$

where n represents the cardinal number of the basis set (e.g., $n=2$ for cc-pVDZ) and $A(\infty)$ corresponds to the estimated CBS limit ($n\rightarrow\infty$) for property A. The parameters $A(\infty)$,

TABLE X. Incremental energy lowerings for addition of selected angular momentum sets to the Hartree–Fock orbitals of the neon atom; each succeeding set includes the previous sets. The angular momentum sets were taken from the cc-pV6Z basis set.

	$\lvert\Delta\epsilon_l(2s2s)\rvert$			$\lvert\Delta\epsilon_l(2s2p)\rvert$			$\lvert\Delta\epsilon_l(2p2p)\rvert$		
l	Present	J&M[a]	Δ	Present	J&M[a]	Δ	Present	J&M[a]	Δ
s	−3.17	−3.18	0.01	⋯	⋯	⋯	−2.28	−2.29	0.01
p	−1.78	−1.84	0.06	−42.45	−42.62	0.17	−96.27	−96.50	0.23
d	−4.60	−4.62	0.02	−16.89	−17.18	0.29	−90.88	−91.09	0.21
f	−1.28	−1.30	0.02	−17.46	−17.64	0.18	−15.60	−15.94	0.34
g	−0.47	−0.50	0.03	−4.91	−5.14	0.23	−7.87	−8.29	0.42
h	−0.20	−0.23	0.03	−1.71	−2.04	0.33	−2.59	−3.15	0.56
i	−0.07	−0.12	0.05	−0.53	−0.97	0.44	−0.77	−1.45	0.68
$\Sigma\Delta\epsilon_l$	−11.57	−11.81	0.24	−83.95	−85.58	1.63	−216.26	−218.71	2.45
ϵ[a]		−12.02	0.21		−87.15	1.57		−220.80	2.09

[a]K. Jankowski and P. Malinowski, Phys. Rev. A **21**, 45 (1980).

TABLE XI. Incremental energy lowerings for addition of selected angular momentum sets to the Hartree–Fock orbitals of the neon atom; each succeeding set includes the previous sets. The angular momentum sets were taken from the cc-pCV6Z basis set.

	$\lvert\Delta\epsilon_l(2s2s)\rvert$			$\lvert\Delta\epsilon_l(2s2p)\rvert$			$\lvert\Delta\epsilon_l(2p2p)\rvert$		
l	Present	J&M[a]	Δ	Present	J&M[a]	Δ	Present	J&M[a]	Δ
s	−3.18	−3.18	0.00	⋯	⋯	⋯	−2.29	−2.29	0.00
p	−1.83	−1.84	0.01	−42.58	−42.62	0.04	−96.44	−96.50	0.06
d	−4.61	−4.62	0.01	−17.12	−17.18	0.06	−90.98	−91.09	0.11
f	−1.28	−1.30	0.02	−17.52	−17.64	0.12	−15.76	−15.94	0.18
g	−0.48	−0.50	0.02	−4.95	−5.14	0.19	−7.97	−8.29	0.32
h	−0.20	−0.23	0.03	−1.72	−2.04	0.32	−2.62	−3.15	0.53
i	−0.07	−0.12	0.05	−0.53	−0.97	0.44	−0.77	−1.45	0.68
$\Sigma\Delta\epsilon_l$	−11.65	−11.81	0.16	−84.42	−85.58	1.16	−216.83	−218.71	1.88
ϵ[a]		−12.02	0.21		−87.15	1.57		−220.80	2.09

[a]K. Jankowski and P. Malinowski, Phys. Rev. A **21**, 45 (1980).

B, and C are determined via a least-squares procedure. No formal justification as to why this functional form seems to work has yet been provided, though the convergence behavior observed in the development of the sets[2] suggested such a form.

We have used Eq. (1) to extrapolate the results from our four test systems to the CBS limit. Although the exponential extrapolation certainly improves the calculated results, the remaining errors are substantial; see Table XII. For Table XII, extrapolations were done including results from three to five levels of basis sets. For instance, ''D-Q'' in the table represents an extrapolation including the results from the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. As seen in Table XII, the root-mean-square (rms) errors in the exponentially extrapolated CBS limits range from 3 to 7.5 mE_h.

To see if we could improve on the exponential function, we also investigated the following functional form:

$$A(l_{\max}) = A(\infty) + \frac{B}{(l_{\max}+d)^m} + \frac{C}{(l_{\max}+d)^{m+1}} + \frac{D}{(l_{\max}+d)^{m+2}}, \tag{2}$$

where $l_{\max}$ is the maximum angular momentum represented in each basis set, d is an angular momentum offset, and $m=3$ or 4. This particular form was inspired by convergence studies of the MP2 energy of the helium atom[26] where it was found that the partial wave increments asymptotically follow ($m=4$, $C=D=0$) for singlet pairs and ($m+2=6$, $B=C=0$) for triplet pairs with $d=1/2$. Additionally, the truncation error behaves as ($m=3$, $C=0$). Martin and Lee have also shown that the form where $C=0$ and $d=1/2$ works quite well for extrapolations of CCSD(T) energies.[30]

The root-mean-square errors resulting from the least-

TABLE XII. Root-mean-square errors in the extrapolated MP2 valence correlation energies obtained from calculations with the cc-pVnZ sets for Ne, H_2O, N_2, and HF.

		(3)			(3,4)			(3,5)			(3,4,5)		
Range	Expt.	$d=0$	1/2	1	$d=0$	1/2	1	$d=0$	1/2	1	$d=0$	1/2	1
D-Q	7.53	12.52	4.67	3.61	1.49	4.16	5.36	0.73	2.89	5.06			
D-5	5.84	9.06	2.90	3.54	1.48	3.34	4.03	0.41	2.46	3.96	1.57	1.33	0.88
D-6	4.89	7.05	2.03	3.19	1.18	2.50	2.88	0.36	1.90	2.96	0.65	0.37	0.81
T-5	3.94	2.38	0.89	3.83	1.52	2.04	2.02	0.94	1.82	2.31			
T-6	3.56	1.75	0.83	3.13	0.83	1.07	0.91	0.49	1.04	1.29	1.08	1.84	2.61
Q-6	3.16	0.52	0.96	2.23	0.41	0.49	0.80	0.42	0.31	0.33			
		(4)			(4,5)			(4,6)			(4,5,6)		
		$d=0$	1/2	1	$d=0$	1/2	1	$d=0$	1/2	1	$d=0$	1/2	1
D-Q		22.16	16.67	10.88	5.97	2.77	0.53	7.56	4.31	1.63			
D-5		16.97	12.64	8.20	4.34	1.97	0.37	5.56	3.13	1.16	0.91	0.43	0.50
D-6		13.68	10.15	6.54	3.49	1.67	0.42	4.46	2.58	1.07	1.06	0.66	0.59
T-5		7.82	5.52	3.38	1.76	0.78	0.37	2.48	1.37	0.55			
T-6		6.22	4.48	2.73	1.64	0.94	0.50	2.18	1.37	0.76	1.39	1.42	1.62
Q-6		3.37	2.51	1.56	1.48	1.21	1.08	1.74	1.39	1.14			

TABLE XIII. Errors in the extrapolated MP2 valence correlation energies obtained from calculations with the cc-pVnZ sets for Ne, H_2O, N_2, and HF.

	(3,5) $d=0$	(4,5) $d=1$		(3,5) $d=0$	(4,5) $d=1$
H_2O (-300.54)			N_2 (-420.37)		
D-Q	-0.38	-0.40	D-Q	0.64	0.34
D-5	-0.61	-0.34	D-5	0.31	0.44
D-6	-0.58	-0.18	D-6	0.28	0.61
T-5	-0.99	-0.24	T-5	-0.24	0.60
T-6	-0.67	0.02	T-6	0.07	0.86
Q-6	-0.17	0.40	Q-6	0.54	1.23
Ne (-320.00)			HF (-319.78)		
D-Q	1.25	0.91	D-Q	0.18	-0.04
D-5	0.35	0.46	D-5	-0.31	-0.13
D-6	0.19	0.53	D-6	-0.28	0.10
T-5	-1.12	-0.22	T-5	-1.12	-0.27
T-6	-0.50	0.40	T-6	-0.52	0.30
Q-6	0.45	1.29	Q-6	0.41	1.14

squares expansions using Eq. (2) are also summarized in Table XII. In addition to using Eq. (2) with $d=0$, 1/2, and 1, we also examined the expansions determined with $D=0$ [(3, 4) and (4, 5) extrapolation] and, separately, $C=0$ [(3, 5) and (4, 6) extrapolation]. Use of Eq. (2) reduces the magnitude of the *minimum* rms error from 3.16 mE_h (exponential) to just 0.42 mE_h [(3, 5) with $d=0$]. In fact, the (3, 5) fit with $d=0$ yields an rms error of less than 1 mE_h for all of the extrapolation sequences studied (D-Q through Q-6). Only for the T-5 and Q-6 extrapolations does one obtain better results with other functional forms, e.g., a (4, 5) fit with $d=1$ reduces the rms error from 0.94 to 0.37 mE_h for the T-5 extrapolations and a (3, 5) fit with $d = 1/2$ reduces the error from 0.42 to 0.31 mE_h for the Q-6 extrapolations.

The results of all of the extrapolations for a (3, 5) fit with $d=0$ and a (4, 5) fit with $d=1$ are listed in Table XIII. For the (3, 5) fit with $d=0$, the only absolute errors larger than 1 mE_h are for the D-Q and T-5 extrapolations for Ne (1.25 and -1.12 mE_h, respectively) and the T-5 extrapolations for HF (-1.12 mE_h). For the (4, 5) fit with $d=1$, the only absolute errors exceeding 1 mE_h are for the Q-6 extrapolations for Ne, N_2, and HF (1.29, 1.23, and 1.14 mE_h, respectively).

As noted in the previous section for Ne, truncation of the radial and angular expansions lead to comparable correlation energy errors for the largest correlation consistent set considered here (cc-pV6Z). Thus, none of the expansions, Eq. (2), represent the ''true'' asymptotic behavior of the MP2 energy with increasing n (cc-pVnZ). However, use of Eq. (2) does lead to a significant improvement over Eq. (1) for extrapolating the finite basis set results to the CBS limit. Overall, the (3, 5) fit with $d=0$ and the (4, 5) fit with $d=1$ seem to provide the most accurate and consistent results, providing estimates of the MP2 correlation energies that are accurate to 1 mE_h. It is interesting to note that in MP2-R12 calculation on He_2, Klopper[12] also found that the (4, 5) fit with $d = 1$ provided an accurate description of the convergence of the MP2 energies.

V. CONCLUSIONS

In this work we examined the convergence of the valence MP2 pair and correlation energies for H_2O, HF, Ne, and N_2 with the correlation consistent basis sets of Dunning and co-workers.[2–4,18–21] These sets result in smooth, monotonic convergence with the cc-pV6Z basis sets yielding 97.4%–98.3% of the complete basis set (CBS) limits reported by Klopper.[12] The calculations with the cc-pV6Z set are the most accurate basis set calculations on these systems reported to date.

However, despite the desirable systematic convergence characteristics of the correlation consistent basis sets, they still show the usual slow convergence associated with basis set expansions. For example, for the molecules considered here, the correlation consistent basis sets recover 58.0%–72.7% of the valence correlation energy at the cc-pVDZ level, 82.6%–88.7% at the cc-pVTZ level, 91.7%–94.7% at the cc-pVQZ level, and 95.7%–97.2% at the cc-pV5Z level. For this same series, the number of functions in the sets increase from 14 (cc-pVDZ) to 30 (cc-pVTZ) to 55 (cc-pVQZ) to 91 (cc-pV5Z) to 140 (cc-pV6Z).

Because of the systematic convergence behavior observed for the correlation consistent basis sets, the energies can be approximately extrapolated to the CBS limit. Extrapolating the valence MP2 correlation energies, $E^{(2)}$, computed with the cc-pVDZ, cc-pVTZ, and cc-pVQZ sets to the CBS limit using

$$E^{(2)}(l_{\max}) = E^{(2)}(\infty) + \frac{B}{(l_{\max}+1)^4} + \frac{C}{(l_{\max}+1)^5},$$

we obtain: -300.94 mE_h(H_2O), -319.09 mE_h(Ne), -319.82 mE_h(HF), and -420.03 mE_h(N_2). These differ by just -0.40, 0.91, -0.04, and 0.34 mE_h from the accurate values reported by Klopper.[12] Although the general form of this expansion was suggested by prior studies of partial-wave expansions of the MP2 correlation energy,[26] calculations on the Ne atom clearly show that this form cannot be exact for the correlation consistent basis sets as the errors in the radial expansions are comparable to those in the angular expansions.

Note added in proof. The authors wish to draw the readers attention to two recent papers by D. Moncrieff and S. Wilson [J. Phys. B **29**, 6009 (1996); J. Phys. B **29**, 2425 (1996)] that have thoroughly examined the correlation energies of H_2O and N_2 using distributed Gaussian basis sets.

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