RESEARCH ARTICLE | JUNE 06 2008

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J. Chem. Phys. 128, 214308 (2008)
https://doi.org/10.1063/1.2927302

Correlation energy and dispersion interaction in the *ab initio* potential energy curve of the neon dimer

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(Received 18 March 2008; accepted 21 April 2008; published online 6 June 2008)

A close approximation to the empirical potential energy curve of the neon dimer is obtained by coupled-cluster singles plus doubles plus noniterative triples calculations by using nonaugmented correlation-consistent basis sets without counterpoise corrections and complementing them by three-term extrapolations to the complete basis set limit. The potential energy is resolved into a self-consistent-field Hartree–Fock contribution and a correlation contribution. The latter is shown to decay in the long-range region in accordance with the empirical dispersion expansion.
 [DOI: 10.1063/1.2927302]

I. OBJECTIVE

Intermolecular interactions play important roles in solid-state, liquid, gas, and biological phenomena.[1–7] Experimental as well as theoretical interest in them has steadily increased over the last decades. In this context, a body of *ab initio* work is developing on the properties of the van der Waals dimers of noble gas atoms using the *supermolecule approach*, where the potential energy curve is calculated by taking differences between molecular energies at finite distances and at infinity (or a large-distance facsimile thereof). For such calculations, the individual energies must sufficiently closely approximate their complete basis set (CBS) limits so that, upon taking the differences, the cancelation of their respective errors is accurate enough for the remaining errors to be small compared to the differences that represent the potential energy surfaces. This objective is manifestly more difficult to achieve when potential energy curves have very small values, as is the case for bonds due to dispersion interactions.

The goal of most *ab initio* work on the noble gas dimers has been the accurate recovery of the binding energy and the equilibrium distance. Our motivating interest is somewhat different. In the context of our work on other molecules,[8–10] it became important for us to know whether the supermolecule approach will, in fact, yield a *correlation potential* curve that decays in the long-range region according to the dispersion expansion $(-C_6/R^6-C_8/R^8-\cdots)$. We therefore resolve the potential energy curve into a Hartree–Fock contribution and a correlation contribution and examine the latter in detail.

A second problem of interest to us was whether it is necessary to invoke the counterpoise correction in order to address this question. Past approaches have almost exclusively treated noble gas dimers by using atomic basis sets that are heavily augmented by diffuse orbitals. Additional functions in the bond region have also been used. Such basis sets were found to generate substantial basis-set-superposition errors[11,12] which were then dealt with by applying counterpoise corrections.[13–15] Alternative approaches[16–19] to reducing the basis-set-superposition error have also been developed. But as yet, a complete elimination of this error does not seem to have been achieved. A recent discussion has been given in Ref. 20.

Since dispersion interactions are long-range correlation effects and not generated by orbital overlap, one can ask oneself how well one can do by using basis orbitals that are not augmented and extrapolating them to the CBS limit without counterpoise corrections. In principle, a basis that approaches the complete orbital space *sufficiently closely for the separated atoms* cannot suffer from a basis-set-superposition error due to possible (approximate) overcompleteness of the basis that is used in the molecule.

In the present study, we shall, in fact, determine a very accurate theoretical potential energy curve of the neon dimer by CBS extrapolation of the energies obtained with nonaugmented basis sets without counterpoise corrections. The analysis of this curve furthermore yields the correct dispersion coefficients.

II. METHOD

We have followed straightforward procedures. Dunning's nonaugmented cc-pV*X*Z basis sets[21] for $X=4,5,6$ were used to express the molecular orbitals. For the sake of comparison, we also considered the corresponding singly augmented analogs.[22] The energies $E(R)$ were calculated by the CCSD(T) method. The total energies $E(R)$ were expressed as the sum

$$E(R) = E_{\mathrm{RHF}}(R) + E_{\mathrm{cor}}(R), \tag{1}$$

where $E_{\mathrm{RHF}}(R)$ is the Hartree–Fock energy, while the correlation energy $E_{\mathrm{cor}}(R)$ is obtained as the difference between $E(R)$ and $E_{\mathrm{RHF}}(R)$.

The extrapolation to the CBS limit was performed by the two-tier approach, i.e., by separately extrapolating the Hartree–Fock energies and the correlation energies. While the exponential extrapolation[23,24] was used for the Hartree–Fock component, i.e.,

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$$E_{\mathrm{RHF}}(R,X) = E_{\mathrm{RHF}}(R,\mathrm{CBS}) + a(R)\exp[-b(R)X], \quad (2)$$

the correlation energy was extrapolated by using the three-term inverse-power expansion,[25–36]

$$E_{\mathrm{cor}}(R,X) = E_{\mathrm{cor}}(R,\mathrm{CBS}) + A(R)X^{-3} + B(R)X^{-5}. \quad (3)$$

This two-tier extrapolation scheme has been developed and well tested[25–32] in the context of achieving chemical accuracy (~1 mhartree) when calculating with nonaugmented cc-pV*X*Z bases. The extent of its validity has been less thoroughly explored for augmented bases, and we shall indeed encounter problems in this respect.

The present approach differs from other work on dispersion forces by including the X^{-5} term. We have found that, for the present purpose, the three-term expression of Eq. (3) yields a significantly superior extrapolation compared to that resulting from using the inverse third power term only.

The potential energy surface $V(R)$ was obtained as the difference

$$V(R) = E(R) - E(60\ \text{Å}), \quad (4)$$

since the Hartree–Fock energy as well as the CCSD(T) energy were found to change by less than 5×10^{-9} hartree from 30 to 60 Å. In analogy to Eq. (1), the potential energy curve was then decomposed into a Hartree–Fock and a correlation contribution according to

$$V(R) = V_{\mathrm{RHF}}(R) + V_{\mathrm{cor}}(R), \quad (5)$$

where

$$V_{\mathrm{RHF}}(R) = [E_{\mathrm{RHF}}(R) - E_{\mathrm{RHF}}(60\ \text{Å})], \quad (6)$$

$$V_{\mathrm{cor}}(R) = [E_{\mathrm{cor}}(R) - E_{\mathrm{cor}}(60\ \text{Å})]. \quad (7)$$

It may be noted that the CBS extrapolation of Eq. (3) can be directly applied to the correlation potential V_{cor}, i.e.,

$$V_{\mathrm{cor}}(R,X) = V_{\mathrm{cor}}(R,\mathrm{CBS}) + A^*(R)X^{-3} + B^*(R)X^{-5}, \quad (8a)$$

$$A^*(R) = A(R) - A(60\ \text{Å}), \quad B^*(R) = B(R) - B(60\ \text{Å}). \quad (8b)$$

For the Hartree–Fock part, the components at RÅ and 60Å must, however, be separately extrapolated before taking the difference of Eq. (6).

The CCSD(T) calculations and the extrapolations were performed at 30 internuclear distances by using the GAMESS (Ref. 37) and the MOLPRO (Ref. 38) suites of molecular programs.

III. POTENTIAL ENERGY CURVE

Based on a comprehensive consideration of experimental data, Aziz and Slaman[39] have derived the following empirical potential for the Neon dimer:

$$V(R) = A\exp(-aR - bR^2) - f(R) \times (C_6/R^6 + C_8/R^8 + C_{10}/R^{10}), \quad (9a)$$

with the damping factor

$$f(R) = \exp[-(1 - d/R)^2] \quad \text{for } R \leqslant d \quad (9b)$$

$$f(R) = 1 \quad \text{for } R \geqslant d$$

and the constants

$$A = 119.8458 \text{ hartree},$$

$$a = 80.983\,667 \text{ bohr}^{-1}, \quad b = 4.433\,359 \text{ bohr}^{-2},$$

$$C_6 = 6.447\,08 \text{ hartree bohr}^6,$$

$$C_8 = 96.501\,20 \text{ hartree bohr}^8,$$

$$C_{10} = 1520.019 \text{ hartree bohr}^{10},$$

$$d = 7.943\,96 \text{ bohr} = 4.203\,76 \text{ Å}.$$

(This type of potential originally goes back to Ahlrichs *et al.*[40]). Aziz and Slaman[39] used the results deduced from atomic data by Kumar and Meath[41] for C_6 (choosing it to be within 1% of the value in Ref. 41) and kept C_8 and C_{10} coefficients within the asymptotic limits derived in the study of Certain and co-workers.[42,43] Within these constraints, Aziz and Slaman[39] were able to determine C_6 and C_8 and the remaining four parameters so that many other properties were well reproduced: Virial coefficients, viscosity, thermal conductivity, internuclear equilibrium distance, binding energy, collision cross sections and ro-vibrational spectrum. Equations (9a) and (9b) imply that, in this system, the "long-range" region starts at 4.2 Å.

The values of the interaction potential that we obtained for the six mentioned AO-bases (viz., aug- and non-aug-4,5,6 zeta) at 29 internuclear distances are listed in Table I. For each calculation, the minimum of the potential is indicated by boldfaced underscored font.

Table II provides a comparison between the experimental interaction potential and several theoretical interaction potentials. The second column lists the values of the experimentally deduced potential of Aziz and Slaman,[39] which was given above. Columns three, four, and five list results of the present work, viz., from the aug-6-zeta, the aug-4,5,6-CBS, and the non-aug-4,5,6-CBS calculations, respectively. Columns six to eight list values published by other authors[44–46] for this potential. *For all theoretical work, the entries listed are the deviations from the experimental values*. In each column, the position of the respective minimum is indicated by boldfaced underscored font. The quality of the three potentials of the present work listed in Table II (i.e., columns three to five) is illustrated in Figs. 1 and 2, which exhibit plots of them together with a plot of the experimental potential.[39]

The CBS extrapolation of the calculations using the non-augmented bases yields a close approximation to the empirical curve. The equilibrium distance is obtained within 0.016 Å. The binding energy of −133.75 μhartree is recovered with an error of 2.09 μhartree. The long-range region of the curve is also very closely reproduced and will be discussed in detail below. The somewhat larger deviations between 3.2 and 4.2 Å will be commented upon in Sec. IV B.

TABLE I. Calculated potential energy curves for the neon dimer. Minima indicated by bold-faced underscored font. Energies in microhartree.

	CCSD(T), nonaugmented bases			CCSD(T), augmented bases		
R (Å)	V4Z	V5Z	V6Z	aug-V4Z	aug-V5Z	aug-V6Z
2.750	110.84	151.81	108.51	−10.97	18.10	23.72
2.800	41.22	85.25	48.03	−62.14	−36.29	−30.31
2.900	−49.69	−1.27	−28.62	−121.87	−102.05	−95.30
3.000	−96.49	−46.83	−66.83	−146.32	−130.38	−123.30
3.050	−108.79	−59.69	−76.86	−150.70	−135.83	−128.73
3.075	−112.86	−64.32	−80.27	−151.55	−137.02	−129.95
3.100	−115.74	−67.97	−82.79	**−151.70**	**−137.39**	**−130.36**
3.125	−117.59	−70.77	−84.55	−151.24	−137.04	−130.08
3.150	**−118.53**	−72.82	−85.65	−150.27	−136.09	−129.23
3.200	−118.10	−75.10	**−86.25**	−147.11	−132.75	−126.13
3.250	−115.26	**−75.49**	−85.21	−142.73	−127.99	−121.69
3.300	−110.64	−74.52	−82.99	−137.49	−122.29	−116.37
3.400	−98.11	−70.02	−76.44	−125.48	−109.43	−104.37
3.500	−83.68	−63.74	−68.55	−112.57	−96.17	−91.99
3.600	−69.37	−56.90	−60.46	−99.64	−83.61	−80.19
3.750	−50.55	−46.91	−49.16	−81.42	−67.17	−64.51
4.000	−28.82	−32.88	−34.12	−56.51	−46.66	−44.34
4.200	−18.81	−24.34	−25.43	−41.88	−35.19	−32.91
4.400	−12.91	−17.89	−19.07	−31.09	−26.72	−24.65
4.500	−10.91	−15.33	−16.56	−26.81	−23.32	−21.43
4.800	−7.01	−9.75	−11.01	−17.22	−15.63	−14.39
5.000	−5.40	−7.34	−8.49	−12.86	−12.08	−11.20
5.400	−3.34	−4.39	−5.19	−7.36	−7.38	−6.95
6.000	−1.75	−2.27	−2.66	−3.47	−3.67	−3.59
6.400	−1.18	−1.53	−1.78	−2.24	−2.37	−2.38
6.600	−0.98	−1.26	−1.47	−1.82	−1.93	−1.95
7.000	−0.68	−0.88	−1.02	−1.25	−1.31	−1.34
7.500	−0.45	−0.58	−0.67	−0.81	−0.84	−0.86
8.000	−0.30	−0.39	−0.45	−0.54	−0.56	−0.57

The present treatment does not include the effects of valence correlations beyond the CCSD(T) level, core correlations, and relativistic corrections. Burda *et al.*[47] as well as Gdanitz[45] and Lee[48] have estimated that these contributions may increase the binding energy by up to 2 μhartree, primarily due to improvements in describing the valence correlations. Their estimates have, in fact, been confirmed by highly accurate recent calculations of Hellmann *et al.*[46] The quantitative values the latter authors reported for these corrections are listed in the last column of Table II. Adding the correction at the equilibrium distance to the nonaugmented CBS limit of the present work (column 5) yields a theoretical value within about 0.3 μhartree of the experiment-deduced value. It is also seen that, for distances smaller than the equilibrium geometry, the combined contributions of the mentioned corrections become considerably larger, as had also been predicted by Gdanitz.[45]

Although the augmented sextuple-zeta basis yields a remarkably accurate curve, the CBS extrapolation of the calculations using the augmented bases yields a poorer curve than the CBS extrapolation of the nonaugmented bases, the error in the binding energy being about 10 μhartree. We shall examine the augmented bases in greater detail in Sec. IV D.

IV. CORRELATION POTENTIAL AND DISPERSION ENERGY

A. Background

London's classical paper[49] of 1937 identified the correlative long-range attractions, which he called dispersion interactions, and established that they decay as the inverse sixth power of the internuclear distance (see also Ref. 50). Numerous subsequent investigations (Refs. 51–57 and other work mentioned therein) have elucidated the nature of these interactions from the point of view of the perturbation theory of the separated atoms. These studies combine experimental atomic spectroscopic information with theoretical considerations, such as sum rules for oscillator strengths, and/or use theoretical derivations of polarizabilities. For the noble gas atoms, they have led to asymptotic expansions of the dimer potentials in terms of inverse powers of R^2, starting with R^{-6}, which determine the dispersion coefficients. In view of the subsequent discussion, Table III lists values obtained by various authors for C_6 and C_8. The values indicated by boldfaced font are generally considered the best. This approach yields of course only information for the *asymptotic* region.

The object of the *empirical* potentials of noble gas dimers is to account for the experimental information of the dimers. An example is the Ne_2 potential of Aziz and

TABLE II. Experimental and theoretical interaction potentials for the neon dimer. Minima indicated by boldfaced underscored font. Energies in microhartree.

		Deviations of theoretical values from experimental values						
		This work CCSD(T)			Previous Work			
R (Å)	Deduced from experiment[a]	V6Z aug	CBS aug	CBS non-aug	r_{12}-ACPF[b] "aug-V5Z"	CCSD(T)[c] aug-V5Z+bf	CCSD(T)[d] t-aug-V6Z+bf	Corrections[e] to CCSD(T)
2.750	10.63	13.09	20.34	−15.95	35.90	13.36	⋯	⋯
2.800	−40.95	10.64	18.61	−11.88	⋯	⋯	7.28	−5.55
2.900	−102.41	7.11	16.52	−5.43	⋯	⋯	4.70	−4.15
3.000	−128.16	4.86	13.98	−0.42	21.19	4.49	3.38	−3.14
3.050	−132.78	4.05	12.61	1.39	⋯	⋯	⋯	⋯
3.075	−133.65	3.70	11.84	**2.09**	18.50	3.69	⋯	⋯
3.100	**−133.75**	**3.39**	11.15	2.76	17.71	**3.31**	**2.73**	−2.39
3.125	−133.20	3.12	**10.41**	3.34	**16.99**	3.07	⋯	⋯
3.150	−132.10	2.87	9.63	3.84	⋯	⋯	⋯	⋯
3.200	−128.57	2.44	8.20	4.68	⋯	⋯	2.41	−1.85
3.250	−123.78	2.09	6.80	5.29	13.93	2.55	⋯	⋯
3.300	−118.15	1.78	5.50	5.82	⋯	⋯	2.29	−1.43
3.400	−105.68	1.31	3.36	6.48	⋯	⋯	2.19	−1.12
3.500	−92.95	0.96	1.84	6.85	9.69	2.04	2.09	−0.89
3.600	−80.89	0.70	0.96	6.93	⋯	⋯	1.99	−0.71
3.750	−64.91	0.40	0.57	6.58	6.84	1.67	⋯	⋯
4.000	−44.44	0.10	1.09	4.96	4.82	1.61	1.30	−0.32
4.200	−32.83	−0.08	1.41	3.29	⋯	⋯	0.95	−0.22
4.400	−24.45	−0.20	1.41	1.79	⋯	⋯	0.68	−0.16
4.500	−21.19	−0.24	1.33	1.27	2.17	0.58	⋯	⋯
4.800	−14.04	−0.35	0.85	0.22	⋯	⋯	0.38	−0.08
5.000	−10.83	−0.37	0.57	−0.01	1.20	0.29	0.30	−0.06
5.400	−6.65	−0.30	0.28	−0.07	⋯	⋯	⋯	⋯
6.000	−3.43	−0.16	0.03	0.03	⋯	⋯	0.10	−0.02
6.400	−2.29	−0.09	−0.05	0.04	⋯	⋯	⋯	⋯
6.600	−1.89	−0.06	−0.03	0.02	⋯	⋯	⋯	⋯
7.000	−1.32	−0.02	−0.04	0.03	⋯	⋯	0.04	−0.01
7.500	−0.86	−0.00	−0.01	0.02	⋯	⋯	⋯	⋯
8.000	−0.58	0.01	−0.01	0.02	⋯	⋯	0.01	0.00

[a]Obtained with the formula of Aziz and Slaman (Ref. 39).
[b]Obtained by Gdanitz (Ref. 45) with a customized "aug-V5Z-type" [18*s*13*p*8*d*6*f*3*g*2*h*] basis and counterpoise correction.
[c]Obtained by Cybulski *et al.* (Ref. 44) with aug-cc-pV5Z basis plus bond midpoint basis functions and counterpoise correction.
[d]Obtained by Hellmann *et al.* (Ref. 46) with t-aug-cc-pV6Z basis plus bond midpoint basis functions and counterpoise correction.
[e]Corrections to the CCSD(T) potential due to core correlation, scalar relativity, and valence correlations beyond CCSD(T), reported by Hellmann *et al.* (Ref. 46).

Slaman,[39] which was quoted in Eq. (9a) of Sec. III. Since the molecular experimental data alone are insufficient to determine the long-range distance dependence, these potentials typically incorporate the asymptotic dispersion expansion described in the preceding paragraph. The extension of the long-range attractive part to shorter ranges is then mediated by inserting empirical damping factors into the asymptotic atomic expansions. In a comprehensive study of all homonuclear and heteronuclear noble gas dimers, which generated a set of consistent empirical potentials, Tang and Toennies[58] have, however, shown that the part of the asymptotic expansion beyond R^{-10} is too small to have any relevance regarding the molecular experimental data. Moreover, these authors essentially require the term C_{10}/R^{10} only for fitting the experimental data at *short* ranges. For instance, in the long-range region of Ne_2, i.e., for $R>4.2$ Å [See Eq. (9b) above], this term has a value of less than a microhartree over most of the range.

When the molecular interaction is calculated via the *supermolecule* route, one explicitly obtains the entire potential energy curve. Here, the question is therefore whether the dispersion expansion can, in fact, be recovered from the long-range part of the theoretical curve. This problem can be approached in different ways. To achieve a direct comparison to the experimentally deduced parameters, Cybulski and Toczyłowski[45] determined a potential expression of an experimental-empirical form similar to that of Tang and Toennies[58] by a least-mean-squares fit to the theoretical potential. Hellmann *et al.*[46] fitted their data to a similar, but more complex potential with more parameters. Monari *et al.*[57] as well as Thom *et al.*,[59] on the other hand, simply tried to fit the total theoretical potential $V(R)$ directly to an

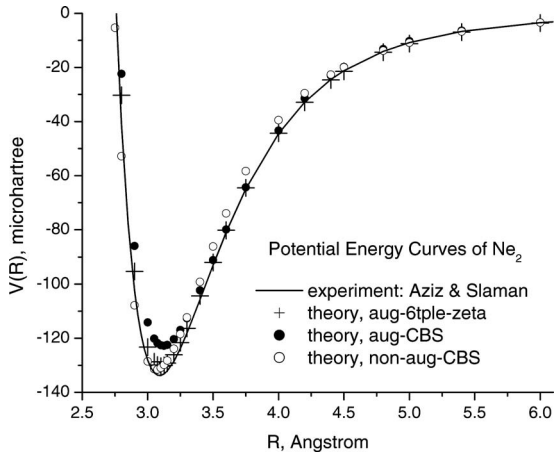

FIG. 1. Potential energy curves of the neon dimer. Experimental curve from Aziz and Slaman (Ref. 39). Theoretical curves from cc-pV(4,5,6)Z-CBS calculations, aug-cc-pV6Z calculations, and aug-cc-pV(4,5,6)Z-CBS calculations of the present work.

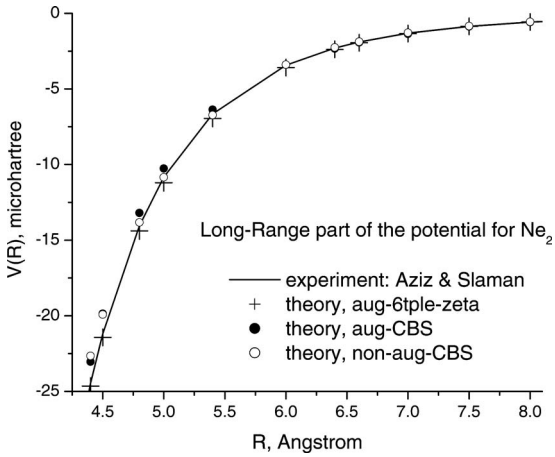

FIG. 2. Long-range parts of the potential energy curves for the neon dimer. Experimental curve from Aziz and Slaman (Ref. 39). Theoretical curves from cc-pV(4,5,6)Z-CBS calculations, aug-cc-pV6Z calculations, and aug-cc-pV(4,5,6)Z-CBS calculations of the present work.

expression $(-C_6/R^6-C_8/R^8)$ over a range starting at about 6 and 4.2 Å, respectively. It stands to reason that one should not expect *close* agreement between coefficients C_k that are obtained via different fitting models.

B. Theoretical and empirical correlation potential

As stated in the Introduction, we pursued a different line of inquiry. Since London's analysis[49] implies that the dispersion forces are a consequence of electron correlation, we investigated whether the correlation part $V_{cor}(R)$ of the theoretical potential, as defined by Eq. (7), in fact, embodies the empirical dispersion interaction potential. To this end, we examined our best potential, viz., the one obtained as the CBS limit using the nonaugmented cc-pVXZ basis sets.

From the derivation[40] of the empirical potential of Aziz and Slaman, it is clear that the exponential first term in Eq. (9a) is an empirical adaptation of the repulsive Hartree–Fock energy, whereas the second part is an empirical representation of the attractive correlation energy and ought to be compared to the theoretical correlation energy V_{cor}. These comparisons are made in Table IV. The second column lists the values of $V_{RHF}(R)$, the third column lists the differences

$$\Delta_{RHF}(R) = V_{RHF}(R) - A\exp(-aR - bR^2), \tag{10}$$

the fourth column lists $V_{cor}(R)$, and the fifth column lists the differences

$$\Delta_{cor}(R) = V_{cor}(R) - [-f(R) \times (C_6/R^6 + C_8/R^8 + C_{10}/R^{10}), \tag{11}$$

where the coefficients C_k are those of Eq. (9a).

Figure 3 displays plots of the correlation differences of Eq. (11) obtained by using the nonaugmented cc-pVXZ basis sets with $X=4,5,6$ as well as those of the CBS extrapolation listed in Table IV.

Table IV and Fig. 3 show that the progression of $V_{cor}(R)$ from $X=4$ to 5 to 6 is very systematic and that the extrapolated CBS correlation values closely agree with the empirical correlation values. Table IV shows that, over the long-range region, the difference decreases from 1.9 μhartree at 4.4 Å to 0.02 μhartree at 8 Å. Even for shorter distances, into the repulsive region of the total potential, the agreement continues to be surprisingly close.

That the excellent performance of the extrapolation procedure is no accident is confirmed by its performance in calculating the correlation energy E_{cor} of the dimer at 60 Å, where one finds the values

Basis set	4Z	5Z	6Z	CBS
E_{cor}(millihartree)	−600.440 12	−623.176 69	−632.402 20	−643.954 02

The CBS value implies the valence correlation energy of −321.975 mhartree for the neon atom. For this quantity, Klopper[27] had obtained the benchmark value of -321.8 ± 0.5 mhartree by using r_{12} terms in addition to a CCSD(T) wavefunction constructed from a very large uncontracted basis.

To obtain a finer comparison in the *long-range* region, Fig. 4 exhibits graphs of $[-R^6V_{cor}(R)]$ for the cc-pVXZ calculations with $X=4,5,6$ and their CBS extrapolation as well as the corresponding empirical term $[f(R)\times(C_6+C_8(R^{-2})+C_{10}(R^{-2})^2]$, all plotted versus $(R)^{-2}$. Even with this magnification of the long-range differences, the systematic

TABLE III. Asymptotic dispersion coefficients of the neon dimer from Atomic Data.

Method of determination	Ref.	C_6 (hartree bohr^6)	C_8 (hartree bohr^8)
Polarizability, spectra, sum rules, 1964	51	6.43	···
Spectra, sum rules, 1964	52	6.31	···
Spectra, sum rules, 1976, 1985	**42 and 43**	**>6.48**	**>55.39**
Spectra, sum rules, 1976, 1985	**42 and 43**	**<7.27**	**<96.39**
Spectra, sum rules, 1985	**41**	**6.383**	···
Polarizability, spectra, sum rules (variat), 1973	53		$15.6C_6$
Polarizability, spectra, sum rules, (perturb), 1973	53		$16.8C_6$
MBPT, 1992	54	···	90.34
TD-DFT & experimental corrections, 2004	55	6.20	···
TD-DFT, HCTH407 functional, 2005	56	6.248	···
TD-DFT, B97-2 functional, 2005	56	6.159	···
TD-DFT, PBE0 functional, 2005	56	6.234	···
MBPT2, 2005	56	6.316	···
FCI, t-aug-vDZ, 2007	57	6.401	19.80

approach toward the CBS limit and the empirical curve is preserved. The most important feature is that for $R \geqslant 4.8$ Å, where $f(R)=1$, the CBS curve very closely agrees with the empirical curve, which is approximately linear, viz., $[C_6+C_8(R^{-2})]$.

TABLE IV. Comparison of the theoretical [nonaugmented CBS limit of CCSD(T) calculation without contributions from core correlation, scalar relativity, and corrections associated with the improvement of valence correlations beyond CCSD(T)] and empirical values for the repulsive and attractive terms in the interaction potential of Ne_2. Energies in microhartree.

R (Å)	$V_{RHF}(R)$	$\Delta_{RHF}(R)$[a]	$V_{cor}(R)$	$\Delta_{cor}(R)$[b]
2.750	456.35	−18.99	−461.67	3.04
2.800	362.15	−16.27	−414.98	4.39
2.900	228.01	−11.77	−335.85	6.34
3.000	143.48	−8.41	−272.05	7.99
3.050	113.79	−7.08	−245.18	8.47
3.075	101.32	−6.51	−232.88	8.60
3.100[c]	**90.22**	**−5.97**	**−221.22**	**8.73**
3.125	80.32	−5.48	−210.18	8.82
3.150	71.51	−5.03	−199.77	8.87
3.200	56.66	−4.24	−180.56	8.91
3.250	44.88	−3.57	−163.36	8.86
3.300	35.54	−3.00	−147.87	8.83
3.400	22.29	−2.10	−121.49	8.58
3.500	14.01	−1.42	−100.11	8.27
3.600	8.84	−0.92	−82.80	7.85
3.750	4.49	−0.41	−62.82	6.99
4.000	1.49	−0.07	−40.96	5.03
4.200	0.58	−0.04	−30.12	3.33
4.400	0.18	−0.07	−22.83	1.86
4.500	0.06	−0.10	−19.98	1.37
4.800	−0.09	−0.13	−13.74	0.35
5.000	−0.11	−0.13	−10.74	0.11
5.400	−0.07	−0.07	−6.65	0.00
6.000	−0.02	−0.02	−3.38	0.05
6.400	0	0	−2.25	0.04
6.600	0	0	−1.88	0.02
7.000	0	0	−1.28	0.03
7.500	0	0	−0.84	0.02
8.000	0	0	−0.56	0.02

[a]Theoretical minus empirical terms, as defined in Eq. (10).
[b]Theoretical minus empirical terms, as defined in Eq. (11).
[c]Minimum of total *empirical* potential energy curve.

It should be noted that the multiplication by R^6 also magnifies the round-off error noise arising from the numerical accuracy limits of the computer programs. For this reason, the linear fit through the last eight or nine points in Fig. 4 will give a more reliable value for the limiting value at $R^{-2}=0$, i.e., C_6, than a fit using only the last three points, say.

Figure 4 reveals a ripple in the CBS curve, which is mainly caused by a similar flaw in the quadruple-zeta ($X=4$) curve. This seems to be a consequence of the fact that, for the quadruple-zeta basis, the Hartree–Fock energy exhibits a spurious minimum of about −20.11 μhartree in the same region. The minimum disappears as one proceeds to using bases for higher zeta values, but a remnant of this quadruple-zeta flaw survives in the Hartree–Fock CBS limit, as can be seen from the second column in Table IV.

It was possible to reduce the irregularity in the CBS curve of V_{cor} somewhat by avoiding the use of the quadruple-zeta results in the CBS extrapolation of the correlation energy by the following *ad hoc* device. Based on our data, we substituted a linear function of R for the ratio $[B^*(R)/A^*(R)]$ in the extrapolation equation (8), viz.,

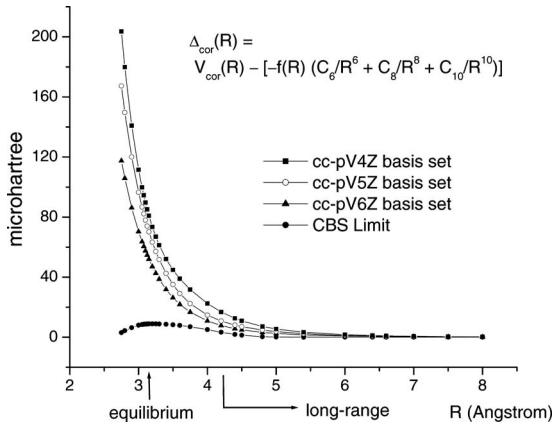

FIG. 3. Plots of $\Delta_{cor}(R)$ as defined by Eq. (11) vs the internuclear distance R. Displayed are the results for the nonaugmented cc-pVXZ basis sets with $X=4,5,6$, and for the extrapolated CBS limit.

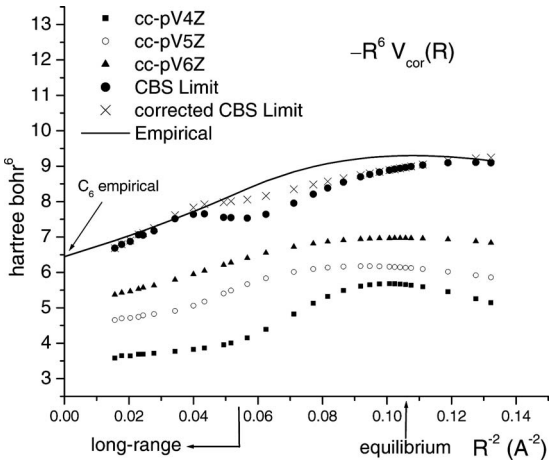

FIG. 4. Plots of $[-R^6V_{\mathrm{cor}}(R)]$ for the nonaugmented cc-pVXZ calculations with $X=4,5,6$, and their CBS limit as well as the corresponding empirical term $[f(R)\times(C_6+C_8(R^{-2}))+C_{10}(R^{-2})^2]$ vs $(R)^{-2}$.

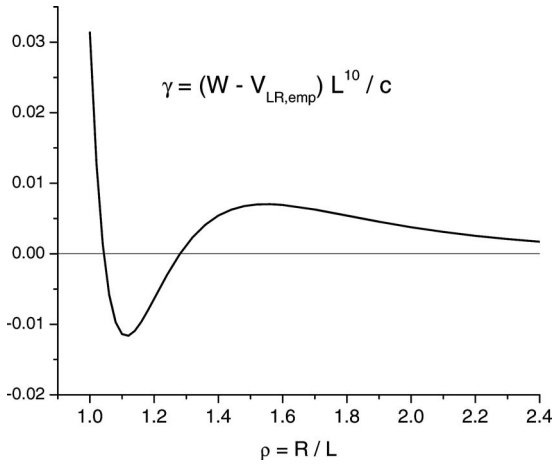

FIG. 5. The function $\gamma(\rho)$ of Eq. (18) in the long-range region $(\rho>1)$.

$$[B^*(R)/A^*(R)] = -12.593\,29 + 0.704\,85R \quad (\text{where } R \text{ in Å}),$$

which we deduced from the overall variation of this ratio between 3.1 and 8 Å. Using this relation eliminated the appreciable deviations of the actual $[B^*/A^*]$ ratios from this average line that were caused by the quadruple-zeta flaws in the region of the ripple (the maximum deviation of ~60% occurred around 4 Å). By using the quoted linear relation, the CBS extrapolation of Eq. (8a) could be performed by using only the quintuple-zeta and sextuple-zeta correlation potentials. The resulting CBS limit for the $[-R^6V_{\mathrm{cor}}(R)]$ curve, entered as "corrected CBS limit" in Fig. 4, manifestly goes more smoothly into the linear long-range behavior.

It is apparent that the ripple in Fig. 4 is related to the inaccuracies we had found in the total potential between 3.2 and 4.2 Å (column 5 of Table II). They, too, can be partially remedied by the correction described in the preceding paragraph.

The discussed results suggest that the observed flaw is likely to disappear when the three-term CBS extrapolation of Eq. (3) is used for calculations performed with quintuple, sextuple, and septuple bases.

C. Dispersion expansion

The objective is to deduce the dispersion coefficients by fitting the dispersion expansion to the long-range values of the correlation potential. The first observation that has to be made in this regard is that *it is not possible to determine the two coefficients C_8 and C_{10} both, if the values of the long-range potential have possible errors of up to* 0.01 microhartree.

To understand the origin of this insensitivity, consider the long-range expression of the empirical correlation potential of Aziz and Slaman,[39] viz.,

$$V_{\mathrm{LR,emp}}(R) = -C_6/R^6 - C_8/R^8 - C_{10}/R^{10}, \tag{12}$$

where the coefficients are those listed above, after Eq. (9a). Consider now also the comparison potential

$$W(R) = (-C_6 + a)/R^6 + (-C_8 + b)/R^8 + (-C_{10} + c)/R^{10}, \tag{13}$$

where we take c to be an arbitrary parameter and optimize a and b, for a given value of c, by least-mean-squares fitting $W(R)$ to the original $V_{\mathrm{LR,emp}}(R)$ over the long-range region $(R=L\to\infty)$. The integrated mean-squares deviation is

$$\int dR[W(R) - V_{\mathrm{LR,emp}}(R)]^2 = \int dR[a/R^6 + b/R^8 + c/R^{10}]^2,$$

the integration going from L to ∞. Minimization of this integral with respect to a and b leads to the closed solution,

$$a = \alpha c/L^4, \quad b = \beta c/L^2, \tag{14}$$

where

$$\alpha = [(13\times17)^{-1} - (15)^{-2}]/[(11\times15)^{-1} - (13)^{-2}] = 0.560\,784\,314, \tag{15}$$

$$\beta = [(13\times15)^{-1} - (11\times17)^{-1}]/[(11\times15)^{-1} - (13)^{-2}] = -1.529\,411\,765. \tag{16}$$

The equations (14) define a straight line in the coefficient space, i.e., the space spanned by C_6, C_8, C_{10}. At any given point on this line, specified by a particular value of c, the difference between $V_{\mathrm{LR,emp}}$ and the optimally fitted W becomes

$$W(R) - V_{\mathrm{LR,emp}}(R) = (cL^{-10})\gamma(R/L), \tag{17}$$

where

$$\gamma(\rho) = 0.560\,784\,314/\rho^6 - 1.529\,411\,765/\rho^8 + 1/\rho^{10}. \tag{18}$$

A plot of the function $\gamma(\rho)$ in the long-range region $(\rho>1)$ is displayed in Fig. 5. The *largest* value of this function occurs for $\rho=1$, i.e., $R=L$, and has the value

$$W(L) - V_{\mathrm{LR,emp}}(L) = (cL^{-10})(\alpha+\beta+1) = 0.031\,372\,549c/L^{10}. \tag{19}$$

For $R=3L$, which would essentially encompass the *practically* considered long range, we have

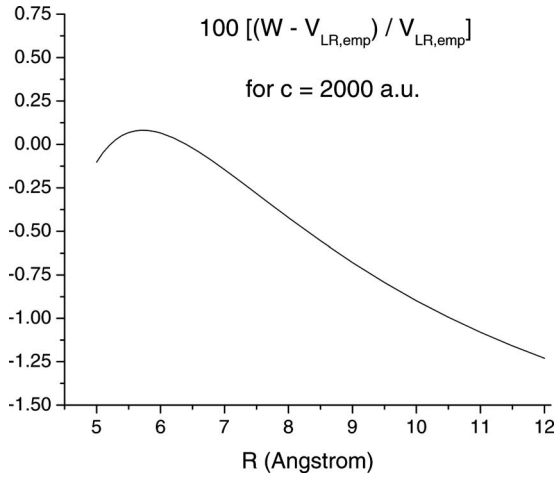

FIG. 6. The *relative* change $\{[W(R)-V_{\mathrm{LR,emp}}(R)]/V_{\mathrm{LR,emp}}(R)\}$, in%, caused in the long-range potential $V_{\mathrm{LR,emp}}(R)$ by a change of $c=2000$ a.u. in the coefficient C_{10} [see Eq. (17)].

$$W(3L)-V_{\mathrm{LR,emp}}(3L)=[c(3L)^{-10}](81\alpha+9\beta+1)$$
$$=0.017\,629\,427$$
$$\times[W(L)-V_{\mathrm{LR,emp}}(L)]. \quad (20)$$

If we now require that the largest difference between W and $V_{\mathrm{LR,emp}}$, i.e., the left-hand side of Eq. (19), should lie between $-\varepsilon$ and $+\varepsilon$, then Eq. (19) yields for c the following restriction

$$-c^{\#}<c<+c^{\#}, \quad c^{\#}=31.875\varepsilon L^{10}. \quad (21a)$$

Equations (14) yield the corresponding values

$$a^{\#}=17.875\varepsilon L^{6}, \quad b^{\#}=-48.75\varepsilon L^{8}. \quad (21b)$$

For the empirical potential of Eq. (9a), the long-range region starts at 4.2 Å. On the other hand, Fig. 4 showed that the theoretical potential V_{cor} settled down from 5 Å on. If we choose $L=5$ Å$=9.448\,63$ bohr and, furthermore, specify that the absolute value of the deviation $[W-V_{\mathrm{LR,emp}}]$ not exceed $\varepsilon=0.01$ μhartree, then Eq. (21a) shows that the limiting value of $c^{\#}$ is

$$c^{\#}=1808 \text{ hartree bohr}^{10}, \quad (22a)$$

for which

$$a^{\#}=0.1278 \text{ hartree bohr}^{6}, \quad b^{\#}=-30.97 \text{ hartree bohr}^{8}. \quad (22b)$$

Thus, the empirical value of the coefficient C_{10} (viz., 1520 a.u.) can be changed by over 100% without changing the value of the potential by more than 0.01 μhartree anywhere in the long-range region. In particular, one can choose C_{10} to be zero. The origin of this indeterminacy is of course the near-linear dependence of R^{-8} and R^{-10}.

Consider the choice $c=2000$ hartree bohr^{10} for the change in C_{10}. The change in the potential will be 0.011 and 0.0002 μhartree for $R=5$ and 15 Å, respectively. Figure 6 exhibits the *relative* deviation $[(W\text{-}V_{\mathrm{LR,emp}})/V_{\mathrm{LR,emp}}]$, which is seen to be less then 1.3% from 5 to 12 Å. Moreover, according to Eqs. (14)–(16), this change of $c=\pm 2000$ hartree bohr^{10} will change the empirical value of $C_6=6.447$ hartree bohr^6 by only ± 0.14 hartree bohr^6. It will, however, change the empirical value of $C_8=96.50$ hartree bohr^8 by ± 34.26 hartree bohr^8. Thus, one can change the numerical values *of the constants* C_8 *and* C_{10} very greatly along the straight line defined by Eqs. (14) without causing the numerical values *of the approximation* $W(R)$ to change by more than 0.01 μhartree in the entire long-range region.

TABLE V. Insensitivity of the three-term dispersion expansion of the long-range correlation potential with respect to the coefficient C_{10}.

C_{10}[a] hartree bohr^{10}	C_6[b] hartree bohr^6	C_8[b] hartree bohr^8	MAD[c] μhartree	MAXD[d] μhartree
		Empirical correlation potential[e]		
1520[f]	**6.447**	**96.50**	**0.000**	**0.000**
400	6.359	116.83	0.002	0.003
0	**6.327**	**124.09**	**0.002**	**0.004**
−400	6.296	131.35	0.003	0.006
−1000	6.248	142.25	0.004	0.007
		Theoretical correlation potential[g]		
1520[f]	**6.346**	**99.98**	**0.020**	**0.060**
400	6.258	120.32	0.019	0.057
0	**6.226**	**127.58**	**0.019**	**0.056**
−400	6.195	134.84	0.018	0.055
−1000	6.147	145.73	0.018	0.053

[a]Fixed input parameter.
[b]Values obtained by LMSQ fitting $[-C_6/R^6-C_8/R^8-C_{10}/R^{10}]$ to the empirical or theoretical correlation potential with the given fixed value of C_{10} over the range of 5–8 Å. An end point was added at $R=1000$ Å with $V_{\mathrm{corr}}=0$ and a weight factor of 4000.
[c]Mean absolute deviation.
[d]Maximum absolute deviation.
[e]Attractive term in Eq. (9a).
[f]This is the value in the empirical potential of Eq. (9a).
[g]CBS limit of V_{cor} obtained with the nonaugmented cc-pV(4,5,6)Z bases.

On the other hand, it is readily verified that the absolute value of the deviation $(W\text{-}V_{\mathrm{LR,emp}})$ rapidly increases with c when one moves at right angles to the "minimum line" defined by Eqs. (14) in the C_8-C_{10} space.

These conclusions are confirmed in the upper part of Table V, which lists the mean absolute deviations and the maximum absolute deviations between $V_{\mathrm{LR,emp}}$ and various functions of an identical algebraic structure that were obtained as follows: The coefficient C_{10} was arbitrarily fixed at several values between −1000 and +1520 a.u. The other two coefficients, C_6 and C_8, were then optimized by a least-mean-squares fit covering the eight points from 5 to 8 Å and an added end point at $R=1000$ Å with $V_{\mathrm{corr}}=0$ and a weight factor of 4000. While C_6 changes relatively little, there occurs a trade-off between C_8 and C_{10} along the straight line

$$C_8=124.092-0.018\,153\,88C_{10}, \quad (23)$$

with the mean absolute deviations remaining less than 0.005μhartree. Equation (23) is manifestly analogous to Eqs. (14).

The lower part of Table V exhibits the coefficients C_k and the mean and maximum absolute deviations that result when one fits the same type of expansions under the same conditions to the *theoretical* correlation potential $V_{\mathrm{cor}}(R)$. Again, the deviations change only by a few thousands of a

microhartree as C_{10} is varied over the same wide range. Here, a trade-off between the C_8 term and the C_{10} term occurs along the straight line,

$$C_8 = 127.578 - 0.018\,154\,75 C_{10}, \tag{24}$$

again without much effect on C_6. Parenthetically, we note that a completely unrestrained least-mean-squares (LMSQ) optimization of all three coefficients yields the values $C_6 = 5.30$, $C_8 = 340$, $C_{10} = -11\,745$ (in atomic units). Even this very large change in the coefficients lowers the mean absolute deviation only by 0.006 μhartree relative to the value given in Table V for $C_{10}=0$. These values of C_8 and C_{10} again satisfy the linear relationship of Eq. (24).

Thus, the numerical long-range values of neither the theoretical nor the empirical potential curve unambiguously determine the magnitude of C_{10}, and its value must therefore be chosen on the basis of other considerations. In empirical potentials, a popular choice manifestly is the value of 1520 hartree bohr[10] deduced from the asymptotic atomic considerations, and it is also used in Eq. (9a) by Aziz and Slaman.[39] From an operational point of view on the other hand, one would argue that nothing is gained by keeping a high-order term that is quantitatively irrelevant for the accessible long-range potential and that it should therefore be abandoned. Both of these choices are indicated by boldfaced font in Table V.

Another conclusion is that, when comparing values of C_8 from different sources, one has to take into account the assumptions that have been made regarding C_{10} and, if necessary, make adjustments by using the linear relations discussed above. It is furthermore to be expected that more extensive trade-offs exist in polyatomic systems, where terms in R^{-7} and R^{-9} can be part of the expansion.

In the present context, the most important result of the preceding analysis documented in Table V is that, for any choice of C_{10}, the values of C_6 and C_8 deduced from the theoretical $V_{\mathrm{cor}}(R)$ are found to be in very close agreement with those obtained for the empirical $V_{\mathrm{LR,emp}}(R)$.

D. Correlation potentials for the augmented basis sets

Figure 7 displays the correlation potential differences defined by Eq. (11) that result from using the *augmented* aug-cc-pVXZ basis sets for $X=4,5,6$ and from the corresponding CBS limit, all plotted versus the internuclear distance. All augmented bases generate correlation potentials V_{cor} that are considerably closer to the empirical potential (note the difference in scale between Figs. 3 and 7). In particular, the augmented sextuple-zeta basis yields a very good potential. However, these curves show a much less systematic progression with increasing X than the curves for the nonaugmented bases, which were shown in Fig. 3. As a consequence, the CBS limit of V_{cor} deviates considerably from the empirical curve. The long-range behavior is elucidated by Fig. 8, which is analogous to Fig. 4. Here, too, the augmented bases exhibit a much less systematic behavior. While the overall thrust is roughly right, the CBS limit curve does not settle down out into the appropriate linear dependency in the long-range region.

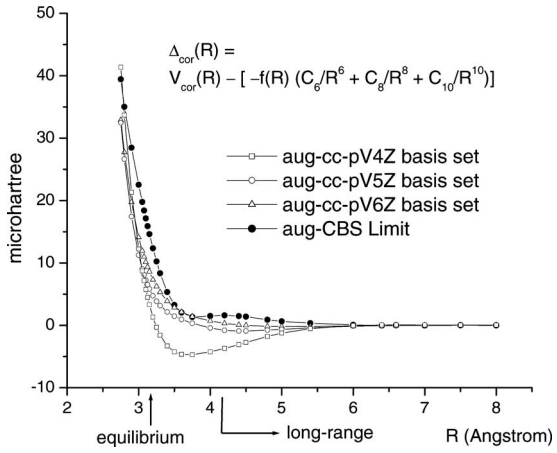

FIG. 7. Plots of $\Delta_{\mathrm{cor}}(R)$ as defined by Eq. (11) with respect to the internuclear distance R. Displayed are the results for the augmented aug-cc-pVXZ basis sets with $X=4,5,6$, and for the extrapolated CBS limit.

The use of the augmented bases seems to pose two problems. First, the successive curves of V_{cor} do not appear to form a systematic progression. This may conceivably be remedied by using counterpoise corrections. Secondly, the extrapolation of the correlation energies to the CBS limit may require procedures different from that given by Eq. (3). More sophisticated CBS extrapolation techniques have recently been advanced by several authors.[29–32,48,60–62]

We note, however, that the application of the extrapolation procedure of Eq. (3) at $R=60$ Å yields the CBS correlation energy of −644.054 mhartree, implying the valence correlation energy of −322.077 mhartree for the neon atom, which differs only by 0.3 mhartree from Klopper's benchmark value[27] mentioned in Sec. IV B [see third paragraph after Eq. (11)]. *For the neon atom*, the extrapolation defined by Eq. (3) works therefore equally well for the augmented bases and for the nonaugmented bases.

V. COMPARISON OF VARIOUS STUDIES

There have been a large number of studies regarding the interaction potential of the neon dimer.[22,39,44–46,57–59,63–78] References 22 and 58 contain a rather thorough list of studies of all homonuclear noble gas dimers.

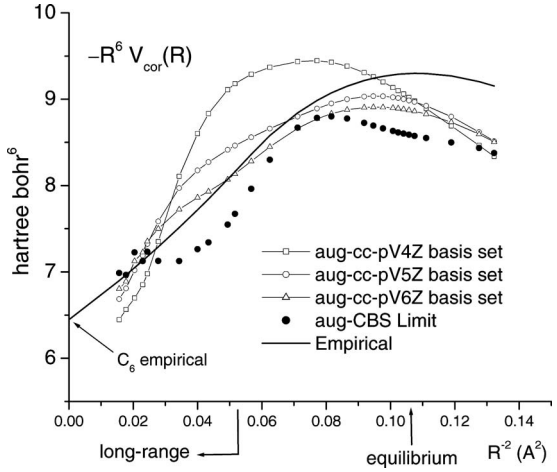

FIG. 8. Plots of $[-R^6 V_{\mathrm{cor}}(R)]$ for the aug-cc-pVXZ calculations with $X=4,5,6$, and their CBS limit as well as the corresponding empirical term $[f(R)\times(C_6+C_8(R^{-2}))+C_{10}(R^{-2})^2]$ vs $(R)^{-2}$.

TABLE VI. Comparison of results from various studies of the neon dimer.

	Ref.	R_e (Å)	$-D_e$ (mhartree)	C_6 (hartree bohr^6)	C_8 (hartree bohr^8)
		Experiment			
From rovibrational spectra, 1974	63	···	0.1303	···	···
From many molecular properties, 1983	64	3.091	0.1307	···	···
From many molecular properties, 1989 (C_{10} assumed to be 1520 (hartree bohr^{10}))	**39 and 41–43**	**3.091**	**0.1338**	**6.447**	**96.50**
Comparative study of rare gas dimers, 2003 (C_{10} assumed to be 1536 (hartree bohr^{10}))	**58, 39, 41, and 54**	**3.090**	**0.134**	**6.383**	**90.34**
From rovibrational spectra, 2003	69	3.094	0.1340	···	···
		Theory			
Present work, CCSD(T), without counterpoise correction					
CBS limit of non-augmented cc-pV(4,5,6)Z bases					
C_{10} assumed to be=1520 (hartree bohr^{10}), see text		**3.075**	**0.1316**	**6.346**	**99.98**
C_{10} assumed to be=0, see text		**3.075**	**0.1316**	**6.226**	**127.58**
Previous work, CCSD(T), without counterpoise correction					
aug-cc-pV6Z, 1999	22	3.102	0.1303	···	···
d-aug-cc-pV6Z, 1999	22	3.082	0.1481	···	···
t-aug-cc-pV6Z, 1999	22	3.030	0.2202	···	···
Previous work, CCSD(T), with counterpoise correction					
CBS via aug-cc-pV(up to 6)Z, 1999	22	3.106	0.1330	···	···
CBS via d-aug-cc-pV(up to 6)Z, 1999	22	3.101	0.1296	···	···
CBS via t-aug-cc-pV(up to 6)Z, 1999	22	3.101	0.1294	···	···
Customized aug-5Z basis+bond functions, 1999	65	3.101	0.1297	···	···
aug-cc-pV5Z, 1999	44[a]	3.125	0.1176	···	···
aug-cc-pV5Z+bond functions, 1999	**44[a]**	**3.100**	**0.1304**	**6.282**	**90.05**
6-311(d)+SPDFG diffuse basis sets, 2003	67	3.2	0.1323	···	···
CBS of d-aug-cc-pV(3,4)Z, 2003	68	3.086	0.1412	···	···
t-aug-vDZ, 2007 (C_{10}=0 assumed)	57[b]	3.267	0.0835	6.543	28.49
q-aug-vTZ, 2007 (C_{10}=0 assumed)	57[b]	3.136	0.1164	7.105	37.88
aug-cc-pV5Z, 2008 (C_{10}=0 assumed)	59[c]	···	···	6.42	77
Previous work, CCSD(T)+corrections, with counterpoise correction					
t-aug-cc-pV6Z+bond functions, 2008	**46[d]**	**3.089**	**0.1334**	**6.355**	**84.92**
Previous work, r_{12}-ACPF, with counterpoise correction					
Customized aug-5Z basis, 2001	45	3.125	0.1162	···	···
Previous work, CCSD, with counterpoise correction					
t-aug-vDZ, 2007 (C_{10}=0 assumed)	57[b]	3.305	0.0700	5.885	21.98
q-aug-vTZ, 2007 (C_{10}=0 assumed)	57[b]	3.183	0.0938	6.172	37.41
aug-cc-pV5Z, 2008 (C_{10}=0 assumed)	59[c]	···	···	5.62	64
Previous work, MP2, with counterpoise correction					
aug-cc-pV5Z, 2008 (C_{10}=0 assumed)	59[c]	···	···	5.56	45
Previous work, Short-range DFT+long-range MP2, with counterpoise correction					
CBS of aug-cc-pV(5,6)Z, 2007	71	···	0.1000	···	···
aug-cc-pVQZ, 2007	71	3.195	···	···	···
Previous work, path integral summation, with counterpoise correction					
aug-cc-pV5Z, 2008 (C_{10}=0 assumed)	59[c]	···	···	4.48	35

[a] C_6 and C_8 obtained by generating an empirical fit to the *ab initio* potential.
[b] C_6 and C_8 obtained by fitting the long-range *ab initio* potential directly to $(-C_6/R^6-C_8/R^8)$.
[c] C_6 and C_8 obtained by fitting the long-range *ab initio* potential directly to $(-C_6/R^6-C_8/R^8)$.
[d] C_6 and C_8 obtained by generating an empirical fit to the *ab initio* potential.

Table VI collects experimental as well as theoretical results that have been obtained for the equilibrium distance, the binding energy, and the dispersion coefficients C_6 and C_8 of the neon dimer.

The highly regarded experimental references of Aziz and Slaman[39] and of Tang and Toennies[58] are indicated by boldfaced font in the table. Among the previous theoretical work, the CCSD(T)-based calculations are clearly superior to the

other approaches. So far, the calculations by Cybulski and Toczyłowski[44] and Hellmann *et al.*[46] using bond functions appear to be the most successful ones, and they have also been indicated by boldfaced font. Hellmann *et al.*[46] have additionally estimated the valence correlations beyond CCSD(T) by means of CCSDT(Q) calculations using smaller basis sets. They have also calculated the corrections due to core correlations and scalar relativity. While the results reported in Refs. 44 and 46 appear to be highly accurate when compared to the empirical curve,[39] much of the work cited in Table VI gives reasonable values for the potential well.

The dispersion coefficients are determined only in four of the previous papers, viz, by Cybulski and Toczyłowski,[44] by Monari *et al.*,[57] by Thom *et al.*,[59] and by Hellmann *et al.*[46] Cybulski and Toczyłowski[44] fitted their data to a generalized Tang-Toennies-type potential and adjusted their dispersion coefficients to some degree to the empirical asymptotic values. Hellmann *et al.*[46] fitted their data to an even more complex potential with nine independent parameters, including C_6, C_8, C_{10}. Only Monari *et al.*[57] and Thom *et al.*[59] determined C_6 and C_8 by straight fitting to a theoretical curve, as is done here.

In accordance with our analysis in Sec. IV, we have entered in Table VI the data of the potential that we obtained as the CBS limit of our calculations with the nonaugmented bases. In view of the discussion in Sec. IV C, we have listed the dispersion coefficients C_6 and C_8 for the two choices $C_{10}=0$ and $C_{10}=1520$ a.u.—the value chosen in the empirical potentials. It would seem that the present investigation is the first to report close agreement between all empirical dispersion coefficients and the corresponding coefficients deduced, without any adjustments, by a direct fit to the long-range potential from an *ab* initio supermolecule calculations.

VI. CONCLUSIONS

In contrast to most other work, the present approach has been based on using nonaugmented quadruple-, quintuple- and sextuple-zeta basis sets without counterpoise corrections and obtaining the CBS limit by a two-tier extrapolation, using a three-term expression for the correlation energy. The two-term correlation extrapolation formula was found to be much less satisfactory in the present context.

The resulting theoretical potential energy curve $V(R)$ very accurately recovers the empirical potential in the long-range region and in the region near the equilibrium geometry. The description of the intermediate region is slightly less accurate, presumably as a consequence of the shortcomings in the Hartree–Fock part of the wavefunction for the quadruple-zeta basis set that enters the three-term CBS correlation energy extrapolation.

The well depth is reproduced with an error of about 2 μhartree. This error is reduced to less than 1 μhartree if valence correlations beyond the CCSD(T) level, core correlations and relativistic corrections are accounted for by using the available estimates[46] for these corrections (see comments at the end of Sec. III).

In the long-range region, the empirical potential is recovered within a fraction of a microhartree and that is also the magnitude of the deviation between the theoretical and the empirical correlation potentials. In this region, the theoretical correlation potential $V_{\mathrm{cor}}(R)$ decays according to the dispersion expansion $(-C_6/R^6-C_8/R^8-C_{10}/R^{10})$, and the coefficients are found to agree closely with those used in the empirical potentials. To the author's knowledge, the present theoretical potential exhibits the closest agreement with the empirical curve of Aziz and Slaman[39] for the internuclear distances larger than 4.8 Å.

It is also shown, however, that it is intrinsically impossible to determine *both* coefficients C_8 and C_{10} from the quantitative values of the (theoretical or empirical) long-range potential if the data contains errors of up to 0.01 μhartree. This is because the absolute deviation of the three-term dispersion expansion from the long-range correlation potential energy changes by only a few thousands of a microhartree along a straight line in the C_8-C_{10} space (see Sec. IV C).

The two-tier extrapolation procedure of Eqs. (2) and (3) to the CBS limit, including the three-term correlation extrapolation, was found to work extremely well for the nonaugmented bases. Consequently, no counterpoise corrections were required. In the case of the augmented bases, these CBS limit procedures were not as successful. This observation is consistent with the results of others[22,44,46,57] who emphasize the importance of counterpoise corrections when using heavily augmented basis sets.

ACKNOWLEDGMENTS

The authors acknowledge stimulating and instructive discussions on long-range interactions with Professor Mark S. Gordon and Dr. Michael W. Schmidt. The present work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-07CH11358 with Iowa State University through the Ames Laboratory.

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