

The Effect of the Basis-Set Superposition Error on the Calculation of Dispersion Interactions: A Test Study on the Neon Dimer

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Abstract: The dispersion interactions of the Ne₂ dimer were studied using both the long-range perturbative and supramolecular approaches: for the long-range approach, full CI or string-truncated CI methods were used, while for the supramolecular treatments, the energy curves were computed by using configuration interaction with single and double excitation (CISD), coupled cluster with single and double excitation, and coupled-cluster with single and double (and perturbative) triple excitations. From the interatomic potential-energy curves obtained by the supramolecular approach, the C₆ and C₈ dispersion coefficients were computed via an interpolation scheme, and they were compared with the corresponding values obtained within the long-range perturbative treatment. We found that the lack of size consistency of the CISD approach makes this method completely useless to compute dispersion coefficients even when the effect of the basis-set superposition error on the dimer curves is considered. The largest full-CI space we were able to use contains more than 1 billion symmetry-adapted Slater determinants, and it is, to our knowledge, the largest calculation of second-order properties ever done at the full-CI level so far. Finally, a new data format and libraries (Q5Cost) have been used in order to interface different codes used in the present study.

1. Introduction

On both the theoretical and the experimental sides, the interest of chemists and physicists in clusters involving rare-gas (Rg) atoms increases.^{1–3} In order to be able to perform simulations on medium-size clusters, very accurate two-body potentials are needed. These potentials can be conveniently

computed by using high-level quantum-chemistry algorithms on Rg dimers, Rg₂.

For two identical interacting atoms (system with spherical symmetry), the long-range tail of the interaction potentials, as far as exchange can be neglected, is conveniently expanded in a series of inverse powers of the internuclear distance

$$E(R) = E(\infty) + \sum_n \frac{C_{2n}}{R^{2n}} \quad (1)$$

where the dispersion coefficients C_{2n} depend only on the electric properties of the atoms involved. Such a formulation,

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like for instance the well-known Lennard-Jones potential, allows a very simple and efficient parametrization of the two-body potential. Because of the smallness of the interaction, a very accurate value of the asymptotic limit of the potential-energy curve is extremely important. Since Rg_2 dimers are closed-shell systems that dissociate into two closed-shell atoms, a single determinant gives a qualitatively correct description of the dimer for any value of the internuclear distance. For this reason, single-reference methods can be successfully used even in the dissociation region, contrary to what happens for most chemical systems. In this context, one must be very cautious toward truncated configuration-interaction (CI) methods, as they suffer from the well-known size-consistency (SC) problem. On the other hand, coupled-cluster (CC) methods are size-consistent, and therefore they are not affected by this kind of problem.

In order to obtain accurate values of the potential-energy curves, it is absolutely necessary to take into account the basis-set superposition error (BSSE), and to accordingly modify the energy values. BSSE arises because the wave function (WF) of the dimer at a finite internuclear distance is better described than the WF of the separated atoms, since the orbitals of the two atoms are simultaneously used. For this reason, BSSE is particularly important for small- or medium-size basis sets, while it goes to zero in the limit of complete basis sets.

It should be stressed that a rigorous solution to this problem is at the moment not available. Indeed, one should use exactly the same basis set for all the calculations at the different geometries. However, in the linear combination of atomic orbitals (LCAO) formalism, the atomic orbitals are generally centered on nuclei, and therefore the basis set depends on the geometry of the system. A possibility one could think of would be the use of plane-wave orbitals, as it is done for periodic and extended systems. Unfortunately, plane waves are unable to correctly describe the behavior of the electronic WF close to the nuclei (the “nuclear cusp”), particularly in the case of heavy atoms.

The most diffuse procedure to overcome this problem is the use of the “counterpoise correction”, proposed by Boys and Bernardi.⁴ In this procedure, a series of atomic energies is computed, by using a basis set (b_i) composed of the atomic orbitals of all the atoms of the system, and the differences between these energies and the atomic values are subsequently used to correct the energy surface of the system. In other words, the energy $E(b_i)$ of the complex, computed by using the basis set b_i is corrected by adding a geometry-dependent energy shift Δ , which is given by

$$\Delta = \sum_I \Delta_I \quad (2)$$

where I labels the atoms in the complex

$$\Delta_I = E_f(b_I) - E_f(b_i) \quad (3)$$

Here, b_I represents the atomic basis set of the atom I , while b_i is the total LCAO basis, given by the union of all the atomic basis sets. This procedure, although not an exact one, gives a satisfactory approximation and leads to a satisfactory

approximation to the BSSE. In the present article, the effect of the BSSE on the calculation of dispersion coefficients at the CI and CC levels is investigated. As already well-known, the BSSE must be corrected in order to obtain reliable potential-energy curves of van der Waals (VdW) systems. However, although the BSSE-corrected curves obtained by the different methods are at first sight qualitatively rather similar, CI and CC methods show very different behaviors as far as the long-range dispersion coefficients are concerned. Indeed, we found that, while CC approaches are well-adapted for these types of calculations, the corresponding truncated-CI values are completely useless. The reason for this striking difference can be traced back to the lack of size consistency of the truncated-CI methods.

Our dimer calculations were compared with full-CI (FCI) results obtained on a single atom by means of a perturbative scheme. In our largest FCI calculation, the CI space contains more than 1 billion partly symmetry-adapted and spin-adapted Slater determinants. This represents, to the best of our knowledge, by far, the largest calculation of second-order properties ever done at the full-CI level.

2. Computational Details

In the present section, the basis sets and computational methods, which have been used in the present study, are described. The use of the interface Q5COST between different computational codes is also illustrated and discussed.

2.1. Basis Sets. The computation of molecular dispersion interaction is very sensitive to the quality of the computed polarizabilities of the constituent atoms. These properties are critically dependent on the quality of the basis sets and, in particular, on the presence of diffuse atomic orbitals. For this reason, diffuse orbitals are usually added to the standard atomic basis sets in these circumstances. Unfortunately, this fact can have the consequence of an even larger effect on the BSSE. Some authors⁵ report the use of the so-called midbond functions, instead of diffuse ones, for the computation of neon dimer potential-energy curves; we decided to discard this possibility mainly in order to use the same basis set in supramolecular and long-range perturbative approaches. The calculations are performed with the correlation consistent basis sets, optimized by Dunning and co-workers.^{6–8} In particular, the following two basis sets, retrieved from the Pacific Northwest Laboratory basis set library EMSL,⁹ have been used: triply augmented valence double- ζ (taug-vDZ) and quadruply augmented valence triple- ζ (qaug-vTZ). Since these are valence basis sets, it does not make sense to correlate core electrons, and in all the correlated computations, the 1s orbitals of the two neon atoms have been kept frozen at the Hartree–Fock level. This fact also presents the advantage of a considerable savings in computation time.

2.2. Computational Methods. The following methods have been used in the present study:

1. Long-Range Perturbative Approach (LRPT). LRPT is an approach where the atom–atom interaction¹⁰ is treated by perturbation theory starting from the product of isolated fragments’ wave functions.

The adopted computation strategy was the following: when the full or string-truncated CI formalism is used, it is

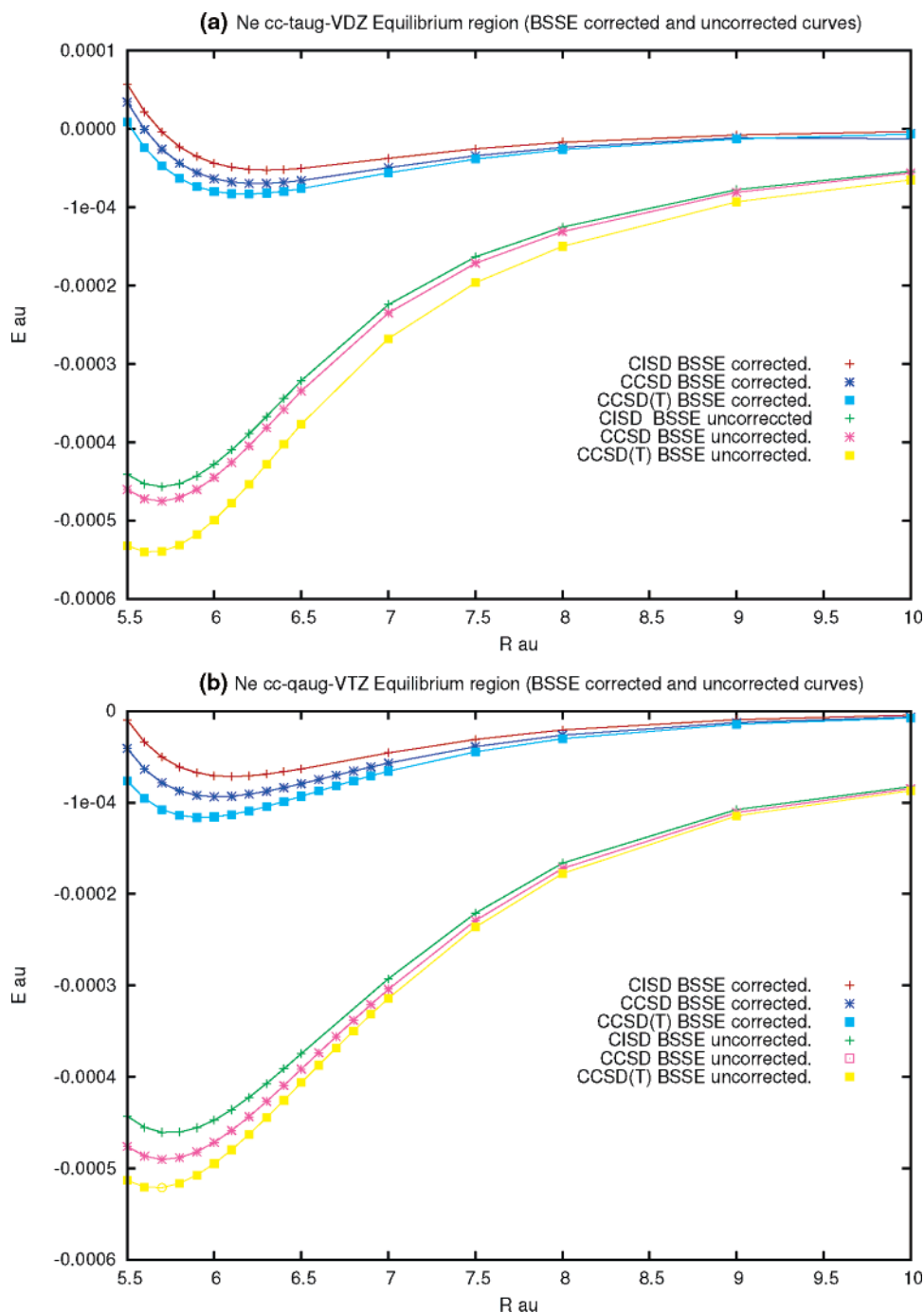


Figure 1. CISD, CCSD, and CCSD(T) potential-energy curves as a function of the internuclear distance. (a) taug-vDZ. (b) gaug-vTZ. Units: distances in bohr and energies in hartree.

possible to immediately get the values of the dispersion coefficients via the use of an innovative perturbation-variational formalism.¹¹ Note that this technique involves only the use of isolated atoms' wave functions, so values obtained can be considered as BSSE-free and size-consistent by construction. Moreover, values of neon atom dipole and quadrupole polarizabilities are obtained as byproducts. The formalism involved implies solving the perturbative equations for the dispersion interaction by expanding the solution as a linear combination of tensor products of suitable FCI vectors. In the present computation, the latter were chosen to be the so-called Cauchy vectors,¹¹ strictly related to the FCI computation of Cauchy moments. An expansion set of 10

Cauchy vectors provided satisfactory convergence. Both FCI and string-truncated CI calculations were obtained with the use of the program VEGA.¹² Molecular orbitals and their integrals were computed with the MOLPRO2000 code.¹³

In the string-truncated CI formalism,¹⁴ the determinants formed by strings having up to a given level of excitation are retained in the CI space: single excitations (CIS); single and double excitations (CISD); and single, double, and triple excitations (CISDT). Notice that, if up to quadruply excited strings are considered, in the case of the neon atom, one gets frozen-core FCI.

2. Supramolecular Approach. In this approach, potential-energy curves for the Ne₂ dimer are computed using (a)

Table 1. CISD, CCSD, CCSD(T) BSSE-Counterpoise-Uncorrected and -Corrected Minimum and Vibrational Frequencies^a

	R_{\min}^{uncorr}	E_{\min}^{uncorr}	R_{\min}^{corr}	E_{\min}^{corr}	N_{bs}	ΔE_0	ω
taug-VDZ							
CISD	5.7025	-456.71	6.3037	-52.675	1	7.2243	
CCSD	5.6862	-475.50	6.2454	-70.022	2	8.2618	6.6990
CCSD(T)	5.6527	-540.83	6.1741	-83.488	2	9.1751	8.3160
qaug-VTZ							
CISD	5.7514	-461.30	6.0995	-71.563	2	8.5749	6.9332
CCSD	5.7188	-490.46	6.0157	-93.766	2	9.9941	9.4897
CCSD(T)	5.6518	-521.52	5.9269	-116.44	2	11.430	11.960
Experiment							
24			5.84	-134			
25 ^b			5.85	-134	2	12.56	13.76

^a R_{\min}^{uncorr} interpolated value of the BSSE-uncorrected energy curve minimum (a_0 bohr); E_{\min}^{uncorr} BSSE-uncorrected potential-energy well depth (μE_h); R_{\min}^{corr} interpolated value of the BSSE-corrected energy curve minimum (a_0 bohr); E_{\min}^{corr} BSSE-corrected potential-energy well depth (μE_h); N_{bs} number of bound states for BSSE-corrected curves; ΔE_0 zero-point energy calculated from the BSSE-corrected well depth (cm^{-1}); ω anharmonic vibrational frequency from BSSE-corrected curves (cm^{-1}). ^b R_{\min} and E_{\min} are obtained fitting a model potential, see text for details.

Table 2. Ne Atom, Taug-VDZ, and Qaug-VTZ Basis Set: Full and String-Truncated CI Properties and Dispersion Coefficients^a

	N_{CI}	E	α_{dip}	α_{quad}	C_6	C_8
taug-VDZ						
CIS	2.929×10^3	-128.663 720	2.436 792	3.097 065	-5.9899	-7.2528
CISD	1.926×10^6	-128.708 024	2.649 742	3.605931	-6.3270	-19.4611
CISDT	1.319×10^8	-128.709 878	2.680 308	3.666 439	-6.3996	-19.7892
FCI	1.044×10^9	-128.709 923	2.680 788	3.667 532	-6.4008	-19.7955
qaug-VTZ						
CI-sd	7.100×10^7	-128.810 697	2.649	7.005	-6.354	-35.550
Interpolated taug-VDZ						
CCSD					-5.8849	-21.9760
CCSD(T)					-6.5433	-28.4863
Interpolated qaug-VTZ						
CCSD					-6.1717	-37.4064
CCSD(T)					-7.1054	-37.8797
experiment ^{29,30}			2.669	7.52	-6.383	

^a Dispersion coefficient interpolated from BSSE-corrected potential-energy curves. N_{CI} is the number of CI determinants in the D_{2h} symmetry point group; E is the total energy of the atom (E_h hartree); α_{dip} is the dipole polarizability (atomic units a_0^3 where a_0 bohr); α_{quad} is the quadrupole polarizability (atomic units a_0^5); C_6 and C_8 are the R^{-6} and R^{-8} dispersion coefficients, respectively ($E_h a_0^6$ and $E_h a_0^8$). When available, the experimental or previous computed best values are also reported.

single-and-double truncated CI, CISD, program CASDI;¹⁵ (b) single-and-double truncated CC, CCSD, DALTON package;¹⁶ (c) single-and-double truncated CC with noniterative triple correction, CCSD(T), DALTON package.¹⁶

At CISD, CCSD, and CCSD(T), the energy curve has been obtained performing energy computation at various values of interatomic separation; the curve has been subsequently counterpoise (CP)-corrected and linearized as described in the next section in order to get the values of the dispersion coefficients. From the energy curves, we also derived values of minimum energy distance, well-depth energy, zero-point energy, and anharmonic vibrational frequency. As concerns the vibrational levels, the computations were performed by the Numerov method¹⁷ in matrix form as formulated by Lindberg¹⁸ implemented in a code described in ref 19.

2.3. The Use of Q5Cost Wrappers. The CASDI program used for the computation of CISD energy curves was originally interfaced with the Molcas²⁰ program suite via the wrapper MOLCOST. In order to perform such a computation

in the same environment as the CC ones, we decided to interface CASDI with DALTON, using the newly developed Q5Cost data format²¹ and library.²² Q5Cost is a new data format and set of Fortran libraries developed by us that allows the easy exchange of the so-called “quantum-chemistry binary data” (mainly molecular integrals) among different codes. In particular, atomic basis integrals produced by Dalton¹⁶ after self-consistent field calculations were processed with a four-indices transformation to get them in molecular orbitals basis and written in Q5Cost format. Subsequently, a wrapper (Q5MOLCOST) was designed and written in order to write molecular orbitals in a MOLCOST format directly accessible by the CASDI program.

3. Results

In Figure 1 (a and b), the potential-energy curves are reported for the different correlated methods and obtained by using the two basis sets. The CISD, CCSD, and CCSD(T) curves are rather similar. It can be seen that the position of the

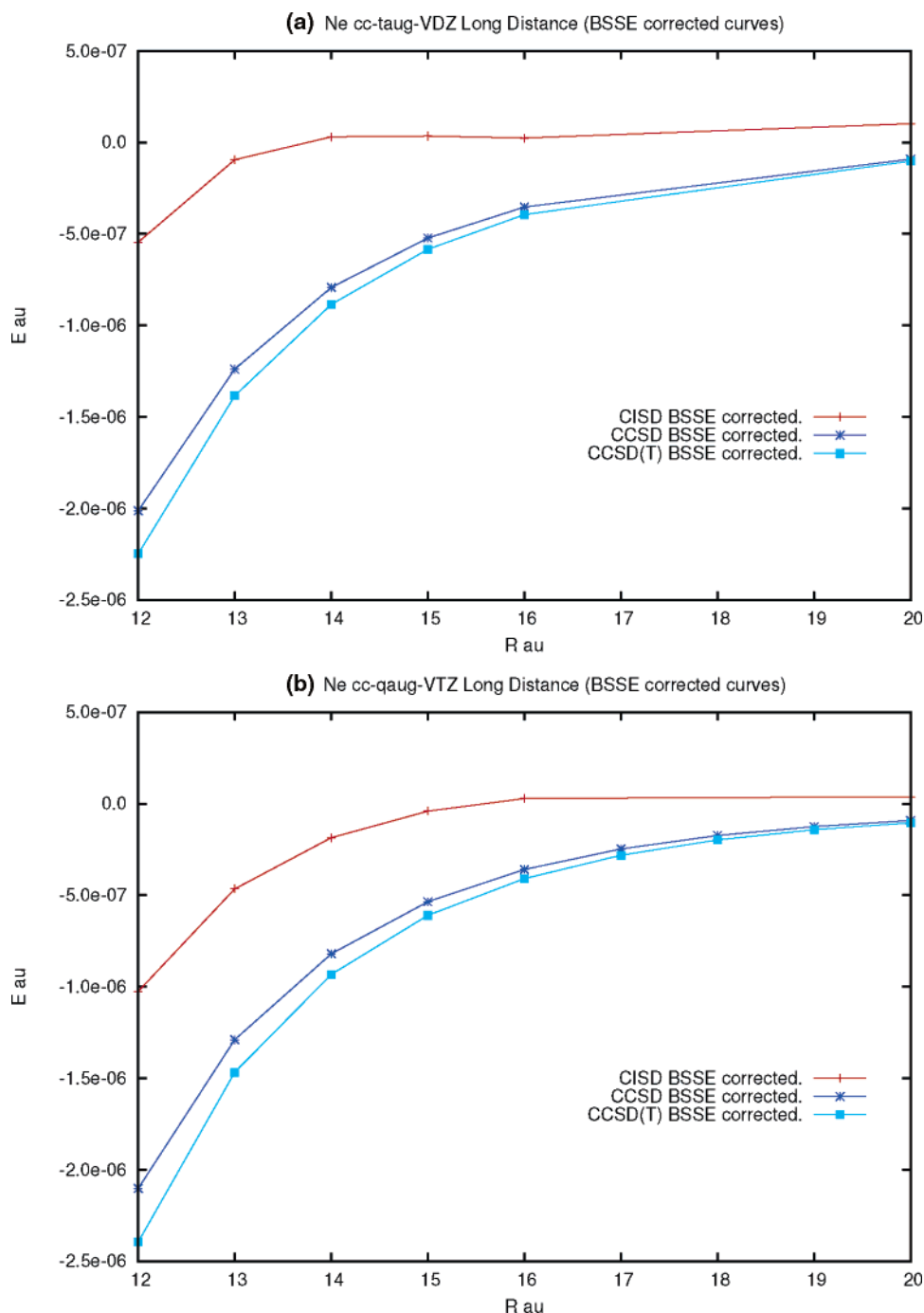


Figure 2. CISD, CCSD, and CCSD(T) BSSE-corrected potential-energy curves in the asymptotic region. (a) taug-vDZ. (b) qaug-vTZ. Units: distances in bohr and energies in hartree.

minimum is not strongly affected by the BSSE correction, while the energy-well shape and depth are completely changed by the BSSE. The curves obtained by using vDZ (Figure 1a) and vTZ (Figure 1b) are extremely similar, a fact that indicates that the BSSE converges very slowly to zero as a function of the basis-set size, probably because of the presence of diffuse functions²³ (we remind the reader that BSSE vanishes for a complete basis set). In Table 1, BSSE-uncorrected and -corrected equilibrium distances and energy-well depths are reported together with the zero-point energy, the number of vibrational bound states, and the anharmonic vibrational frequency, determined after coun-

terpoise correction. Again, these parameters show the same behavior as the ones previously described.

In Figure 2 (a and b), the same curves are displayed, relative to the asymptotic region (from 12.0 to 20.0 bohr). Again, the curves obtained by using vDZ (Figure 2a) and vTZ (Figure 2b) are very similar, but it appears now that the behavior of CI is extremely different than that of CC.

As discussed in the Introduction, the leading terms of the asymptotic energy are given by the equation

$$E(R) = E_{\infty} + C_6 R^{-6} + C_8 R^{-8} \quad (4)$$

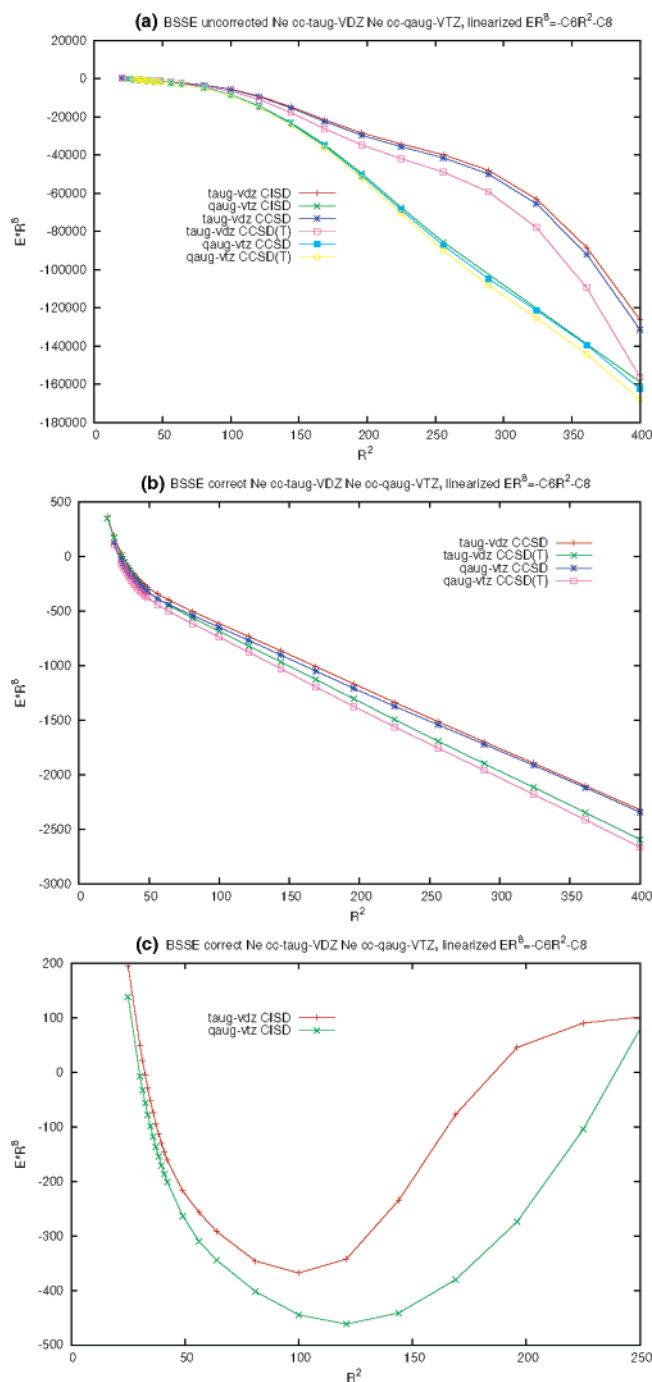


Figure 3. $E R^8$ as a function of R^2 (see text), in the asymptotic region. (a) taug-vDZ and qaugg-VTZ CISC, CCSD, and CCSD(T) BSSE-uncorrected. (b) taug-vDZ and qaugg-VTZ CCSD and CCSD(T) BSSE-corrected. (c) taug-vDZ and qaugg-VTZ CISC BSSE-corrected. Units: bohr² versus hartree·bohr⁸.

By multiplying this expression by R^8 and rearranging the different terms, one gets

$$[E(R) - E_\infty]R^8 = C_6R^2 + C_8 \quad (5)$$

This means that, if one plots the quantity $[E(R) - E_\infty]R^8$ as a function of R^2 , the result should be a straight line for large values of R . The results of these plots are shown in Figure 3, for four different cases: uncorrected CI and CC (3a) and BSSE-corrected CC (3b) and CI (3c). It is clear that, in the

case of uncorrected energies, either CI or CC, the long-range curves are far from being straight lines. This implies that the BSSE completely masks the correct long-range behavior of the potential energy for this VdW species. On the other hand, once the BSSE has been corrected, the CC results [either CCSD or CCSD(T)] have a correct linear behavior. Rather surprisingly, however, this is not true for the CISC results, as it could have been guessed from the long-range tail of the potential, Figure 2. When a linear least-square regression was used, it was possible to obtain values of the dispersion coefficients from the coupled cluster, BSSE-corrected, potential curves: results are collected in Table 2. These values can be compared with the results obtained from LRPT treatment and are collected and, with experimental ones, reported again in Table 2. In Table 2, computed or experimental values of polarizabilities are presented too (see also Figure 4).

4. Discussion

Two main aspects can be underlined from the analysis of the data: the long-range behavior of the potential-energy curves with the determination of dispersion coefficients, in particular, for the failure of CISC, and the determination of spectroscopic properties from the analysis of the equilibrium region of the curves.

4.1. Dispersion Coefficients: The Failure of CISC. The remarkable difference in the long-distance part of potentials that are overall substantially similar is rather unexpected. The reason can be traced back to a subtle interplay between two different sources of error that affect CI calculations: basis-set superposition error and size-consistency error (SCE). SCE originates from the fact that, in truncated-CI calculation, determinants that are present in the product of the monomer WF are absent in the dimer WF. For this reason, the CISC energy of two fragments separated by such a large distance, that they are physically noninteracting, is different from the sum of the CISC energies of the isolated fragments. The SCE is far from being negligible: in fact, the CISC energy of two noninteracting neon atoms is about 0.15 hartree higher than the sum of the corresponding energies of isolated atoms. However, the SCE depends only weakly on the geometry: once the BSSE has been taken into account via the counterpoise correction, the CISC values for the equilibrium distance and dissociation energy are in reasonable accord with the corresponding CCSD values (which are SCE-free) and also in a reasonable accord with the experimental^{24,25} and previously computed values.^{26,27} For this reason, CISC can be used to compute the spectroscopic quantities of a VdW dimer as Ne₂, although the obtained results are certainly less accurate than those obtained from CCSD, and much less accurate than those from CCSD(T). As expected, the use of diffuse functions appears to be of great importance to improve the computation of dispersion interactions; as an example, we can consider the Ne₂ CISC BSSE-corrected energy-well depth computed with the vDZ basis set during a preliminary study: in that case, a value of about 30 μ hartree was obtained to be compared with 83.5 μ hartree for taug-vDZ (experimental value 134 μ hartree).

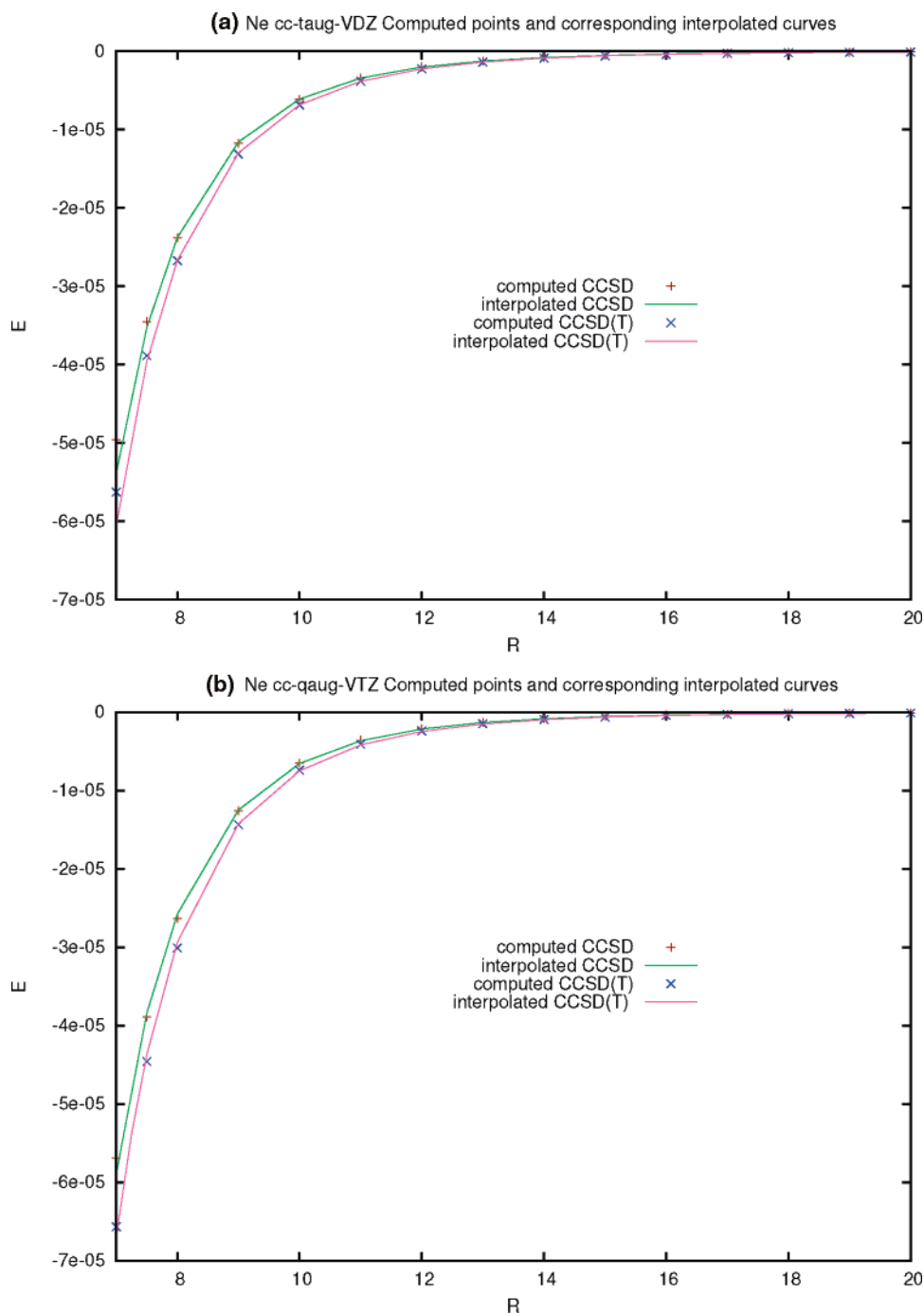


Figure 4. Computed points and the corresponding interpolated curves, in the asymptotic region. (a) taug-vDZ. (b) qaug-vTZ. Units: distances in bohr and energies in hartree.

Let us consider now the dispersion coefficients. Before being corrected to take into account the BSSE, the long-range tail of the potential-energy curves gives absolutely unreliable results. Once the BSSE has been taken into account via the CP correction, the CC curves fit very well into the long-range expression, and the values of the dispersion coefficients are in good agreement with both the FCI and experimental values. The situation is completely different for the CISD calculations, which cannot be fitted with the theoretical expression at large distances. In this case, the CP correction overcorrects the energy values, which become even higher than the corresponding asymptotic values. This is because the CP correction is extracted from

atomic calculation, while it is used to correct **molecular** energies. The (relatively small) error due to the lack of size consistency of the CI results has a dramatic effect on the long-range tail of the potential-energy curves. In fact, the sum of the atomic energies is larger than the energy of noninteracting atoms, giving therefore a too-large correction. For this reason, the CP correction **overestimates** the effect of BSSE, thus giving a long-range tail of the potential that is completely artificial.

4.2. Spectroscopic Properties. As the spectroscopic properties are concerned, as already stated, our values can be compared with a recent experimental work by Wüest and Merkt.²⁵ In that paper, the authors determine the position of

rovibrational energy levels of the Ne₂ dimer using vacuum ultraviolet laser spectroscopy. The potential curve for the ground electronic state was subsequently determined by means of a nonlinear fitting of a model interaction potential to the measured position of the rovibrational levels. It is quite interesting to see how the zero-point energy level lies very high in energy; in fact, it accounts for about 40% of the well depth, leading to a very low binding of the complex; this fact is anyway confirmed by experimental results. Moreover, Wüest and Merkt²⁵ observe only two vibrational levels, in agreement with our results, but from the analysis of the potential, they predict the existence of a third vibrational level with a very low binding energy. The existence of this level is, anyways, still uncertain and depends strongly on the energy-well depth and from the form of the long-range tail of the potential due to the high diffuse nature of the vibrational WF. The computed spectroscopic properties can be improved toward the basis set limit using a two-point basis set extrapolation formula.²⁸ Applying this formula to the CCSD(T) BSSE-corrected results, we obtain $E_{\min} = -130$ μ hartree, $R_{\min} = 5.82$ bohr, $\Delta E_0 = 12.38$ μ hartree, and $\omega = 13.5$ cm⁻¹.

5. Conclusions

It has been shown that the BSSE plays a key role in the numerical calculation of the dispersion coefficients of VdW species. No reasonable value of dispersion constants or equilibrium properties can be obtained for the Ne₂ dimer if one does not take into account the BSSE correction. The use of counterpoise correction allows one to obtain satisfactory results provided one uses size-consistent methods for the computation of the potential-energy curves of the dimer. Values obtained in such a way with CCSD or CCSD(T) agree quite well with experimental values and with the BSSE-free LRPT values. On the other hand, the application of the counterpoise correction to curves obtained with non-size-consistent methods gives quite good values for the equilibrium properties but totally wrong dispersion coefficients. This fact is due to a subtle interplay between basis-set-superposition and size-consistency errors. By using the potential-energy curves obtained at CI and CC levels, we computed the zero-point energy and the anharmonic vibrational frequency for the fundamental electronic state of Ne₂, showing the existence of two bound vibrational states; our results agree quite well with spectroscopic experiments. Finally, we show that a new data format and set of libraries (Q5Cost) were used in our calculations in order to interface the different codes used in the present study.

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