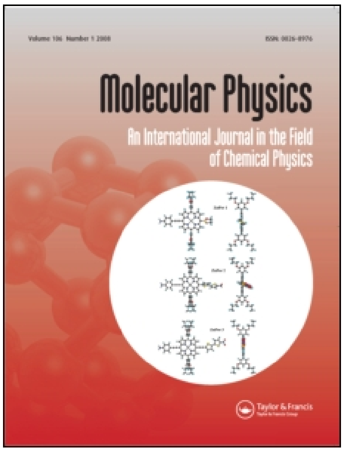

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On the treatment of long-range interactions in global potential energy surfaces for chemically bound systems

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RESEARCH ARTICLE

On the treatment of long-range interactions in global potential energy surfaces for chemically bound systems

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The convergence of undamped, inverse power series asymptotic van der Waals expansions for the hydrogen molecule is tested. The role of this kind of expansion in the description of global potential energy surfaces for strongly bound molecules is discussed. The single-bond breaking dissociation channel of the water molecule is shown to display the same behaviour. It is suggested that such expansions do not provide a good starting point for this problem as they only become reliable when the interaction energy is very small.

Keywords: intramolecular van der Waals forces; potential energy surfaces; asymptotic expansions

1. Introduction

Long-range intermolecular interactions [1,2] such as those found in weakly bound van der Waals complexes [3] have been well studied. On the other hand, the behaviour of long-range *intra* molecular interactions in strongly bound systems (i.e. systems where breaking a bond takes more than about $10,000\,\mathrm{cm}^{-1}$ or $30\,\mathrm{kcal\,mol}^{-1}$) upon bond-breaking processes have received less attention. An exception is the model case of the hydrogen molecule which has been studied many times [4–13]. However there are increasing efforts being made to find global methods of representing potentials for chemically bound molecules [14]. Several methods either implicitly or explicitly assume that, at long range, the interactions can be represented using potential forms developed for van der Waals systems [15–20]. Indeed, Ho *et al.* [21] developed a procedure for building potential energy surfaces for chemically bound systems that assumes that such surfaces go asymptotically as R^{-6}, where R is the length of the bond being stretched, as this is the expected leading term in the long-range form of the van der Waals interaction.

Asymptotic R^{-n} expansions have proved useful for representing global surfaces for systems with shallow wells; see, for example, the extensive work on the alkali metal complexes by Hutson *et al.* [22,23]. However, it would appear that their usefulness is largely untested by either experiment or theory for the case of more strongly bound systems, such as the water molecule. For such strongly bound molecules, one is generally interested only in the region close to equilibrium as the high-energy, near-dissociation behaviour of the potential cannot be easily investigated by spectroscopic measurements.

At short and intermediate range the $R=0$ divergence of expansions in R^{-n} hinders their practical implementation. A common remedy is to multiply each term by an empirical, sigmoid-type 'damping' function $f_n(R)$ defined to both suppress the singularity at $R=0$ and to allow for exchange effects as the charge clouds of the separated functions overlap. Such functions are defined such that $\lim_{R\to+\infty} f_n(R)=1$ so that the asymptotic limit is recovered.

Koide *et al.* [24] proposed the use of a damping function of the form $f_n(R)=(1-\exp(-a_nR-b_nR^2-c_nR^3)^n$, while another well-known form is that suggested by Tang and Toennies [25] and modifications thereof [26]. These damped expansions are widely used in potentials of weakly bound systems where long-range interactions are fundamental for their description. However, they require further parameters that can only be obtained from fitting rather than by theoretical asymptotic calculations. For strongly bound molecules, like water, a common practice is to incorporate in the potential an asymptotic behaviour of the simple C/R^6 type [15,27]. As we demonstrate in this work, it is important that this form should not be enforced as soon as the region covered by the *ab initio* points ends if, as is often the case, points stop at $R < 5a_0$.

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Two recent developments make it timely to reconsider the precise representation of these potentials at their dissociation limit. The first is the discovery that chemically bound polyatomic molecules support a series of long-range bound states, so-called asymptotic vibrational states (AVS), in the region between their classical and quantal dissociation limits [28,29]; analysis of these states suggests they should be ubiquitous and may only depend weakly on the form of the long-range potential [30]. The second is the development of a multiphoton technique capable of probing the vibration–rotation states of water just above and just below its dissociation limit with spectroscopic accuracy [31]. A good representation of the potential energy surface in this region is essential for analysing these spectra and this was in fact our initial motivation for addressing the issues discussed in this work.

The purpose of this work is to assess the relevance of intramolecular van der Waals interactions in the design of global potential energy surfaces to be used, for example, for the calculation of highly excited rotational–vibrational states of small, strongly covalently bound molecules. We shall first consider the case of the hydrogen molecule as this is a well-analysed system; we will then use a similar analysis for the single-bond-breaking dissociation channel in the water molecule.

All energies were converted from Hartrees to cm^{-1} using the CODATA 2006 [32] value $1E_h = 219{,}474.6313705\,\mathrm{cm}^{-1}$.

2. The London interaction in molecular hydrogen

Hydrogen is the simplest molecule and, as mentioned above, its asymptotic properties have been well studied and the divergence problems of asymptotic expansions of the long-range energy are well understood. We use H_2 to underline some features that are also present in larger systems.

2.1. *Series expansion of the interaction energy*

The analytic treatment of the long-range interaction between two ground-state hydrogen atoms is a paradigmatic example of the London dispersion interaction and has been studied in many papers [4–12]. The simplest treatment is based on Rayleigh–Schrödinger perturbation theory and is discussed in books [33,34] and reviews [1,2]. The final result is a series expansion in inverse powers of the interatomic distance R of the kind

$$E = \sum_{n=6}^{+\infty} C_n R^{-n}, \tag{1}$$

where each C_n is in turn given by a sum of contributions from various orders of perturbation theory,

$$C_n = \sum_{p=2}^{\infty} C_n^{(p)}. \tag{2}$$

Although the procedure is conceptually simple, calculations involving third and higher order of perturbation theory are rare and involve a great amount of both algebra and computation [4]. It was first conjectured [11] and later proven [35] that the series expansion thus obtained is asymptotic in character [36–39] and is in fact divergent as $n \to +\infty$ for all values of R.

The convergence problems of expansion (1) have been extensively discussed in the literature. Kreek and Meath [13] derived a second-order perturbative expression for the long-range energies without performing the multipole expansion. This avoids the divergence problems, but the resulting expressions are of little practical use in the fitting of potential surfaces based on the use of *ab initio* calculations.

To our knowledge the explicit comparison of the asymptotic expansion with accurate *ab initio* data is restricted to a few cursory remarks by Kolos and Wolniewicz [40]. This matter is therefore treated below.

In an asymptotic divergent power series of the form given by Equation (1) a criterion is needed for truncating the expansion at some R-dependent $n_{\max}(R)$ so that the truncated sum is in some sense optimal. The choice of such a criterion has been discussed in the mathematical literature [36–38] and the recommendation is to sum terms until they start to increase. Furthermore, if $C_n R^{-n} \ll C_{n-1}\, R^{-(n-1)}$, then $C_n R^{-n}$ may be used as a non-rigorous estimate of the residual error $\varepsilon(R)$ of the truncated expansion [36]. This recipe was applied to the recent, very accurate all-order C_n up to $n = 30$ by Ovsiannikov and Mitroy [4].

To obtain $n_{\max}$ we proceeded as follows. A simple numerical examination shows that plotting $(C^n)^{1/n}$ against n yields approximately a straight line, so that $(C_n)^{1/n} \approx An + B$. A and B were therefore obtained by a linear fit and then the integer $n_{\max}$ at which the series should be truncated was found by taking the derivative of $(An+B)^n R^{-n}$ with respect to n, setting it equal to zero and numerically solving for n. The final results for H_2 can be summarized as $n_{\max} = \lfloor 1.8R/a_0 \rfloor$. This truncation criterion, together with the non-rigorous estimate of the residual error mentioned above, leads to an expression for ε that can be well approximated for H_2 by an exponential function: $\varepsilon(R) \approx 10^{-0.72(R/a_0 - 5.34)}\,\mathrm{cm}^{-1}$. This result already suggests that series expansions should probably not be used for values of R less than about $5a_0$.

2.2. *Accurate reference points*

There is a long history of accurate calculations of the electronic potential of the hydrogen molecule [41]. Comparing the recent values from Sims and Hagstrom [42] with those from Rychlewski and Komasa [41] we estimate the energies by Sims and Hagstrom [42] to be accurate to at least $10^{-4}\,\mathrm{cm}^{-1}$; we label these results 'exact' below.

We computed a series of full-CI energies using MOLPRO 2002.6 [43] and various basis sets of the aug-cc-pV*n*Z family [44]. Basis-Set Superposition Error was estimated by calculating the counterpoise (Boys–Bernardi) correction [45] $\Delta E^{\mathrm{CP}}(R) = 2[E_{\mathrm{H}} - E_{\mathrm{HG}}(R)]$, where E_{H} is the energy of the hydrogen atom with the given basis set, and $E_{\mathrm{HG}}(R)$ is the energy of a hydrogen atom in the presence of the basis sets for the two hydrogens, for the aug-cc-pVQZ points. ΔE^{CP} is $0.311\,\mathrm{cm}^{-1}$ at $5a_0$ and decreases rapidly with R. Its effect is therefore small. Unsurprisingly, absolute values of the energy obtained in this way are much less accurate (e.g. the full-CI aug-cc-pV6Z energies near equilibrium are about $25\,\mathrm{cm}^{-1}$ too high), but results for energy differences at long bond lengths are much more encouraging.

Results are collected in Table 1 and are discussed in the following section.

2.3. *Analysis*

An overview of some of the truncated expansions, Equation (1), is presented in Figure 1. It is apparent that all the expansions are essentially useless for bond lengths less than about $5a_0$, as already suggested by the analysis of the expansion coefficients.

In the region $5 < R < 8a_0$, asymptotic expansions are still not very accurate, and the improvement on adding terms of higher n (within the limit of the truncation criterion) is slow. Expansions with $n < 18$ underestimate the interaction energy, while those with $n > 24$ overestimate it. In the range $8 < R < 10a_0$ the $n = 6$ term still performs rather poorly, for example at $9a_0$ the errors are about $1\,\mathrm{cm}^{-1}$ while the exact energy is only $-4.5\,\mathrm{cm}^{-1}$. Adding terms with higher n only improves the values very slowly, with the $n = 24$ curve still lying relatively far from the exact one. Finally, it is only for $R > 10a_0$ that the expansions give accurate values of the interaction energy. We note that terms with n higher than about 12 seem to only become useful for values of R greater than about $11a_0$, when the residual interaction energy is a mere $1\,\mathrm{cm}^{-1}$. The main conclusion of this analysis is that the high-order dispersion coefficients C_n computed by many authors [4–10] have little practical usefulness as they are applicable only at very long range, R greater than about $10a_0$, when their effect is very small.

It can be seen from Table 1 that full-CI, aug-cc-pV*n*Z calculations describe the London interaction rather well. Already with an aug-cc-pVTZ basis set the interaction energy is, for $R < 10a_0$, better than those obtained by asymptotic expansions of any order. The importance of diffuse basis functions was tested by removing the 'aug' function from the aug-cc-pV*n*Z basis sets and also by adding to these basis sets a further set of diffuse functions for every value of the angular momentum. The extra diffuse functions were obtained by logarithmic extrapolation (i.e. following an even-tempered scheme). The conclusion is that diffuse functions are essential in the description of the long-range interaction, but double augmentation does not lead to a significant improvement.

3. Long-range interaction for O–H stretching in H_2O

The long-range interaction upon stretching of one O–H bond inside the water molecule was studied. More specifically, this corresponds to the reaction $H_2O(^1A_1) \rightarrow H(^2S) + OH(^2\Pi)$.

For simplicity, the bond angle θ and the unstretched bond length r_2 were fixed to the equilibrium values of 104.52° and $1.8096a_0$, respectively. This reaction path differs slightly from the real dissociation channel of water because, in that case, r_2 and θ relax as r_1 is stretched. However, tests (not reported) showed that this small difference has no influence on our conclusions.

3.1. *Calculations*

All H_2O calculations are for the ground-state singlet $^1A'$ electronic state and make use of the standard, non-relativistic Hamiltonian. Spin-orbit and relativistic effects are not considered. Computations were performed with MOLPRO 2002.1 [43] and the IC-MRCI + Q method, i.e. internally contracted multi-reference configuration interaction including the (renormalized) Davidson correction. The computation of each point consists of three subsequent steps, namely Hartree–Fock, CAS-SCF (complete active space self-consistent field) and IC-MRCI. Two different active spaces were considered. The first is an (eight electrons, eight orbitals) complete active space (CAS) constituted by 6a′ orbitals and 2a″ orbitals; the lowest-energy a′ orbital, corresponding to the 1s atomic orbital of oxygen, was kept uncorrelated at the step. This is known to be a very good one for water [48–51]. A second, larger (eight electrons, 10 orbitals), which includes two further a′ orbitals,

Table 1. Long-range values for the interaction energy $E(+\infty) - E(R)$ of H_2, comparison of truncated asymptotic expressions with quantum chemistry calculations. R is in a_0, all energies in cm^{-1}. Full-CI energies were obtained as $E(R) - E(70)$. The distance of $70a_0$ was chosen because of numerical limitations for longer R. The true $E(70)$ is 0.001 cm^{-1}. A*n*Z stands for aug-cc-pV*n*Z; *n*Z stands for cc-pV*n*Z; AA*n*Z stands for a double-augmented cc-pV*n*Z basis set obtained as described in the text.

		Series expansion up to *n*					Full-CI									
R	Literature	6	12	18	24	30	ATZ	AQZ	A5Z	A6Z	TZ	QZ	5Z	6Z	AATZ	AAQZ
5.0	−830.856[a]	−91.288	−329.7375	−2406.20	-3×10^5	-2×10^8	−808.712	−823.262	−826.605	−828.427	−716.607	−765.199	−794.252	−810.635	−811.654	−824.997
8.0	−12.204[b]	−5.441	−8.043	−8.610	−11.793	−127.950	−11.255	−11.649	−11.786	−11.917	−9.560	−6.565	−7.664	−8.633	−11.838	−12.267
9.0	−4.341[c]	−2.684	−3.596	−3.672	−3.855	−7.118	−4.048	−4.102	−4.163	−4.212	−3.145	−1.969	−2.434	−2.771	−4.432	−4.461
10.0	−1.922[c]	−1.426	−1.791	−1.804	−1.817	−1.950	−1.838	−1.842	−1.844	−1.866	−0.740	−1.028	−1.179	−1.354	−2.150	−2.004
11.0	−0.989[c]	−0.805	−0.966	−0.969	−0.970	−0.977	−0.943	−0.968	−0.954	−0.964	−0.327	−0.515	−0.609	−0.698	−1.213	−1.071
12.0	−0.559[c]	−0.478	−0.555	−0.555	−0.556	−0.556	−0.532	−0.548	−0.544	−0.547	−0.169	−0.284	−0.349	−0.400	−0.707	−0.641
15.0	na	−0.125	−0.137	−0.137	−0.137	−0.137	−0.133	−0.135	−0.135	−0.136	−0.041	−0.070	−0.088	−1.101	−0.145	−0.147
20.0	na	−0.022	−0.023	−0.023	−0.023	−0.023	−0.023	−0.023	−0.023	−0.023	−0.007	−0.012	−0.015	−0.018	−0.031	−0.028
25.0	na	−0.006	−0.006	−0.006	−0.006	−0.006	−0.006	−0.006	−0.006	−0.006	−0.002	−0.003	−0.004	−0.005	−0.009	−0.008

[a] From [42], should be exact to the given precision.
[b] From [46], should be exact to the given precision.
[c] From [47], should be accurate to about 0.005 cm^{-1}.

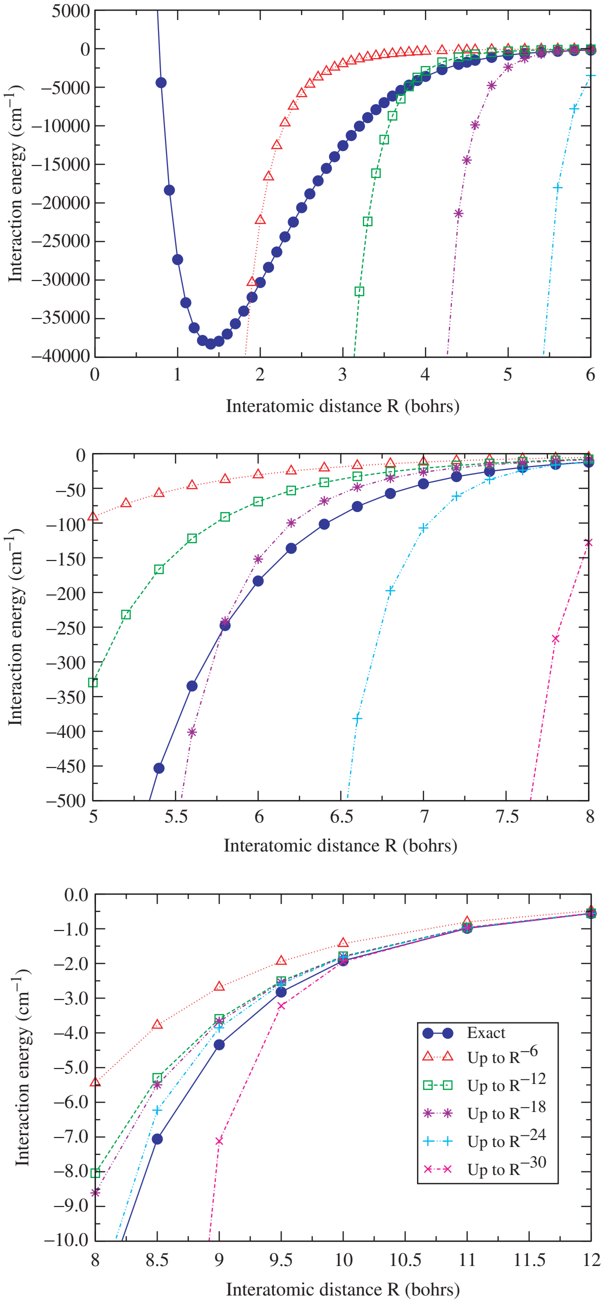

Figure 1. Comparison of potential energy curves for H_2 with several truncated asymptotic expansions of the long-range interaction energy.

was also examined. The basis sets used are those from the aug-cc-pV*n*Z series for $n = $ T, Q, 5 [44]. A total of 32 values for $r_1 = 1.0$ to $r_1 = 25.0a_0$ were computed and are reported in Table 2. All computations were done on a standard PC Pentium IV 3 GHz with 3 GiB (gibibytes) of RAM memory. Each of the aug-cc-pV5Z computations took about one hour and the other smaller computations between 5 and 30 min each.

3.2. *Analysis*

Looking at the data reported in Table 2 it can be seen that, as in the case of H_2, the calculated interaction energies for r_1 greater than about $5a_0$ are rather insensitive to the basis set used; already with the aug-cc-pVTZ basis set they are converged with respect to basis set increases to within 5 cm^{-1} or better. A similar level of convergence is observed with respect to increasing the CAS. Considering that the typical accuracy of potential energy surfaces for water near equilibrium is only of about 100 cm^{-1} [51], the aug-cc-pVTZ values can already be considered as quite accurate.

It should be noted that the long-range energies given by the CAS-SCF step differ significantly to the IC-MRCI + Q ones. While they show the same level of stability as IC + MRCI + Q energies with respect to basis set augmentation, they depend appreciably on the size of the CAS selected. These observations support the conventional view that an accurate description of long-range interactions requires an extensive treatment of dynamical electron correlation.

Once the accuracy of the computed values was evaluated, the range where the asymptotic behaviour of the kind $Ar_1^{-\alpha}$ effectively begins was ascertained, $\alpha = 6$ being the expected value. To do this we plotted the quantity $-r\,(\mathrm{d}/\mathrm{d}r_1)\log(|V(r_1)|)$ for the aug-cc-pV5Z energies, calculating the necessary derivative by finite differences (see Figure 2). If $V(r_1)$ had a form of the kind $Ar_1^{-\alpha}$, the plot would yield a constant value equal to α, so that the curve can be interpreted as a 'local exponent' as a function of r_1. This is also the value of α that would be obtained if a small portion of $V(r_1)$ were fitted to the functional form A/r_1^{α}. It can be observed from Figure 2 that the curve is not a constant, even at large r_1, indicating that, in the plotted range, asymptotic behaviour is not yet reached; the figure shows that H_2 behaves similarly.

The plot suggests that the curve does indeed approach the expected value of 6, but it is still away from it at $r_1 = 10a_0$ when the interaction energy is less than 4 cm^{-1}. This situation is thus quantitatively similar to that found above for H_2.

4. Conclusions

We show that undamped high-order asymptotic expansions in powers of R^{-1} of the interatomic energy for the hydrogen molecule are only useful for $R > 10a_0$. Furthermore, we show that these long-range interactions can be modelled accurately with standard quantum chemistry methods even with relatively small basis sets, provided the model includes sufficient treatment of dynamical electron correlation.

Table 2. Interaction energies for the single-bond stretching of water. Energies, in cm^{-1}, were obtained as $E(r_1) - E(25)$, where r_1, in a_0, is the length of the stretched OH bond.

	IC-MRCI + Q			
	(6a′, 2a″)			(8a′, 2a″)
CAS r_1	ATZ	AQZ	A5Z	ATZ
1.0	90,626.95	89,213.62	88,751.50	90,516.84
1.2	10,539.00	9521.35	9223.82	10,425.88
1.4	−25,198.84	−25,991.83	−26,187.15	−25,312.78
1.6	−39,467.82	−40,088.80	−40,233.26	−39,581.98
1.8	−43,119.11	−43,605.91	−43,722.31	−43,233.12
2.0	−41,554.90	−41,943.86	−42,040.76	−41,668.47
2.2	−37,552.12	−37,879.65	−37,961.89	−37,664.77
2.4	−32,583.77	−32,874.80	−32,945.04	−32,694.45
2.6	−27,445.97	−27,708.55	−27,768.61	−27,552.47
2.8	−22,563.30	−22,795.69	−22,847.03	−22,660.57
3.0	−18,151.87	−18,351.27	−18,394.88	−18,228.94
3.2	−14,311.19	−14,477.06	−14,513.50	−14,362.83
3.4	−11,072.87	−11,206.58	−11,236.13	−11,106.72
3.6	−8423.40	−8527.45	−8550.37	−8446.51
3.8	−6316.07	−6393.71	−6410.64	−6332.51
4.0	−4681.69	−4736.97	−4748.91	−4693.74
4.5	−2145.48	−2165.25	−2169.34	−2151.33
5.0	−967.34	−973.69	−974.41	−970.21
5.5	−440.68	−442.77	−442.40	−442.07
6.0	−206.70	−207.58	−206.98	−207.34
6.5	−101.47	−101.74	−101.27	−101.76
7.0	−52.94	−52.70	−52.41	−53.06
8.0	−17.63	−17.24	−16.94	−17.65
9.0	−7.45	−7.15	−6.92	−7.45
10.0	−3.68	−3.46	−3.36	−3.69
11.0	−2.01	−1.87	−1.82	−2.01
12.0	−1.16	−1.06	−1.03	−1.17
13.0	−0.70	−0.64	−0.62	−0.71
14.0	−0.43	−0.40	−0.39	−0.44
15.0	−0.27	−0.26	−0.25	−0.28
20.0	−0.03	−0.03	−0.03	−0.03
25.0	0.00	0.00	0.00	0.00

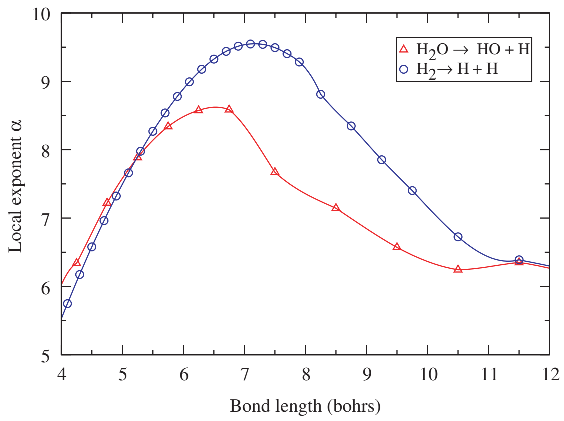

Figure 2. Plot of the quantity $-r(\mathrm{d}/\mathrm{d}r_1)\log(|V(r_1)|)$, corresponding to the local exponent α (see text). The plot shows that the asymptotic form A/R^6 is only reached for r_1 greater than about $10a_0$.

Conversely, we show that the asymptotic van der Waals regime, taken as the region where the potential can be reliably represented by the functions AR^{-6}, starts only at $R \approx 10a_0$ for both hydrogen and water. In both cases the interaction energy in this region is $3\,\mathrm{cm}^{-1}$ or less away from dissociation. It is true that there are some important cases where the very long-range form of the interaction determines the physics of the system, two notable examples being collisions of ultra-cold molecules and atoms [52] and near-dissociation rotation–vibration levels in diatomic molecules [53]. However, in the case of strongly bound polyatomic molecules, such binding energies are less than the error encountered in standard least-squares fits to global *ab initio* potential energy surfaces.

Our conclusion is that for global potential surfaces of strongly chemically bound systems, in most cases it will be unnecessary, and possibly harmful, to force the surface to have an asymptotic form of the kind AR^{-6} except when considerably larger values of R are used than is currently the case. In particular, one should be cautious about the use of undamped expansions for these systems for values of R below about $10a_0$.

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