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Recommended Citation

Studies of dispersion energy in hydrogen-bonded systems. H[sub 2]O--HOH, H[sub 2]O--HF, H[sub 3]N--HF, HF--HF M. M. Szczesniak and Steve Scheiner, J. Chem. Phys. 80, 1535 (1984), DOI:10.1063/1.446903

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Studies of dispersion energy in hydrogen-bonded systems. H_2O–HOH, H_2O–HF, H_3N–HF, HF–HF

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(Received 3 October 1983; accepted 8 November 1983)

Dispersion energy is calculated in the systems H_2O–HOH, H_2O–HF, H_3N–HF, and HF–HF as a function of the intermolecular separation using a variety of methods. Møller–Plesset perturbation theory to second and third orders is applied in conjunction with polarized basis sets of 6-311G** type and with an extended basis set including a second set of polarization functions (DZ + 2P). These results are compared to a multipole expansion of the dispersion energy, based on the Unsöld approximation, carried out to the inverse tenth power of the intermolecular distance. Pairwise evaluation is also carried out using both atom–atom and bond–bond formulations. The MP3/6-311G** results are in generally excellent accord with the leading R^{-6} term of the multipole expansion. This expansion, if carried out to the R^{-10} term, reproduces extremely well previously reported dispersion energies calculated via variation-perturbation theory. Little damping of the expansion is required for intermolecular distances equal to or greater than the equilibrium separation. Although the asymptotic behavior of the MP2 dispersion energy is somewhat different than that of the other methods, augmentation of the basis set by a second diffuse set of *d* functions leads to quite good agreement in the vicinity of the minima. Both the atom–atom and bond–bond parametrization schemes are in good qualitative agreement with the other methods tested. All approaches produce similar dependence of the dispersion energy upon the angular orientation between the two molecules involved in the H bond.

A basic understanding of the forces between molecules is a central goal of chemical physics. Accurate intermolecular potentials are crucial to understanding of dynamic phenomena like scattering, relaxation, lattice dynamics, energy transfer processes,[1] etc. They are also a vital ingredient in studies of the structure of liquids and solutions.[2] In recent years, considerable progress has been achieved in the calculation of interaction energies of closed-shell systems at the SCF level. Development of numerical methods along with high-speed computers has made it possible to perform *ab initio* SCF calculations even for systems containing a relatively large number of electrons.[3] However, it is now clearly recognized that intermolecular potentials based on the one-electron approximation are generally insufficient for high-quality studies. For example, Hartree–Fock (HF) potentials fail to indicate van der Waals minima for rare gas atom interactions.[4] These minima are predicted only when dispersion forces are directly included in the calculations via consideration of electron correlation. In addition to a general deepening of the interaction potential in the vicinity of the minimum, dispersion forces have also been demonstrated to alter the anisotropy of the interaction.[5]

The various methods for calculating the correlation contribution to the interaction energy—the dispersion energy—generally fall into one of two categories. The supermolecule approach may be used to calculate the dispersion energy indirectly via CI, MCSCF, etc. treatments or it may be evaluated directly with perturbational methods where the interaction operator is considered the perturbation.

A recently developed indirect method which shows great potential consists of application of many-body Rayleigh–Schrödinger perturbation theory (MB–RSPT) with Møller–Plesset partitioning of the Hamiltonian.[6,7] This method represents a significant step forward since it is more efficient and less time consuming that the technique of configuration interaction truncated after double substitutions.[8] A second advantage of the Møller–Plesset method is its size consistency.[7] Recent calculations have demonstrated that this method is applicable to van der Waals interactions[9,10] as well as to donor–acceptor complexes[11] and to strong H-bonded systems.[12] However, one shortcoming of the approach is that the size of the system is severely limited in the number of electrons which may be treated.

Significant progress has been made as well in methods of direct evaluation of the dispersion energy based on perturbation (or variation-perturbation) theory.[13,14] However, the complexity of the calculations increases dramatically when the influence of intrasystem correlation is taken into account.[15] Therefore accurate calculations with this approach are also limited to systems containing small numbers of electrons.

An alternative and much more efficient means of calculation of dispersion energy arises from the use of the multipole expansion of the interaction operator and replacement of the sum-over-states evaluation of transition moments by the Unsöld approximation.[16] The procedure proposed by Mulder *et al.*[17] leads to an expression for the dispersion energy in the expanded form

$$E_D^{\text{mult}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots, \tag{1}$$

where C_6, C_8, C_{10}, ... are the dispersion coefficients and R is

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the distance between subsystems. These coefficients have been evaluated in application to ethylene[17] and simple hydrides of first-row atoms.[18] The usefulness of the procedure is exemplified by its successful application to systems containing more than 80 electrons and its potential use with much larger systems.[19] The method does suffer from a number of drawbacks such as its failure to provide a strict upper bound to the interaction energy and the fact that the expansion (1) is not required to converge in the region of the van der Waals minimum.

A different class of methods allows a very efficient evaluation of dispersion energy by the use of parameters that are transferable from one molecule to another. These parameters are typically calibrated to reproduce the dispersion energy in a pairwise form, of either atom–atom or bond–bond type. Moreover, this approach does not suffer from size limitations or from convergence problems. The bond–bond approach takes advantage of the fact that an estimation of the C_6 dispersion coefficient may be provided by either experimental values of bond polarizabilities[20] or theoretical values based on a localized orbital description.[21] The alternative atom–atom potential parameters, derived on experimental bases, have been in use for years to furnish predictions and analyses of the structures and interactions in molecular crystals.[22] A theoretical set of atom–atom dispersion coefficients has recently been proposed by Mulder and Huiszoon[23] for molecule–molecule interactions as well. This set leads to an expression of the dispersion energy in the following form:

$$E_D^{\text{A-A}} = \sum_{i\in X}\sum_{j\in Y}\frac{A_{ij}}{r_{ij}^6}, \tag{2}$$

where X and Y are interacting molecules and r_{ij} are the distances between atoms i and j.

The diversity of aforementioned methods leads to a number of very interesting and important questions such as the following: What are the relative merits of MB-RSPT within the supermolecule approach vs direct calculation of dispersion forces via variation-perturbation theory? What is the range of convergence of the multipole expansion of the dispersion energy? It would be useful to determine whether some damping procedures can extend this range and how far in the expansion it is necessary to go in order to get good accuracy. How well do the atom–atom and bond–bond parametrization schemes work and is one preferable to the other?

The work described in this paper was carried out in an effort to help provide answers to some of these questions. The specific subject of our calculations is a series of hydrogen-bonded systems containing HF, OH_2, and NH_3. We are particularly interested in identifying an efficient and reliable method of calculating dispersion energy in these types of systems with potential application to very large systems. Since very little is known thus far about the applicability of Møller–Plesset theory to hydrogen-bonded systems, a central topic of our study is the use of this approach to calculate dispersion energy in these complexes.

METHODS

Hartree–Fock calculations were carried out with the polarized triple-valence[24] 6-311G** basis set as were the Møller–Plesset treatments to second (MP2) and third (MP3) orders.[7] For certain systems, an extended basis set containing two sets of d functions, denoted DZ + 2P, was also used. The MP interaction energies were computed as the difference in total energy between the complex and the isolated monomers. The GAUSSIAN-80 set of computer programs[25] was used to perform the above calculations. The dispersion energy was also evaluated by the multipole expansion in Eq. (1) using C_6, C_8, and C_{10} coefficients of Mulder *et al.*[18] The value of the leading C_6R^{-6} term in the multipole expansion is designated below as M(6) while the cumulative sum to the $C_{10}R^{-10}$ term is referred to as M(10). (R is evaluated as the distance between centers of mass in the expansion.)

An alternative means of calculating the dispersion energy involves a pairwise sum over interactions between bonds on different molecules, making use of experimental bond polarizabilities.[26] There is some uncertainty, however, in the choice of the molecular excitation energy to be used in the London formula. For OH_2 and NH_3, this energy was estimated from experimentally determined values of the C_6 coefficients for the homodimers H_2O–HOH and H_3N–HNH_2[27] and from the experimental mean polarizabilities. Since the C_6 coefficient for HF–HF has not been determined to date, the assumption was made that the excitation energy is proportional to the ionization energy for the series H_3N, H_2O, HF[26] leading to a value of 23.0 eV for HF. The dispersion energy computed using this bond–bond formulation is abbreviated as B–B, the parameters of which are collected in Table I.

Another pairwise formulation of the dispersion energy involves summing over pairs of atoms, designated A–A below. The A_{ij} parameters needed for evaluation of Eq. (2) were taken from Ref. 23. Whereas the B–B dispersion energy serves as an approximation to the R^{-6} leading term of the multipole expansion, the A_{ij} parameters have been chosen to fit data calculated with the first three terms of Eq. (1).

The four H-bonded systems studied in this work are H_2O–HOH, H_2O–HF, H_3N–HF, and HF–HF, the geometries of which are illustrated in Figs. 1–5. The relative orientations of the monomers in H_2O–HOH[28] and H_3N–HF[29] were taken directly from experiment and contain linear H bonds. Geometry optimization at the MP3/6-311G** level was used to determine the relative orientation in H_2O–HF.[30] In the above cases, the internal geometries of the individual monomers were taken as the experimental structures of the isolated molecules. The geometry of the HF–HF dimer is that of a previously reported complete optimization (including internal HF bond lengths) at the CEPA level.[31] Disper-

TABLE I. Average excitation energies (U) and longitudinal (α_L) and transverse (α_T) bond polarizabilities.

	NH_3	H_2O	HF
U, eV[a]	15.2	17.7	23.0
α_L, Å^3[b]	0.50	0.58	0.98
α_T, Å^3[b]	0.83	0.79	0.76

[a] See the text for definition.
[b] From Ref. 26.

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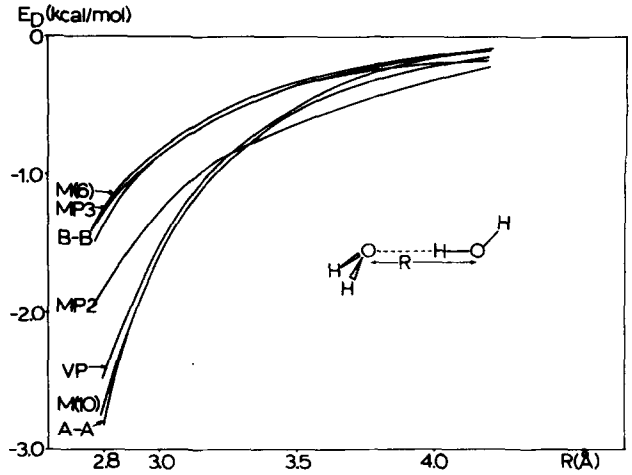

FIG. 1. Dispersion energy for H_2O–HOH. For both H_2O units, r(OH) = 0.957 Å, θ(HOH) = 104.5 °. The complex belongs to the C_s point group with an angle of 120 ° between the O—O axis and the bisector of the left-hand water.

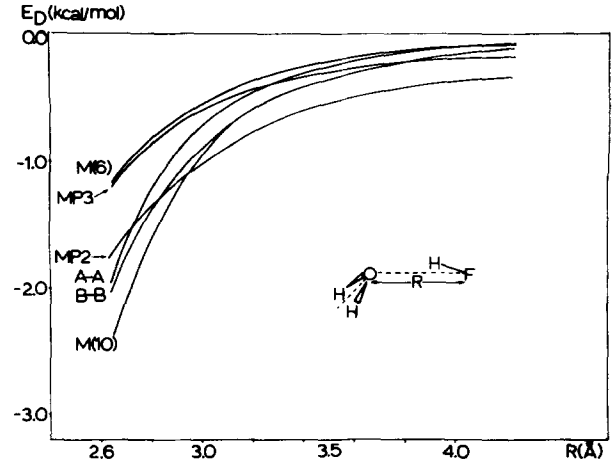

FIG. 3. Calculated dispersion energy for C_s complex of H_2O–HF. r(OH) = 0.957 Å, θ(HOH) = 104.5 °, r(FH) = 0.921 Å. The intermolecular orientation is such that θ(HFO) = 2.5 ° and the HOH bisector makes an angle of 136.9 ° with the O—F axis.

sion energies for each of the systems were calculated as a function of R, the distance between first-row atoms, over a range extending from slightly less than the equilibrium separation to 4.0 Å. The internal geometries of the monomers were held fixed as R was varied as were the relative orientations.

RESULTS

Figures 1–5 illustrate the dependence of the dispersion energy upon the distance between molecules. We begin our analysis by pointing out a few general features of the results. In all four cases, and over the entire range of intermolecular separation, second-order Møller–Plesset theory leads to a greater (i.e., more negative) dispersion energy than does MP3. When compared to MP3, or to any other method for that matter, the MP2 dispersion energy appears to have different asymptotic behavior. The MP2 dispersion approaches zero much more slowly for large R and increases less rapidly as R decreases. Over most of the R range for all four systems, the extra two terms included in the M(10) multipole expansion lead to significantly greater dispersion energies than the leading term proportional to R^{-6}. In three of the cases examined, the latter M(6) energy is in remarkable coincidence with the supermolecule MP3 results. The exception to this rule is HF–HF which will be discussed in greater detail below. The parametrized A–A and B–B dispersion energies generally fall in the range between the M(10) values and the smaller MP3 energies. (Again HF–HF proves an exception.)

At this point, it would be most illuminating to discuss each case on an individual basis. We begin with H_2O–HOH for which there is available the most extensive theoretical

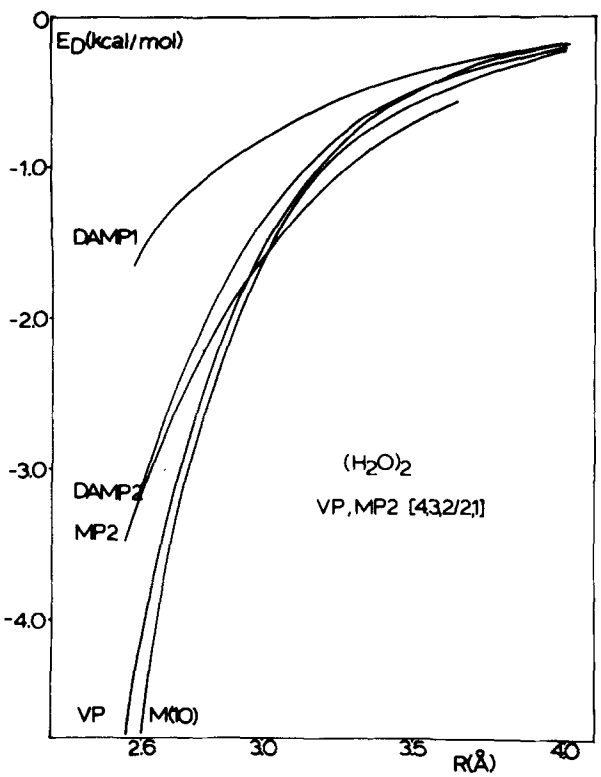

FIG. 2. Dispersion energy for $(H_2O)_2$. VP and MP2 values calculated with identical basis sets. DAMP1 and DAMP2 results were obtained using Eqs. (3)–(5) and respective values of $\zeta = 0.949$ and $\zeta = 1.344$.

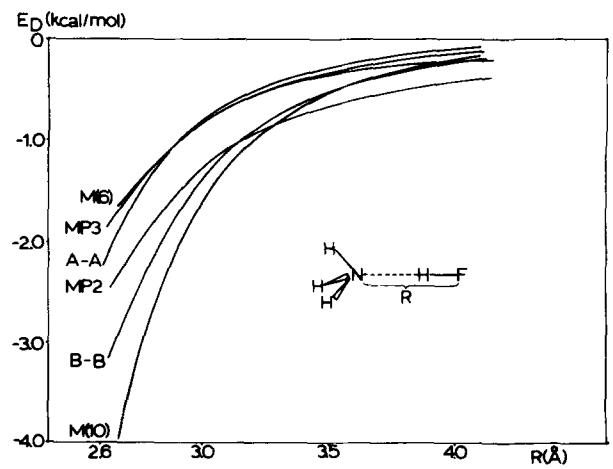

FIG. 4. Dispersion energy for C_{3v} complex of H_3N–HF. r(NH) = 1.012 Å, r(HF) = 0.92 Å. The internal θ(HNH) angle is 106.5 °.

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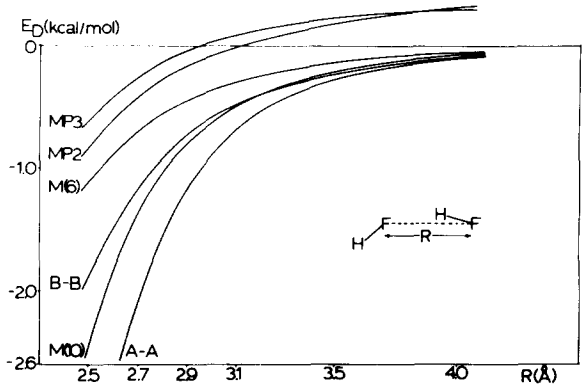

FIG. 5. Calculated dispersion energy for $(HF)_2$. For the left-hand molecule, $r(FH) = 0.902$ Å and $\theta(HFF) = 123.2°$. $r(FH) = 0.904$ Å and $\theta(HFF) = 6.0°$ in the other molecule.

and experimental data base with which to compare our results. Included in Fig. 1 and labeled as VP are the dispersion energies of this system calculated by Jeziorski and van Hemert using a direct variation-perturbation method.[32] This procedure was applied directly to the uncorrelated subsystem wave functions, calculated with a fairly extended [432/21] basis set and an unexpanded interaction Hamiltonian. These results may be taken as the most accurate evaluation of the dispersion energy in the water dimer system to date. We note from Fig. 1 that the multipole expansion through the $C_{10}R^{-10}$ term furnishes dispersion energies in excellent agreement with the accurate VP data. Significant discrepancies arise only for distances smaller than the equilibrium separation of 3.0 Å. Differences in this region are not unexpected owing to charge overlap effects. However, these effects appear to be minimal in the vicinity of the equilibrium structure and for larger distances where M(10) and VP dispersion energies are in excellent agreement. The atom–atom parametrized dispersion energy mimics quite well the M(10) data, which is not surprising since it is against this data that the A_{ij} parameters were fit.

Smaller in magnitude, but in excellent accord with one another, are the dispersion energies calculated by the MP3, M(6), and B–B procedures. The agreement between the latter two methods is gratifying since the pairwise bond–bond formalism was devised in an attempt to efficiently reproduce the leading term of the multipole expansion. However, the nearly identical MP3 dispersion energies are rather unexpected due to the drastically different formulation of this quantity. It is further noted that a very different approach; namely, the CI treatment with a comparable basis set,[33,34] yields dispersion energies quite close to the MP3, M(6), and B–B results.

For distances less than about 3.2 Å, the MP2 dispersion energies are smaller in magnitude than the VP values which might be explained on the basis of the larger basis set used in the latter calculations, and by the fact that MP2 accounts for different types of excitations (intersystem and intrasystem type) than does VP. However, the situation is reversed for longer distances where the MP2 dispersion energies are the most negative of all those calculated. This result is most likely connected with the supermolecular nature of the calculations, resulting in the interaction-induced change of the HF potential[35] as well as basis set superposition effects, which may exaggerate the magnitude of the dispersion energy at the MP2 level. For purposes of direct comparison between the MP2 and VP approaches, additional calculations were carried out at the MP2 level using a [432/21] basis set identical to that used by Jeziorski and van Hemert (denoted DZ + 2P here). These results are presented in Fig. 2 where it may be seen that in the vicinity of the van der Waals minimum ($R = 3.0$ Å), the MP2 and VP methods yield almost the same dispersion energies. For shorter intermolecular separations, the MP2 correlation contribution is less negative than the VP results whereas the situation is reversed for longer distances. The latter fact may possibly be attributed to mutual improvements of the subsystem basis sets; we will return to this point below.

For all intermolecular distances, the MP2 dispersion energies are greater than the MP3 values. This observation may be explained most simply by describing the third-order MBPT interaction energy roughly as the interaction of the uncoupled HF polarizability of molecule X with the correlation-corrected polarizability of Y,[36] which is known to be a positive quantity.

While MP3/6-311G** furnishes an excellent estimate of the leading term in the multipole-expanded dispersion energy, it does appear to be significantly different than the more complete M(10) multipole values. The accuracy of the MP3 treatment is verified in part by basically similar results using the CI method and a comparable basis set.[33,34]

In an effort to improve the agreement between the VP results and the multipole expansion M(10) in the region of small R, some damping of the latter expression was carried out. The doubly corrected damping procedure recently proposed by Douketis *et al.*[37] was used.

$$E_D^{\text{mult}} = \left[\sum_{n=6,8,10} C_n R^{-n} g_n(\zeta R) \right] f(\zeta R), \tag{3}$$

where C_n are the usual dispersion coefficients and ζ is a scaling parameter characteristic of the interaction. The damping functions

$$g_n(R) = [1 - \exp(-2.1\,R/n - 0.109\,R^2/n^{1/2})]^n \tag{4}$$

correct the various terms for charge overlap effects while the function f,

$$f(R) = 1 - R^{1.68} \exp(-0.78\,R) \tag{5}$$

corrects the expansion for exchange overlap and other effects. The damped E_D^{mult} was calculated with two different values of ζ. These were 0.949 which was obtained for H_2O–HOH interactions from the empirical formula given in Ref. 37 (denoted DAMP1 in Fig. 2) and 1.344, the value adopted by these authors for He–He interactions (DAMP2). Use of the first value leads to very strong damping such that the scaled dispersion energy is even smaller than the MP3/6-311G** values. The second value of 1.344 also leads to an overcompensation, although somewhat less dramatic, and the corrected dispersion energy is smaller than the VP results. We conclude that only a very small damping of the multipole expansion is necessary in H_2O–HOH and probably other H-bonded systems as well; this damping is unnec-

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essary for the equilibrium separation and larger distances.

We now turn to the H_2O–HF system for which the dependence of the dispersion energy upon intermolecular separation is presented in Fig. 3. As in the previous case of the water dimer, the MP3 and M(6) results are in close coincidence while the M(10) expansion of the multipole expression leads to much higher values, particularly at small distances. The atom–atom parametrized dispersion energies are not as close to the M(10) values here as in the previous water dimer case nor are the B–B estimates in as good agreement with M(6). The second-order Møller–Plesset energy is a much flatter function of the intermolecular distance than the other quantities.

The situation for H_3N–HF, illustrated in Fig. 4, is in many ways similar to H_2O–HF. The multipole expression carried to the R^{-10} term is substantially greater than the M(6) and MP3 results which are quite similar to one another. In this case, the A–A dispersion energy matches the latter two curves quite closely, whereas the B–B energies are larger, falling in the range between M(6) and M(10). The MP2 curve again has different asymptotic behavior than the others.

In comparison to the previous three cases, the results for HF–HF (Fig. 5) are anomalous in a number of ways. The MP3 dispersion energies are substantially smaller than the M(6) values. In addition, the correlation interaction energies calculated with Møller–Plesset theory are positive over a fairly wide range of R. Of course, dispersion is by definition a negative quantity and these positive values warrant some discussion. Some enlightening information in this regard comes from a previous study of $(HF)_2$ by Lischka using the CEPA method.[38] While his [7s, 3p, 2d /4s, 1p] basis set was larger than ours and the geometry of the complex somewhat different ($C_{\infty v}$), the qualitative conclusions are expected to be quite relevant. A partitioning of the CEPA interaction correlation energy indicated that the change in the intrasystem correlation energy due to the interaction is a positive quantity whereas the intersystem term is negative. Lischka found that combination of the two terms led to large scale cancellation with a slightly positive net interaction correlation energy. It is thus clear that proper evaluation of the dispersion energy within the supermolecule framework relies on a delicate balance between the two terms and small inadequacies in the basis set can result in a positive "dispersion" energy. Similar cancellation most likely occurs in the HCN···HF system studied recently by Benzel and Dykstra[39] where correlation effects calculated via the SCEP and coupled-cluster approaches were found to make negligible contributions to the H-bond energy.

The 6-311G** basis set used here does indeed have some deficiencies as illustrated by the overestimation of the interaction energy at the HF level, calculated to be -5.4 kcal/mol, as compared to Lischka's recent[31] value of -3.8 (for the quasilinear C_s geometry). Moreover, it is known that a basis set of 6-311G** type is unable to properly describe the subsystem properties of HF (e.g., multipole moments, polarizability) essential to reproduction to the interaction energy.[40] A second and very diffuse set of d functions ($\zeta = 0.15$) was therefore added to the F atoms. As may be seen in Table II, the MP3 dispersion energies with this 6-311G** (2d) basis set are much closer to the M(6) values. Moreover, there is excellent agreement between the MP2/6-311G** (2d) and M(10) dispersion energies. However, the problem of incorrect asymptotic behavior at large R is not completely removed as both MP2 and MP3 values become positive (albeit only slightly) for $R = 4.0$ Å. Improved results would probably result from further extension of the basis set or carrying the MP expansion to higher orders.

TABLE II. Dispersion energies[a] calculated for HF–HF.

			6-311G**		6-311G**(2d)	
R, Å	M(6)	M(10)	MP2	MP3	MP2	MP3
2.83	−0.52	−0.95	−0.24	−0.10	−0.94	−0.60
3.10	−0.30	−0.49	−0.02	+0.08	−0.60	−0.35
3.50	−0.15	−0.22	+0.18	+0.22	−0.18	−0.05
4.00	−0.06	−0.08	+0.30	+0.29	+0.15	+0.17

[a] All entries in kcal/mol.

DISCUSSION

From the foregoing arguments, it is clear that the choice of basis set plays a major role in calculation of dispersion energy with the Møller–Plesset method. The 6-311G** basis set used here does have a number of deficiencies. Despite its inclusion of polarization functions on all atoms, it leads to overestimation of interaction energies of the various complexes considered here at the Hartree–Fock level. These overestimates are due to incorrect multipole moments, particularly exaggerated dipole moments, in addition to basis set superposition errors. Because of these deficiencies, it is rather surprising that this basis set leads to generally quite satisfactory values of dispersion energies for a wide range of intermolecular distances, including the equilibrium separation. Although basis sets like 6-311G**, containing only a single set of polarization functions, are not capable of properly describing the dipole polarizability,[41] the MP3 dispersion energies generally agree quite well with the M(6) values. Moreover, the basis set, when augmented by a second set of d functions, reproduces extremely well the M(10) multipole expansion dispersion energies for HF–HF despite the fact that a basis set of this type should not in principle properly describe the quadrupole polarizability.[42]

A major source of this unexpected agreement may lie in mutual improvements of the subsystem basis sets. Karlström and Sadlej[43] have described a partitioning of the basis set superposition effects into primary and higher-order categories. The primary effect is associated with an artificial lowering of the subsystem energies in a purely mathematical manner. Higher-order effects result in changes in the electric properties, such as multipole moments and polarizabilities, of each subsystem. Karlström and Sadlej argue that while the primary effect is an undesirable artifact, the higher-order effects may lead to improvements in calculated interaction energies. In our application of calculation of dispersion energies, the polarizabilities of each subsystem may be improved considerably by the presence of the basis set of the other subsystem. (This is precisely the result found by Karlström

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and Sadlej at the SCF level and would be enhanced at correlated levels.) The resulting increase in the polarizabilities of the two subsystems introduces into the correlated interaction energy a purely attractive contribution of proper dispersion type. For example, it has been demonstrated that functions of f type are required for correct evaluation of the quadrupole polarizabilities.[42] Within the supermolecule treatment of the HF dimer, the d functions of one molecule may act as substitutes for the f functions of the other, absent within the 6-311G** ($2d$) basis set. This hypothesis is confirmed in part by the observation that addition of a second and diffuse set of d functions on the F atom results in close agreement between the MP2 dispersion energies and the M(10) values which explicitly include interactions between quadrupole polarizabilities of the two HF molecules. Thus, while primarily an undesirable artifact at the SCF level, basis set superposition may lead to improved results at correlated levels.

Certainly the use of large, doubly polarized basis sets with Møller–Plesset theory beyond MP2 is severely limited by rapidly increasing computer time required for MP3 and MP4 calculations. Therefore, an effective compromise between computer resources and accuracy is highly desirable. In particular, it is frequently necessary to choose between smaller basis set calculations up to fourth order of perturbation theory (as, e.g., in Ref. 44) or use of a large basis set and truncation of the calculations at second order. The recent MBPT calculations of dipole polarizabilities by Diercksen *et al.*[45] provide some relevant information. These investigators found a high degree of cancellation between third-order and full fourth-order contributions of MBPT theory, with the largest contribution to the latter term arising from triple excitations. We expect that similar cancellation will occur in the case of dispersion energy. (The importance of triple excitations in intermolecular interactions has not yet been studied in the literature.) Therefore, there are reasons to believe that the MP2 dispersion energy, derived with a sufficiently polarized basis set, represents a good estimate of the accurate dispersion energy.

While the bond–bond parametrization leads to excellent agreement with MP3 and M(6) for the water dimer, it is in general larger than those terms and rather closer to M(10) in magnitude. The reasons for these differences may be traced to the participation of HF in all the other complexes studied. As described above, the excitation energy needed to evaluate the parameters in the B–B expression is somewhat uncertain for HF. As another approach, we recalculated $E_D^{\text{B-B}}$ using the experimental value of the molecular polarizability of HF and the Unsöld value of the C_6 coefficient (from HF–HF) along with a new value of excitation energy of 21.6 eV. The results were little changed from those already provided in Figs. 1–5. A second choice was to fit the excitation energy such that $E_D^{\text{B-B}}$ would reproduce $E_D^{\text{M(6)}}$ as closely as possible. Using this excitation energy (14.0 eV) the recalculated B–B dispersion energies were much closer to M(6) for both H_3N–HF and H_2O–HF.

The atom–atom parametrization scheme appears to offer a very efficient and reasonably reliable means of estimating dispersion energy in H-bonded systems. For the water dimer, the A–A results reproduce the multipole expansion to inverse tenth power of R extremely well, even in the region below the van der Waals equilibrium contact. The agreement with M(10) is less precise in the other cases however. This discrepancy is attributed to the presence of the F atom in these systems. The A–A parameters for this atom were extracted from calculations involving largely isotropic molecules such as CHF_3 whereas we are using these parameters in this study on the highly anisotropic HF molecule. The excellent agreement between A–A and M(10) dispersion energies for the H_2O–HOH system may similarly be attributed to the fact that the A–A parameters for O were extracted from calculations involving the water molecule. It is therefore expected that agreement between A–A and M(10) for systems containing HF might be greatly improved by fitting the parameters to a larger number of molecules containing F.

In addition to the contribution of dispersion forces to the interaction energy as a function of intermolecular distance, it is important to consider as well the manner in which these forces may influence the dependence on the relative orientations. This question is addressed in Fig. 6 which illustrates the calculated dispersion energy as a function of the direction of approach of the HF molecule towards water in H_2O–HF. Specifically, α refers to the angle between the HOH bisector and the O–F axis; the R distance is held fixed at 2.68 Å. All methods agree that the magnitude of the dispersion energy increases as the plane of the water approaches the perpendicular arrangement relative to the H-bond axis; i.e., as α decreases from 180 ° towards 90 °. Superimposed on Fig. 6 as a dashed curve is the potential energy calculated at the HF level (with the 6-311G** basis set) which contains a minimum at $\alpha = 145$ °. The MP3 equilibrium angle is slightly smaller (138 °) and therefore represents a compromise between dispersion and forces accounted for at the HF level which follow opposite trends in the vicinity of the minimum.

While all methods show a decrease in the dispersion energy as α approaches 180 °, there are some differences in the slopes of each. The MP2 dispersion energy is most sensitive to the angle with MP3 slightly less so. The size of the

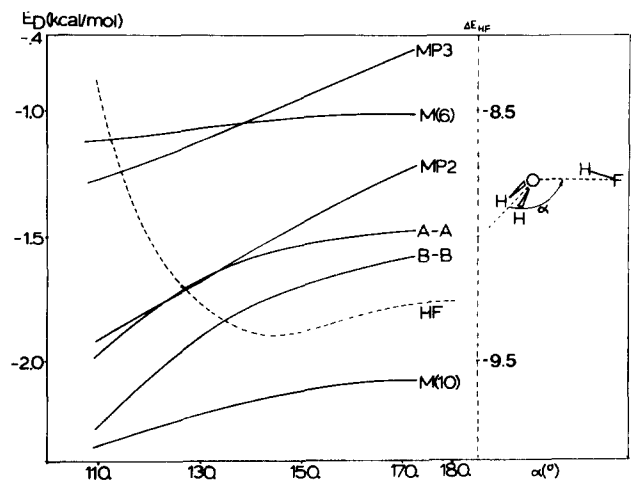

FIG. 6. Dispersion energy in H_2O–HF as a function of relative orientation α. R (OF) is held fixed at 2.68 Å. The dashed curve refers to the Hartree–Fock interaction energy, the scale of which is on the right.

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basis set may be expected to have a large effect on these results since it is known that the perpendicular polarizabilities saturate less quickly than parallel properties as the basis set is enlarged. The A–A and B–B parametrized energies are less linear than the MP curves although the slopes in the region of the minimum (135°–145°) are not very different. The functional dependence of the M(6) and M(10) multipole dispersion energies are notably smaller than the other procedures. This difference may be a result of the fact that the C_n coefficients in the multipole expression are isotropic and the change in dispersion energy with α is caused only indirectly by the change in distance between centers of mass as the OH_2 molecule rotates.

TABLE III. The equilibrium values of HF interaction and dispersion (MP2, MP3) energies derived with (DZ + 2P) basis sets; M(10) values added for comparison. All entries in Å and kcal/mol.

	$(H_2O)_2$[a]	$(HF)_2$[b]	$H_3N\cdots HF$[c]
R_{eq}	2.92	2.83	2.69
ΔE^{HF}	−3.89	−5.87	−11.80
MP2	−1.82	−0.94	−3.25
MP3	...	−0.60	−2.84
M(10)	−1.96	−0.95	−3.11

[a] Values derived for MP2/DZ + 2P minimum; basis set from Ref. 32.
[b] Values derived for CEPA (Ref. 31) minimum; 6-311G**(2*d*) basis set.
[c] Taken from Ref. 48 values derived for MP3/6-311G** minimum; M(10) obtained by damping of multipole expansion [Eqs. (3)–(5)].

SUMMARY

Several different procedures have been applied to the calculation of dispersion energy in a number of H-bonded systems. Møller–Plesset theory appears to represent a very attractive means of incorporating dispersion contributions within the supermolecule framework. When used in conjunction with a polarized basis set such as 6-311G**, third-order MP theory closely reproduces the interactions between the dipole polarizabilities contained in the leading R^{-6} term of the multipole expansion. Dispersion energies calculated with second-order MP theory are of greater magnitude and lead to somewhat different asymptotic behavior, approaching zero more slowly for large R than the other procedures tested. On the other hand, MP2 reproduces quite closely the dependence of the MP3 dispersion energy on the relative orientation of the two subsystems. Anomalous behavior is noted when Møller–Plesset theory is applied to the HF dimer with a 6-311G** basis set. This situation is improved markedly, though, when the basis set is enlarged by addition of a second set of d functions on F. In fact, the resulting MP dispersion energies are in close agreement with values calculated using the multipole expansion. MP2, applied to basis sets equipped with at least two sets of polarization functions, gives very reliable estimates of the accurate dispersion energy in the region of the H-bond minima. Correction of MP2 and MP3 values of interaction energies for BSSE by the use of the functional counterpoise method,[46] as suggested in the literature,[47] seems to be unnecessary. This procedure can lead to an overcorrection of the dispersion-type terms arising from mutual improvements of the subsystems' basis sets.

The results have also demonstrated the usefulness of the multipole expansion as formulated by Mulder. The leading C_6R^{-6} term is generally in close agreement with MP3/6-311G** values. Carrying the expansion through the $C_{10}R^{-10}$ term results in extremely good agreement with the accurate results of a previous variation-perturbation treatment of the water dimer. Of particular interest is the observation that little or no damping of the multipole expression is required in the vicinity of the equilibrium confomations of the weak H-bonded dimers with equilibrium H-bond lengths of 2.9–3.0 Å whereas moderate damping is required for stronger systems like $H_3N\cdots HF$ with R_{eq} around 2.7 Å.[48]

Both types of treatments mentioned above would generally be precluded in applications to larger systems. It is therefore with some optimism that we note that the atom–atom and bond–bond parametrization schemes seem capable of describing rather well the functional dependence of the dispersion energy on both the distance and angular features of the H-bonded complexes. As described in some detail above, careful parametrization of these two schemes can lead to excellent agreement with much more time-consuming means of calculating dispersion energies.

We note finally that there are tendencies in the literature to apply the MP2 method with very limited basis sets, e.g., 6-31G*, 4-31G or even STO-3G, to the SCF-optimized minima. Due to the fact that the MP2 dispersion energy is very strongly basis set dependent, the results obtained give very poor estimates of this quantity. Moreover, these basis sets are so far from the Hartree–Fock limit that the validity of Møller–Plesset partitioning of the total Hamiltonian is in question. In the systems studied here, the magnitude of the dispersion energy is approximately one third that of the HF interaction energy as may be seen in Table III. It is therefore not surprising that the positions of the HF minima differ markedly from those including correlation effects. We believe that a more appropriate procedure to locate the equilibrium structure consists of minimization of the sum of ΔE^{HF} and either atom–atom or bond–bond-formulated dispersion energies.

ACKNOWLEDGMENTS

We are grateful to A. Sadlej for helpful discussions and to P. Hobza for transmitting to us the parameters of Ref. 23 and for reading and commenting on the manuscript. Computer time was provided by the Southern Illinois University Computing Services. Grants to S. S. from the National Institutes of Health (GM29391 and AM01051) and the Research Corporation are acknowledged.

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