Use of a non-pair-additive intermolecular potential function to fit quantum-mechanical data on water molecule interactions*

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Permanent and induced multipole, repulsion, and dispersion terms are proposed as a model for the nonadditive potential of water molecules. 229 quantum-mechanical dimer energies of near Hartree–Fock accuracy which have been published by Popkie, Kistenmacher, and Clementi and by Kistenmacher, Lee, Popkie, and Clementi have been fit to an approximation to this model. The standard deviation 0.0019 of calculated dimerization energies for one simple form of the present model compares with a standard deviation 0.0023 given by an additive analytical fit developed by the above group. Nonadditive contributions calculated for the present model are compared with those given by the HF calculations of Hankins, Moskowitz, and Stillinger and by Kistenmacher, Lee, Popkie, and Clementi. The proposed model is compared with other models, and results to aid in the choice of multipole expansion orders in applications are given.

I. INTRODUCTION

Although direct quantum-mechanical calculations provide reference standards for the energies of intermolecular interactions, such calculations have the following disadvantages which have led to other approaches for the calculation of interaction energies of rather small groups of even simple molecules such as water: (i) Since the intermolecular energy is obtained as a difference, the calculated water dimer energies have been decreased from 12.6 to 3.67 kcal/mole by increasing the size and number of harmonic types of basis functions.[1–6] This points out the importance of using a more costly basis set approximating the Hartree–Fock limit. (ii) It is necessary to perform calculations on different polymer orientations, since it has been shown that the interactions show significant orientationally dependent deviations from additivity[5(a),7(a)] (*vide infra*). The nonadditive contribution of only about 10% has possible structural importance as a consequence of the fact that it exceeds the ΔE of transformation of the various ice forms,[8] with their drastically different relative orientations. (iii) Even in the case of four water molecules, the costliness of direct calculations excludes extensive variations of orientational parameters and consequently led to incorrect selection of the preferred orientation.[7(b),9(a)] Clementi, Kistenmacher, Lie, and Popkie sought to circumvent the costliness of such polymer calculations by developing analytical potential functions to fit a set of Hartree–Fock dimer energies.[6,7] Subsequently, Matsuoka, Clementi, and Yoshimine fit configuration interaction data.[10] Their function consists of a sum of functions $f(r_{ij})$, where each r_{ij} is the distance between a point i on one monomer and a point j on another. Their representation is not only simple enough to allow more adequate search of orientational parameters for polymers, but even Monte Carlo calculations on liquid water structure.[11]

The present paper reports the test of an alternative analytical model which includes a representation of the nonadditive contribution in quantum-mechanical calculations. Section II describes the model and the methods of calculation. Section III presents and discusses numerical results, and Sec. IV compares it with other analytical models.

II. PROPOSED MODEL

Classically, the interaction of discrete polarizable charge distributions is a cooperative problem. Therefore, the proposed model for the interaction energy of n molecules has the form

$$U(n) = U_p(n) + U_i(n) + U_d(n) + U_r(n), \tag{1a}$$

$$U_p(n) = \sum_{k=j+1}^{n} \sum_{j=1}^{n} U_p(j, k), \tag{1b}$$

where $U_p(j, k)$ is the electrostatic energy for the relative orientations of molecules j and k corresponding to the charge distributions of the isolated monomers, $U_i(n)$ the additional electrostatic energy arising from the induced molecular multipole moments; this is *not* given as a pairwise sum, $U_d(n)$ the dispersion contribution, and $U_r(n)$ the repulsion contribution.

The argument previously raised against the use of this classical contribution to the nonadditivity was based upon a point dipole approximation.[5(c)] Since this approximation has been shown to yield quantitatively and even qualitatively incorrect results (cf. Sec. IIIB), the argument is not applicable.

The first of the two tests of this model consists of a fit of Hartree–Fock energies of dimerization $U_{\mathrm{HF}}(2)$. Although preliminary calculations were performed on the dimer energies of Diercksen,[4] the 229 Hartree–Fock dimer points of Popkie, Kistenmacher, and Clementi[6] and of Kistenmacher, Lie, Popkie, and Clementi[7] with their more extensive angular variation were chosen for detailed analysis. Although in principle it would have been desirable to use the results of recent CI calculations,[10,12] two reasons made this impossible: (i) Whereas it was feasible to regenerate the HF solutions (*vide infra*), the regeneration of CI solutions would have been far more costly; (ii) the number of configurations required to represent the correlation has thus far prohibited CI water trimer calculations. Thus, there would have been no basis for testing the nonadditivity of the model.

The four terms in $U_{HF}(2)$ were computed as follows: (i) $U_p(2)$: Since the molecular orbital coefficients were not available, they were regenerated for the molecular geometry $(\langle x, y, z\rangle = \{\mathrm{O}: \langle 0, 0, 0\rangle, \mathrm{H}: \langle 1.1028459, \pm 1.4337993, 0\rangle$ a.u.,$\}$ 1 a.u. $= 0.529167$ Å$)$[13] using the Polyatom system of programs on the CDC 6600 at New York University. This gave a total energy of $-76.05525209 \pm 0.00000003$ a.u., which agrees with the published value -76.05525. $U_p(2)$ defined by this wavefunction was computed by a multipole expansion using the following sequence of new more efficient techniques: (a) The molecular electronic density was partitioned in that particular way which has been called a "very extreme split."[14] This transferred all overlap density to the O atom. (b) The procedure of Mezei and Campbell[15] was used to generate the multipole moments and characteristic directions. (c) $U_p(2)$ was calculated by method IV of Campbell and Mezei.[16] (ii) $U_i(2)$: The second order approximation used in the calculations reported here is characterized as follows: It includes induced dipole–permanent multipole and induced dipole–induced dipole contributions, but ignores the contributions of induced multipoles of orders ≥ 2. Thus, the energy retains only terms quadratic in the field components and ignores the contribution of the field gradients so that the ith component of the induced dipole vector is

$$\mu_{\mathrm{ind},i} = \Sigma_j \alpha_{ij} \mathbf{E}_j \,, \qquad (2)$$

where α_{ij} is the i, j element of the polarizability tensor, and $\mathbf{E}$ the electric field. Although there is debate[17] about the adequacy of various techniques used to calculate the α_{ij}, since the trace given by the α_{ii} calculated by Liebmann and Moskowitz[18] agrees to within ~0.7% with the experimental value, their α_{ii} have been used. The induced dipole vector components were obtained as the solutions of a set of simultaneous linear equations[19,20] modified for the case of molecules at random sites. The $U_i(2)$ was then calculated by the procedure of Mandel and Mazur.[21] (iii) $[U_d(2) + U_r(2)]$: Consider the difference between the energy of the dimer interaction $U(2)$ and the permanent and induced moment contributions

$$\Delta U(2) = U(2) - [U_p(2) + U_i(2)]. \qquad (3)$$

The proposed model interprets $\Delta U(2)$ as $[U_d(2) + U_r(2)]$. Since the Hartree–Fock formalism considers the interaction of each electron with the average field of the others, in this approximation

$$U(2) \cong U_{HF}(2); \quad \Delta U_{HF}(2) \cong U_r(2). \qquad (4)$$

The proposed model satisfies the following qualitative requirement posed by Eq. (4): Whereas $[U_{HF}(2) - U_p(2)]$ shows both positive and negative values in the set of 229 data points,[6,7] $\Delta U_{HF}(2)$ shows only positive values. In lieu of a good theoretical estimate of $\Delta U_{HF}(2)$, the latter was determined by a least squares fit of the data. One of the simplest choices for a spherically asymetric potential approximation to $\Delta U_{HF}(2)$ is a sum of functions

$$\Delta U_{AHF}(2) = \sum_{i,j,k} f_k(|\mathbf{r}^{\beta i} - \mathbf{r}^{\gamma j}|), \qquad (5)$$

where $\mathbf{r}^{\beta i}$, $\mathbf{r}^{\gamma j}$ are the positions of the nuclei i and j of dimers β and γ, respectively. In this test each f_k was chosen to be one of the conventional forms for which the least squares parameters appear linearly:

$$f_k(|\mathbf{r}^{\beta i} - \mathbf{r}^{\gamma j}|) = c(i, j, k)\,|\mathbf{r}^{\beta i} - \mathbf{r}^{\gamma j}|^{-n_k}, \qquad (6)$$

n_k fixed, and $c(i, j, k)$ are least squares parameters. Various choices of the n_k in the conventional range for such an empirical approximation $n_k \geq 9$ were considered.

The use of a scaling function for $[U_p(2) + U_i(2)]$ was also tested. Consider two charge distributions β and γ. Whereas the multipole series about two points P_β and P_γ converges if and only if β and γ are contained within nonoverlapping spheres centered at P_β and P_γ, Pack, Wang, and Rein[22] have shown that truncations of the multipole series can yield good approximations for regions of interest in intermolecular interaction. Since the minimum HF dimer energy occurs at O–O distances of about 3.0 Å, it seemed desirable to see whether a simple approximation such as Eq. (6) would be more accurate if $[U_p(2) + U_i(2)]$ were multiplied by Rahman and Stillinger's[2] scaling function which has continuous vanishing first derivatives at R_L and R_U:

$$S(r_{12}) \equiv \begin{cases} 0 \leq r_{12} \leq R_L, & 0, \\ R_L < r_{12} < R_U, & (r_{12} - R_L)^2 (3R_U - R_L - 2r_{12})/(R_U - R_L)^3, \\ R_U \leq r_{12}, & 1, \end{cases} \qquad (7)$$

where r_{12} is the distance between a point in molecule 1 and a point in molecule 2.

As a second test of this model, the nonadditive contribution to the interaction energy was calculated for the trimer orientations for which HF energies had been published either by Kistenmacher, Lie, Popkie, and Clementi[7] or by Hankins, Moskowitz, and Stillinger.[5] The HF nonadditive contribution for a set of n molecules is defined as the difference

$$U_{HF}(n, 2) \equiv U_{HF}(n) - \sum_{k=j+1}^{n} \sum_{j=1}^{n} U_{HF}(2, j, k), \qquad (8)$$

where $U_{HF}(2, j, k)$ is the HF interaction energy of molecules j and k in the absence of other molecules. Since the MO coefficients of the water wavefunction of Hankins, Moskowitz, and Stillinger[5] were not published, they too had to be regenerated. This gave a monomer energy of $-76.0413592355 \pm 0.0000000005$ a.u., in excellent agreement with the published value[5(a)] of

TABLE I. The errors of the different least squares fits.

Exponent set	Weighted standard relative deviation for $\Delta U_{AHF}(2)$	Standard deviation for $\Delta U_{AHF}(2)$ (i)	(ii)
{8, 12}	0.21	0.0022	0.00087
{9, 12}	0.19	0.0019	0.00093
{9, 13}	0.20	0.0020	0.00098
{9, 14}	0.20	0.0022	0.0010
{12, 15}	0.23	0.0035	0.0017
{9, 11, 13}	0.16	0.0012	0.00083
{9, 12, 15}	0.16	0.0012	0.00085

Legend: (a) The values quoted are in a.u.; (b) the results refer to the fit of all 229 data points of Refs. 6 and 7; (c) for the definition of the quantities listed see Eqs. (10) and (11); (d) column (i) is for the use of relative criterion of Eq. (10) for the minimization, column (ii) is for the use of the criterion of the minimization of the sum of the squares of deviations for $\Delta U_{AHF}(2)$.

−76.041361 a.u. According to the present model, the nonadditivity is approximated as the induced moment contribution

$$U_i(n) - \sum_{k=j+1}^{n} \sum_{j=1}^{n} U_i(2,j,k), \qquad (9)$$

where $U_i(2, j, k)$ is $U_i(2)$ for molecules j and k.

III. NUMERICAL RESULTS

A. The fit of the Hartree-Fock dimerization energies

As a guard against the error in $\Delta_{HF}(2)$ appearing magnified in $U_p(2)$ because of the least squares procedure, a multipole expansion of order 10 was used. The accuracy of the values $U_p(2)$ was estimated by examining increments $|U_p(2, m) - U_p(2, m-2)|$ for multipole expansions of different orders m. The estimated errors were at most ~0.01% at O–O distances greater than or equal to the near neighbor distances in ice and in almost all cases were less than 1%.

The criterion used to determine the $c(i, j, k)$ coefficients of Eq. (6) was the minimization of the weighted squares of the relative errors

$$\sum_q w_q \{[\Delta U_{HF}(2)_q - U_{AHF}(2)_q]/\Delta U_{HF}(2)_q\}^2. \qquad (10)$$

The choice of the weighting factors w_q was based on two considerations: (a) For sufficiently large distances $U_{HF}(2)$ approached its asymptotic form $[U_p(2) + U_i(2)]$; (b) the values for $U_{HF}(2)$ were quoted to 10^{-5} a.u. The w_q used were

$$|U_{HF}(2)|_q < 3\times10^{-5} \text{ a.u.}, \qquad w_q = 0.0,$$

$$3\times10^{-5} \le |U_{HF}(2)|_q \le 3\times10^{-4} \text{ a.u.}, \qquad w_q = 0.1,$$

$$|U_{HF}(2)|_q > 3\times10^{-4} \text{ a.u.}, \qquad w_q = 1.0. \qquad (11)$$

The results can be summarized as follows: (i) *Test of consistency of the calculated values of* $[U_p(2) + U_i(2)]$ *with the assumed wavefunction.* One advantage of the proposed potential, that it is asymptotically exact as the distance between the molecules increases, affords a simple consistency check of all steps from input through the permanent moment calculation. In all cases $[U_p(2) + U_i(2)]$ converged asymptotically and in those orientations for which sufficiently great distances (>≈ 5–6 Å) were available agreed with $U_{HF}(2)$ within the 10^{-5} a.u. accuracy of the published data. (ii) *Choice of the number of exponents in the set* $\{n_k\}$. According to the discussion of Sec. II, $[\Delta U_{AHF}(2)]_q$ is positive for each data point q. Nevertheless, when sets of three exponents were used, one of two results were obtained: (a) For some q, $[\Delta U_{AHF}(2)]_q$ showed negative values, which were very small compared to $[U_{HF}(2)]_q$; (b) Although $[\Delta U_{AHF}(2)]_q$ was positive for each q, the ratios of the coefficients in the potential function were such that the potential would surely become negative for smaller distances and it was by no means clear that negative values would not occur with more extensive orientational variation over the range of distances used. Thus, the further minimization of the sum of the square deviations by the introduction of a third exponent was introducing a correction for the angular dependence of $\Delta U_{HF}(2)$ at the cost of possible spurious local extreme values and the sacrifice of the qualitative consistency of its interpretation as $U_r(2)$. Such an improved angular representation could be more satisfactorily made by inclusion of surface spherical harmonics in the representation. Therefore, without such an extension, the choice should be limited to sets of two exponents. (iii) *Effect of a scaling function.* The introduction of a scaling function was tried for the following sets of the parameters in Eq. (7):

$$\langle R_L, R_U\rangle = \langle 4.3, 4.9\rangle \text{ or } \langle 3.8, 5.0\rangle \text{ a.u.} \qquad (12)$$

In each case the result was a significant increase in the standard deviation. Therefore, for this particular fit the scaling function should not be used. (iv) *Results of the least squares fits.* Although it is obvious that lower standard deviations could be obtained by using as a criterion the minimization of the sums of the squares of deviations (cf. Table I) rather than the sums of the squares of the relative deviations [cf. Eq. (10)], the latter was adopted since it seemed desirable to minimize the relative accuracy. The results of the fits are shown in Table I. The values for the coefficients for $\{n_1, n_2\} = \{9, 12\}$, which gave the lowest deviations, are

$$n_1 = 9:\ c(\text{H},\text{H},1) = -5.5284\times10^2;\ c(\text{H},0,1) = 9.8636\times10^2;\ c(0,0,1) = 2.5762\times10^3;$$

$$n_2 = 12:\ c(\text{H},\text{H},2) = 9.1906\times10^3;\ c(\text{H},0,2) = -1.2374\times10^4;\ c(0,0,2) = 4.5431\times10^5. \qquad (13)$$

It should be noted that although some coefficients are negative, their magnitudes compared to those of the other positive coefficients for the same n_i are small and, therefore, are unlikely to give rise to negative $\Delta U_{AHF}(2)$ values, even for orientations which were not sampled in the set of 229 points.

TABLE II. Comparison of the nonadditive trimer contributions of this model with the HF values.

				Trimer nonadditive contributions	
R(O–O)	Type	θ_{12}	θ_{23}	HF	This approximation
Data of Hankins, Moskowitz, and Stillinger[5(a),(b)]:					
2.76	Sequential	−54.7	−54.7	−0.942	−0.767
3.00	Sequential	−54.7	−54.7	−0.573	−0.378
3.15	Sequential	−54.7	−54.7	−0.442	−0.255
3.00	Sequential	+54.7	−54.7	−0.635	−0.439
2.76	Double donor	−54.7	−54.7	1.295	1.09
3.00	Double donor	−54.7	−54.7	0.606	0.595
3.15	Double donor	−54.7	−54.7	0.377	0.422
2.76	Double acceptor	−54.7	−54.7	0.767	1.26
2.90	Double acceptor	−54.7	−54.7	0.529	0.869
3.00	Double acceptor	−54.7	−54.7	0.372	0.677
3.15	Double acceptor	−54.7	−54.7	0.236	0.476
3.39	Double acceptor	−54.7	−54.7	0.102	0.282
3.00	Double acceptor	−54.7	−25.0	0.490	0.293
3.00	Double acceptor	−54.7	−70.0	0.364	0.854
Datum of Kistenmacher, Lie, Popkie, and Clementi[7a]:					
	Optimal closed trimer			−1.13	−1.12

Legend: (a) The oxygen–oxygen distances R(O–O) are in Å; (b) the type, θ_{12} and θ_{23} are defined by Ref. 5, Figs. 4–6; (c) the energies are in kcal/mole; (d) the contribution of the present model is computed by Eq. (9).

B. Calculations of nonadditivities

Only the dimer data of Popkie, Kistenmacher, and Clementi[6] together with that of Kistenmacher, Lie, Popkie, and Clementi[7] covered sufficiently extensive variation to permit the least squares determination of the parameters for a repulsive potential. The sensitivity of the HF interaction energies and electron densities to the basis set used denies the possibility of using the fit of one set of HF results for comparison with data from another. For the orientation they found to be optimal they obtained a HF trimerization energy of −0.02128 a.u. This compares with −0.01962 a.u. (error = +0.00266 a.u.) from their analytical two-body potential and −0.02157 a.u. (error = −0.00029 a.u.) from the present nonadditive approximation.[24]

Of course, the nonadditive contribution itself can be calculated according to Eq. (9) for different HF wavefunctions. The values have been collected in Table II for comparison with the HF data of Hankins, Moskowitz, and Stillinger[5] and of Kistenmacher, Lie, Popkie, and Clementi.[7] The induced dipole–permanent multipole approximation of this report has given a very good value for the optimal trimer orientation, a useful first approximation for the sequential and double donor orientations, and the correct sign but quantitatively poor representation for the double acceptor orientations. Thus, this approximation has given from very good to useful first approximations for the optimal trimer orientation and for those orientations that occur with probabilities of 4/6 (sequential) and 1/6 (double donor) in ice. The following arguments supports our contention that the inclusion of an improved approximation for induced dipoles and at least the first order induced quadrupole contribution can be expected to substantially reduce all discrepancies and that, therefore, the induced multipole model in this approximation will provide a useful interpretation of the nonadditivity: (i) Previous calculations on ice Ih[25] have shown that premature truncation of the permanent multipole expansions, which yields an inadequate representation of the molecular symmetry, gives serious errors whose magnitudes are strongly orientationally dependent. For example, whereas inclusion of higher order multipoles narrows the range of permanent multipole energies for different site orientations to approach agreement with the experimental observation that all orientations are approximately equally probable, the dipole approximation gives values at 0 °C ranging from 3.56 to 4.98 kcal/mole.[26] Also, calculations on a wavefunction of near HF accuracy[27] have confirmed previous qualitative conclusions and have yielded a dipole–dipole energy only about 30% of the total permanent multipole energy. New calculations of the induced dipole contribution once again introduced a spread in energies as a function of orientation.[27] This can be expected to be removed with an improved approximation to the molecular symmetry by higher order induced multipoles, just as in the case of the permanent multipole contribution. (ii) For the double donor and double acceptor orientations used by Hankins, Moskowitz, and Stillinger[5] the dipole contribution to the permanent multipole energy has a sign opposite to that of the total permanent multipole energy. Conversely, inclusion of all terms up to the order of quadrupole–quadrupole in a single center expansion[14] yields about 90% of the total. Thus, it is plausible to expect that an adequate approximation to the induced dipole and quadrupole should be required to obtain an adequate account of the induced energy. (iii) The calculations reported here in-

TABLE III. Effect of order on internal extrema as a function of ϕ, $0° \leq \phi \leq 180°$.

Type	R(O–O)		n_{max}				
			4	6	8	10	ΔE
1	2.72	ϕ_0	30.	30.	30.	30.	
		E_0	−0.2277E-2	−0.2636E-2	−0.2585E-2	−0.2593E-2	0.11E0
2		ϕ_0	60.				
		E_0	−0.2715	...	...	...	0.18E0
3		ϕ_0	150.	150.			
		E_0	0.9257E-2	0.9812E-2	...	...	0.17E-1
4		ϕ_0	150.				
		E_0	0.9883E-2	...	...	...	0.23E-1
1	3.00	ϕ_0	45.	45.	45.	45.	
		E_0	−0.6185E-2	−0.6258E-2	−0.6254E-2	−0.6246E-2	0.11E-0
2		ϕ_0	45.	45.	45.	45.	
		E_0	−0.6577E-2	−0.6836E-2	−0.6840E-2	−0.6834E-2	0.77E-1
3		ϕ_0	165.				
		E_0	0.6384	...	...	...	0.11E-1
4		ϕ_0					
		E_0	...	...	...	...	
1	3.40	ϕ_0	45.	45.	45.	45.	
		E_0	−0.5475E-2	−0.5501E-2	−0.5501E-2	−0.5498E-2	0.94E-1
2		ϕ_0	45.	45.	45.	45.	
		E_0	−0.5811E-2	−0.5927E-2	−0.5830E-2	−0.5829E-2	0.79E-1
3		ϕ					
		E_0	...	...	...	...	
4		ϕ_0					
		E_0	...	...	...	...	

Legend: (a) R(O–O): oxygen–oxygen distance in Å; (b) $E_0 = E(\phi_0)$ a.u., where $E = U_p(2) + U_i(2) + \Delta U_{AHF}(2)$; (c) ϕ_0: the ϕ_k for which $|E(\phi_k)| <$ both $|E(\phi_{k+1})|$ and $|E(\phi_{k-1})|$, where $\phi_k = k(15°)$, $0 \leq k \leq 12$; (d) n_{max}: the highest order used in the multipole expansions in the calculation of $U_p(2)$ in the $E(\phi_k)$; (e) the last column expresses the importance of the extremum in terms of the greater of the two relative variations $|[(E(\phi_0 - 15) - E(\phi_0)]/E(\phi_0)|$ and $|E(\phi_0 + 15) - E(\phi_0)]/E(\phi_0)|$; (f) the exponential convention:. 16E-4 = 1.6×10^{-5}.

clude only the uniform field contributions to the induced dipoles. Terms in the energy that involve both the field and its gradient[28] yield the first approximation to the induced quadrupole tensor and the next correction to the induced dipole. The double acceptor orientation type is both the type with the largest absolute field gradients and the only type for which the induced dipole energy in the uniform field approximation gives a quantitatively poor account of the induced energy. Thus, the agreement for the nonadditive contribution for the other orientation types also makes it plausible to assume that the induced multipole energy in this approximation will give an adequate account of the nonadditivity for the double acceptor orientation as well. A method which applies to nonuniform fields and extends the approximation to higher order induced moments is being developed.[29]

C. Choice of expansion order in applications

The computational effort and accuracy as a function of both order and expansion type has been analyzed in detail.[14] As a test of the appropriate choice of order for many practical applications the variation of the positions of local extreme values in the dimer energy with angles has been investigated as a function of order for the expansion called the "very extreme split," the type of greatest accuracy. This is viewed as a valid indication of the effect of order upon the practically important problems of determining preferred orientations in larger groups of molecules. In this test calculations were made for each of the four types of orientations used by Popkie, Kistenmacher, and Clementi[6] in their first 190 HF dimer calculations. For this set of calculations their O_1 was translated to the origin. The results are recorded in Table III. The column labeled ΔE for the relative deviations yields the following conclusions about the location of internal extreme values when the very extreme split is used: (i) $n_{max} = 6$ locates reasonably well the extrema at $R \gtrsim \sim 2.7$ Å, (ii) $n_{max} = 4$ locates them reasonably well at $R \gtrsim \sim 3$ Å. This also illustrates how the appropriate choice of order will decrease as the distance of separation increases.

IV. COMPARISON WITH OTHER MODELS; DISCUSSION OF RESULTS

The present model should be viewed as an extension of those which Stockmayer[30] (dipole, Lennard-Jones 6-12 potential) and Rowlinson[31] (dipole, zonal quadrupole, Lennard-Jones 6-12 potential) used in their analyses of second virial coefficient data. The necessity for this extension is established by the following two observations: (i) At distances important in condensed phases, single center multipole expansions including quadrupole-quadrupole and dipole–octupole contributions can give serious errors.[25] This is illustrated by recent calculations[14] based on one wavefunction used in this study[4] where errors in sign with significantly large absolute values are recorded. The significance of this assertion is as follows: The basic model makes no explicit mention of multipole moments but only of $U_p(n)$, the interaction energy of charge distributions corresponding to the densities of the isolated molecules (in this study approximated by wavefunctions of near HF accuracy). Although direct calculation of the integrals

$$\iint \rho(\mathbf{x}_\beta)\,\rho(\mathbf{x}_\gamma)/\left|\mathbf{x}_\beta-\mathbf{x}_\gamma\right| d\mathbf{x}_\beta d\mathbf{x}_\gamma \qquad (14)$$

is too costly for a large number of relative positions and orientations, multipole calculations can be executed much more economically even for the higher orders required to obtain satisfactory accuracy using a single center expansion. (ii) The data given in the following paragraph show that $U_i(2)$ makes an important contribution. Moreover, the results of Sec. IIIB indicate that the induced dipole interactions in the uniform field approximation can be used to provide a useful first approximation to the nonadditive energy.

At one of the orientations for which Popkie, Kistenmacher, and Clementi obtained their most negative dimer interaction energy [$R(O_1{-}O_2)=5.67$ a.u., $\alpha=30.0°$, $\beta=0.0°$ in Table I[6]] the relative contributions are $U_p(2)/U_{\mathrm{HF}}(2)=1.43$, $U_i(2)/U_{\mathrm{HF}}(2)=0.18$, and $U_r(2)/U_{\mathrm{HF}}(2)=0.62$. The importance of the induced contribution is illustrated by another orientation $R(O_1{-}O_2)=5.14$ a.u., $\phi=45.0°$ for type 1 in Table II of Ref. 6 for which $U_p(2)/U_{\mathrm{HF}}(2)=-0.98$, $U_i(2)/U_{\mathrm{HF}}(2)=-0.66$, and $U_r(2)/U_{\mathrm{HF}}(2)=2.63$. Three points should be stressed for the interpretation of these ratios: (i) $U_p(2)$ is what Coulson has called the electrostatic contribution in his discussion of the decomposition of the energy of the hydrogen bond.[32] (ii) As noted in Sec. II, $U_{\mathrm{HF}}(2)$ must be supplemented by a dispersion contribution before comparison with experimental data. (iii) As an indication of the quality of the electron density defined by this wavefunction, the calculated dipole moment of 0.8645 a.u. = 2.20 D compares with the experimental value of 1.8546 ± 0.0004 D[33] and the Neumann and Moskowitz[34] value of 1.995 D. The principal quadrupole moments in the units of 10^{26} esu cm^2 relative to the O atom of

$$Q_{xx}=-5.716, \quad Q_{yy}=-4.171, \quad Q_{zz}=-7.493$$

compare with the values of Neumann and Moskowitz[34] for their most extensive basis set of

$$Q_{xx}=-5.708, \quad Q_{yy}=-4.180, \quad Q_{zz}=-7.482.$$

The axes are those of Ref. 6.

Next, consider a comparison of the proposed model with an additive one developed by Clementi, Kistenmacher, Lie, and Popkie for an analytical fit of the same set of dimerization energies.[6,7] In addition to the inclusion of nonadditivity, the proposed model has two advantages: (i) Whereas the other authors observe that their analytical function should not be interpreted physically, the proposed model is based on a simple physical picture; (ii) the proposed model is asymptotically exact as the intermolecular separation increases. Conversely, the additive model[6,7] is computationally more efficient. However, the cost of application of the present model can be reduced by appropriate choice of the order of the multipole expansion (cf. Sec. IIIC).

The fits can also be compared with regard to accuracy over different ranges of the energy of interaction. First, inspection of their standard deviations σ for the 229 HF points[7(d)] (all points, $\sigma=0.0023$ a.u.; $E_{\mathrm{HF}}>5$ kcal/mole, $\sigma=0.0004$ a.u.; $E_{\mathrm{HF}}>0$, $\sigma=0.0002$ a.u.) shows that the attractive orientations must have been much more heavily weighted than the criterion used in this paper, relative accuracy. This means that their function should be expected to have the advantage of a better fit over the range of orientations and distances which are so heavily weighted. This conclusion was supported by our own calculations. On the other hand, the present function with its somewhat lower standard deviation for all points can be expected to be more accurate for some repulsive orientations, which occur, for example, in ice.

A third extremely important additive model is the analytical fit of 66 CI dimer energies by Matsuoka, Clementi, and Yoshimine.[10] Compared with the model developed in this paper it has the marked advantage for pair interactions of including some dispersion contributions which are omitted in the HF data used here.

Before application to experimental data the HF contributions included should be supplemented with an independent determination of the dispersion contribution. Ultimately, it would be desirable to extend the present model with its nonadditive contribution to such CI data.

Stillinger[35] (1970) proposed an important alternative approach to nonadditivity with his suggestion of an effective pair potential for nonadditive interactions. Ben-Naim and Stillinger and Rahman[36–39] developed and applied a revised model (ST2). The latter even yields good agreement with experimental values for the zeros of the O–O pair distribution function in liquid water, although the peaks show significant discrepancy in magnitude.[38(a)] In general, it has achieved impressive success in reproducing the properties of liquid water.

However, the work of several investigators has indicated limitations on the applicability of such effective pair potentials. For example, Present[40] has warned that an effective pair potential, which is consistent with experimental data for a many-body system but differs from the pair potential in a two-body system, has the limitation that the relation between the two depends upon which property is to be treated. Thus, it is questionable whether parameters in an effective pair potential selected to reproduce properties of one state involving an important nonadditive contribution (e.g., liquid water) will reproduce those of another state involving different orientations and, therefore, a different nonadditive contribution (e.g., surface states, solvation, etc.). Similarly, Rae's[41] calculations on HCN suggest that parameters adjusted for one bulk state of simple H-bonded systems will not reproduce the properties of smaller groups of molecules. Thus, parameters adjusted to give a good account of the structure of HCN(s) were not satisfactory for the dimer. Whereas the effective pair potential model has yielded extremely important results in the study of liquid water, the preceding discussion supports the conclusion that a model such as the present one with an explicit nonadditive contribution is preferable for applications to different states.

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