

Evaluation of the Dispersion Contribution to the Solvation Energy. A Simple Computational Model in the Continuum Approximation

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We present a simple computational method for the evaluation of solute-solvent dispersion energy contributions in dilute isotropic solutions, supplementing the method with an analysis of its sensitivity with respect to several parameters (or features of the solvation model) which are left free in the general formulation. The method is a natural complement of the electrostatic solvation procedure described in preceding articles.

I. INTRODUCTION

The elaboration of solvation models in the continuum approximation has been mainly addressed, in the last years, to improve the description of the electrostatic contribution to the solvation energy.¹⁻²¹ In fact the technical progress in the quantum mechanical description of molecular system has made possible the study of solvation effects also for solutes of complex internal structure (isolated in the solution or interacting) for which a realistic and detailed description of the electrostatic solvation energy is a necessary prerequisite. Dispersion energy contributions, which represent in some cases a sizable portion of the total solvation energy, generally are less critical, and for this reason perhaps the elaboration of new algorithms for this term lagged behind. The extension of the range of applicability of the more recent continuum models makes necessary however the consideration of the dispersion energy, computed with a method coherent with those employed for the others contributions. Most of the evaluation of dispersion energy contributions currently done are based on discrete models, where packing of the solvent molecules around the solute are estimated in more or less sophisticated ways, and the dispersion term is appreciated as a sum of separate contributions involving the solute (or some substructures inside it)

and a cluster of solvent molecules (or some substructures inside them). This method is not congruent with the philosophy of the continuum model approach, which is based on the use of averaged and continuous distributions of the solvent, represented by some experimental quantities (e.g., the dielectric constant). In this article we refer to a simple numerical method relying on the use of continuous distributions for the solvent. As in the electrostatic part of the method,^{7,13,16} of which the present is a supplement, we abandon the usual technique of volume integration, in favor of a direct numerical integration of an appropriate function over the cavity surface. In such a way the calculation of dispersion contributions becomes quite inexpensive because a part of the necessary calculations are in common with the electrostatic part. The solute-solvent dispersion energy is given in terms of atom-atom contributions, using for the solvent distribution a flexible expression of solute-solvent correlation functions. We think that this formulation is flexible enough to permit a subsequent elaboration for more complex condensed phase systems (e.g., solutions in presence of massive bodies, or solutions at finite concentrations). The formal expressions, and the numerical results will be limited here, however, to the simpler realization of the model.

Before entering into the details of the method, it is worthwhile to recall here another approach, congruent with the philosophy of the continuum model, which has been pioneered by Linder²² and recently extended by the Rivail group.^{23,24} According to this approach the dispersion energy is evaluated in terms of a fluctuating reaction field coupled to the instantaneous value of the solute charge distributions; Linder's article gives the formulas for the dipole component in a spherical cavity, Rivail et al.^{23,24} extend the approach to further terms in the multipolar expansion and introduces the method in an already working electrostatic energy package.² The use of the fluctuation reaction field in a formulation suitable for our procedure which avoids multipole expansions is at present under examination in a cognate laboratory.²⁵

OUTLINE OF THE METHOD

According to the atom-atom model, the dispersion energy between two molecules A and S , is written as:

$$E_{\text{disp}}(A, S) = - \sum_{n=6}^{\infty} \sum_{t \in S} \sum_{a \in A} d_{at}^{(n)} r_{at}^{-n} \quad (1)$$

where $d_{at}^{(n)}$ is the atom-atom dispersion coefficient of order n . It will be convenient, for practical applications, to discard in the following the contributions with $n > 6$. Extending the resulting simplified expression of $E_{\text{disp}}(A, S)$ to a solvation cluster, AS_m , we have:

$$E_{\text{disp}}(A, S_m) = - \sum_{S_i} \sum_{t \in S_i} \sum_{a \in A} d_{at}^{(6)} r_{at}^{-6} \quad (i = 1, m) \quad (2)$$

which can be extended to very large clusters, representative of a dilute solution of A in S .

In real solutions, the detailed description of the relative distances between the atoms of the solute and all the atoms of the solvent, may be replaced by distribution functions of the type:

$$\rho_{at}(r_{at}) = N_t \rho_s g_{at}(r_{at}) \quad (3)$$

where N_t is the number of atoms of type t for each molecule of the solvent, ρ_s is the macroscopic numeral density of the solvent and g_{at} is a correlation function, which has been here assumed to be dependent on the $a-t$ distance only. The use of a continuous function leads to

the substitution of the summation on S_i with an integral:

$$G_{\text{disp}}(A \text{ in } S) = - \sum_{t \in S} \sum_{a \in A} d_{at}^{(6)} N_t \rho_s \cdot \int_{C_t} d\mathbf{r}_{at} g_{at}(r_{at}) r_{at}^{-6} \quad (4)$$

and, making a change of variables: $\mathbf{r}_{at} = \mathbf{r}_t - \mathbf{r}_a$

$$G_{\text{disp}}(A \text{ in } S) = - \sum_{t \in S} \sum_{a \in A} d_{at}^{(6)} N_t \rho_s \cdot \int_{C_t} d\mathbf{r}_{at} g_{at}(r_{at}) r_{at}^{-6} \quad (5)$$

The replacement of a discrete distribution with a continuous distribution is a common practice in solution studies, and for dispersion energy contributions dates back as far as Hamaker:²⁶ the "realism" of the model, in specific application, will be done by the actual definition of ρ_{at} . The integrals in (4) exclude the portion of volume forbidden for atoms of the solvent of type t . The presence of a forbidden volume derives from the assumed presence of repulsion forces between atoms. The indication of different excluded volumes for different t introduces a further degree of freedom which will be exploited to make the model more realistic. The envelope of these volumes define the cavity containing the solute A . In a first approximation this cavity may be defined as the set of intersecting van der Waals spheres centered on the atoms (or groups) of A : with the approximation of using atom-atom interaction contributions, the van der Waals cavity must be enlarged to take into account also the van der Waals radii of the solvent atoms. We remark also that in Eq. (4) we have explicitly indicated that the computed quantity has the status of a free energy, the Gibbs free energy, or the Helmholtz free energy, according to the actual definition of ρ_{at} . To transform the volume integrals of Eq. (5) into surface integrals, we follow here a derivation done by Claverie, in a set of articles^{1,27,28} which represented a landmark in the evolution of models for solvent effects. Making use of the divergence theorem:

$$\begin{aligned} \int_{C_t} d\mathbf{r}_{at} F(\mathbf{r}_{at}) &= \int_{\Sigma_t} \mathbf{A}(\mathbf{r}_{at}) \cdot \mathbf{n}_{\Sigma_t} d\sigma \\ &+ \lim_{R \rightarrow \infty} \int_{S(R)} \mathbf{A}(\mathbf{r}_{at}) \cdot \mathbf{n}_S d\sigma \end{aligned} \quad (6)$$

where Σ_τ is the surface of the cavity related to the C_i volume, $S(R)$ is the surface of a sphere, centered in a , with radius R , \mathbf{n}_{Σ_τ} is a unit vector directed from the surface towards the interior of the cavity containing A , while the unit vector \mathbf{n}_S is directed towards larger R . $\mathbf{A}(\mathbf{r}_{at})$ in (6) satisfies the equation:

$$\nabla \cdot \mathbf{A}(\mathbf{r}_{at}) = F(r_{at}) \quad (7)$$

Assuming for $A(r_{at})$ the form:

$$\mathbf{A}(\mathbf{r}_{at}) = f(r_{at})\mathbf{r}_{at} \quad (8)$$

one has:

$$\nabla \cdot \mathbf{A}(\mathbf{r}_{at}) = r_{at}f(r_{at}) + 3f(r_{at}) \quad (9)$$

and

$$d[r_{at}^3 f(r_{at})] = r_{at}^2 F(r_{at}) dr_{at} \quad (10)$$

from which

$$\begin{aligned} f(r_{at}) &= (1/r_{at}^3) \int_{r_{at}^0}^{r_{at}} x^2 F(x) dx \\ &= (1/r_{at}^3) [I(r_{at}) - I(r_{at}^0)] \end{aligned} \quad (11)$$

and finally:

$$\mathbf{A}(\mathbf{r}_{at}) = \left[(1/r_{at}^3) \int_{r_{at}^0}^{r_{at}} x^2 F(x) dx \right] \mathbf{r}_{at} \quad (12)$$

The lower integration limit in (12) can be fixed in different ways, according to the boundaries of the specific system under investigation. For dilute isotropic solutions it is convenient to define it in such a way that the second integral of Eq. (6) goes to zero. To do this it is sufficient to impose that $g_{at}(r_{at}) \rightarrow 1$ as $r_{at} \rightarrow \infty$; this condition is congruent with the properties of solutions at infinite dilution. Using elementary calculus it is immediate to verify that this condition corresponds to put $r_{at}^0 = \infty$. We may thus use the following integral expression to compute the dispersion energy:

$$G_{\text{disp}}(A \text{ in } S) = - \sum_{t \in S} \sum_{a \in A} d_{at}^{(6)} N_t \rho_S \int_{\Sigma_t} \mathbf{A}(\mathbf{r}_{at}) \cdot \mathbf{n}_{\Sigma_t} d\sigma \quad (13)$$

with

$$\mathbf{A}(\mathbf{r}_{at}) = - \left[(1/r_{at}^3) \int_{r_{at}}^{\infty} g_{at}(x)/x^4 dx \right] \mathbf{r}_{at} \quad (14)$$

The surface integral of Eq. (13) is computed with the same technique employed for the electrostatic problem. In the last version of the program,¹⁶ the spheres centered on the

atoms a are approximated by a hierarchy of convex polyhedra, with geodetical notation $\{3, 5_+\}_{p,p}$.²⁹ The first member of the family, $\{3, 5_+\}_{1,1}$, is the pentakis dodecahedron, composed by 60 equivalent triangles, and it is used to define a set of points, the center of the triangles, where the integrand of Eq. (13) is computed. The following members of the $\{3, 5_+\}_{p,p}$ family, with $p = 2, 4, 8, \dots$, are used to set a better appreciation of the surface elements ΔS_k in the regions where the intersection of two or more atomic spheres occurs. The integral (13) is thus reduced to a discrete summation over a limited number of points k , with the integrand weighted by numerical factor given by the appropriate tesseral surface area

$$G_{\text{disp}}(A \text{ in } S) = \sum_{t \in S} \sum_{a \in A} d_{at}^{(6)} N_t \rho_S \sum_k \mathbf{A}(\mathbf{r}_{ak}) \cdot \mathbf{n}_{\Sigma_t} \Delta S_k \quad (15)$$

In the following the summation over k will be divided into contributions related to different atomic spheres, in the search of possible numerical simplifications. The integrands $\mathbf{A}_{at}(r_{at})$ of Eq. (13) are in general obtained by one-dimensional integrations Eq. (14). A noticeable portion of the physics of the model is contained in this term, through the expression of the dispersion energy (the selection we have made of using an atom-atom expansion interrupted at R^{-6}), the definition of the numerical values of the $d_{at}^{(6)}$ coefficients, the actual expression of $g_{at}(r_{at})$.

All these factors can be modified without altering the structure of the mathematical method. Other factors related to the modelling of the physical interaction are the limits for the C_i cavities, which are accounted for in Eq. (15): these factors too may be varied at some extent, in the search of a more realistic description. In the following section of the article we report some preliminary information about the influence of some of these factors on the numerical evaluation of G_{disp} . In future communications, at present under elaboration, the attention will be shifted to the consideration of other interaction terms (G_{rep}) which can be treated in a similar way, to the examination of the effects due to consideration of a boundary surface of the liquid, not too far from the spatial location of A , to the analysis of models containing two or

more solute molecules, with the aim of testing the capabilities and limits of this computational scheme on a wider range of physical situations.

NUMERICAL RESULTS

A very simple approximation of Eq. (15) can be obtained when one replaces the correlation functions, with a constant value:

$$g_{at}(r_{at}) \rightarrow 1 \quad (16)$$

The integration of (14) is in this approximation immediate. We shall make use of the approximation (16) in the following analyses.

The Shape of the Cavity

We report in Tables I, II, and III some values of G_{disp} (A in water) for the first members of the families of linear alkanes, alcohols, and amines computed with two models for the cavity. In all cases standard geometries and

linear conformations have been employed. The models present a progressive reduction of the numbers of spheres: model I has a sphere for each solute atom, model II a unique sphere for each CH_3 and CH_2 group, model III a unique sphere also OH and NH_2 groups. The cavities C_t are defined in terms of van der Waals radii, $R_w(A)$, incremented of a factor $\delta_t(a)$. The $R_w(A)$ values are in Table IV, the $\delta_t(a)$ contribution is equal to 1.385 Å (the mean H_2O radius) for all a and t in all the cases considered here. The dispersion coefficients used here are reported at the bottom of the tables. The data are analyzed under the form:

$$G_{\text{disp}}(\text{A in water}) = a + bn(\text{CH}_2) \quad (17)$$

and the numerical coefficients are reported in Table V, accompanied by the mean square deviation s and the correlation factor r . The data makes evident the superiority of the model II for alkanes: for this reason we have considered unnecessary to repeat the calcu-

Table I. Effect of changes in the shape of the cavity: *n*-alkanes in water.

Solute	Model I			Model II ^d		
	G_{disp}^a	TCA ^b	TCV ^c	G_{disp}	TCA	TCV
CH_4	-4.72	140.900	152.086	-4.50	143.988	162.467
C_2H_6	-7.33	174.448	206.734	-6.77	176.610	217.185
C_3H_8	-8.71	210.384	265.136	-8.72	205.718	268.208
C_4H_{10}	-10.50	241.790	318.774	-10.59	234.337	318.652
C_5H_{12}	-12.33	269.464	366.777	-12.38	263.313	369.618
C_6H_{14}	-13.96	303.711	424.763	-14.31	292.289	420.646
C_7H_{16}	-15.69	333.630	476.142	-16.16	320.927	471.008
C_8H_{18}	-17.24	366.077	531.477	-17.98	349.884	522.117

^ain kcal/mol.

^bin Å².

^cin Å³.

^dThe dispersion coefficients used are reported in Table XX (set 1): $d_{\text{CC}}^{(6)} = 39.1$ a.u., $d_{\text{HH}}^{(6)} = 1.8$ a.u., $d_{\text{CH}}^{(6)} = (d_{\text{CC}}^{(6)}d_{\text{HH}}^{(6)})^{1/2}$.

Table II. Effect of changes in the shape of the cavity: *n*-alcohols in water.

Solute	Model II			Model III ^d		
	G_{disp}^a	TCA ^b	TCV ^c	G_{disp}	TCA	TCV
CH_3OH	-5.67	160.76	187.72	-5.55	163.13	192.93
$\text{C}_2\text{H}_5\text{OH}$	-7.79	192.72	241.90	-7.66	193.81	245.77
$\text{C}_3\text{H}_7\text{OH}$	-9.72	221.31	291.96	-9.55	222.73	296.72
$\text{C}_4\text{H}_9\text{OH}$	-11.55	250.09	342.79	-11.43	251.44	347.23
$\text{C}_5\text{H}_{11}\text{OH}$	-13.31	279.06	393.76	-13.18	280.42	398.20
$\text{C}_6\text{H}_{13}\text{OH}$	-15.28	308.21	444.82	-15.15	308.30	449.14

^ain kcal/mol.

^bin Å².

^cin Å³.

^dThe dispersion coefficients used are reported in Table XX (set 1) $d_{\text{CC}}^{(6)} = 39.1$ a.u., $d_{\text{HH}}^{(6)} = 1.8$ a.u., $d_{\text{OO}}^{(6)} = 15.3$ a.u.

Table III. Effect of changes in the shape of the cavity: *n*-amines in water.

Solute	Model II			Model III ^d		
	G_{disp}^a	TCA ^b	TCV ^c	G_{disp}	TCA	TCV
CH ₃ NH ₂	-6.31	168.98	200.66	-6.25	168.67	202.80
C ₂ H ₅ NH ₂	-8.32	199.42	253.59	-8.27	198.70	254.97
C ₃ H ₇ NH ₂	-10.22	228.22	304.30	-10.16	227.52	305.71
C ₄ H ₉ NH ₂	-12.09	257.28	355.32	-12.03	256.58	356.73
C ₅ H ₁₁ NH ₂	-13.95	277.15	390.35	-13.89	276.45	391.76
C ₆ H ₁₃ NH ₂	-15.76	305.63	439.01	-15.53	302.14	437.59

^ain kcal/mol.^bin Å².^cin Å³.^dThe dispersion coefficients are reported in Table XX (set 1).**Table IV.** van der Waals radii in Å.

<i>a</i>	$R_w(a)$
C	1.60
H	1.20
O	1.40
N	1.50
CH ₃	2.00
CH ₂	2.00
OH	1.70
NH ₂	1.85

lation with model I for alcohols and amines. Also the reduction of the asymmetric OH and NH₂ groups to a unique sphere seems to be an acceptable approximation. Obviously the reduction in the number of spheres makes the calculations easier for larger molecular systems. In Tables I–III we have also reported the total surface and volume of the cavity (TCS and TCV respectively). There has been

a long discussion in the literature about the connection of these geometrical parameters with thermodynamical quantities (see e.g., references 3, 30–33) but the present set of results is too limited and homogeneous to make possible a discussion on this subject. The TCS and TCV data are here employed as supplementary indexes for the assessment of the validity of our reduction of the number of spheres in the definition of the cavity. The data for regression analysis, with formulas similar to Eq. (17) are reported in Tables VI and VII. In passing from model I to model III (we remark that for alkanes models II and III coincide) there is a better correlation between G_{disp} and TCS or TCV. The numerical correlations, expressed under the form:

$$G_{\text{disp}}(A \text{ in } S) = c + dX \quad X = \text{TCS or TCV} \quad (18)$$

Table V. Parameters of regression analysis: $G_{\text{disp}} = a + bn(\text{CH}_2)$.

	<i>n</i> -alkanes		<i>n</i> -alcohols		<i>n</i> -amines	
	I	II	II	III	II	III
<i>a</i>	-7.20	-6.82	-5.81	-5.67	-6.39	-6.39
<i>b</i>	-1.68	-1.86	-1.90	-1.90	-1.89	-1.86
<i>s</i>	0.12	0.04	0.11	0.10	0.07	0.10
<i>r</i>	0.99960	0.99996	0.99960	0.99970	0.99986	0.99960

Table VI. Parameters of regression analysis $\text{TCS} = a + bn(\text{CH}_2)$.

	<i>n</i> -alkanes		<i>n</i> -alcohols		<i>n</i> -amines	
	I	II	II	III	II	III
<i>a</i>	176.62	176.61	162.14	164.18	171.91	171.90
<i>b</i>	31.55	28.86	29.29	28.98	27.01	26.57
<i>s</i>	1.92	0.11	1.02	0.82	3.26	3.57
<i>r</i>	0.99967	0.99999	0.99986	0.99991	0.99834	0.99794

Table VII. Parameters regression analysis: $TCV = a + bn(CH_2)$.

	<i>n</i> -alkanes		<i>n</i> -alcohols		<i>n</i> -amines	
	I	II	II	III	II	III
<i>a</i>	209.02	217.23	189.16	193.89	205.80	208.12
<i>b</i>	53.65	50.80	51.20	51.11	47.23	46.72
<i>s</i>	2.47	0.19	1.09	0.71	5.75	6.01
<i>r</i>	0.99981	0.99999	0.99995	0.99998	0.99831	0.99811

Table VIII. Parameters of regression analysis: $G_{disp} = c + dTCS$.

	<i>n</i> -alkanes		<i>n</i> -alcohols		<i>n</i> -amines	
	I	II	II	III	II	III
<i>c</i>	2.68	4.77	4.70	5.08	5.56	5.64
<i>d</i>	-0.55	-0.06	-0.06	-0.06	-0.07	-0.07
<i>s</i>	0.26	0.07	0.06	0.07	0.19	0.19
<i>r</i>	0.99838	0.99989	0.99987	0.99983	0.99888	0.99886

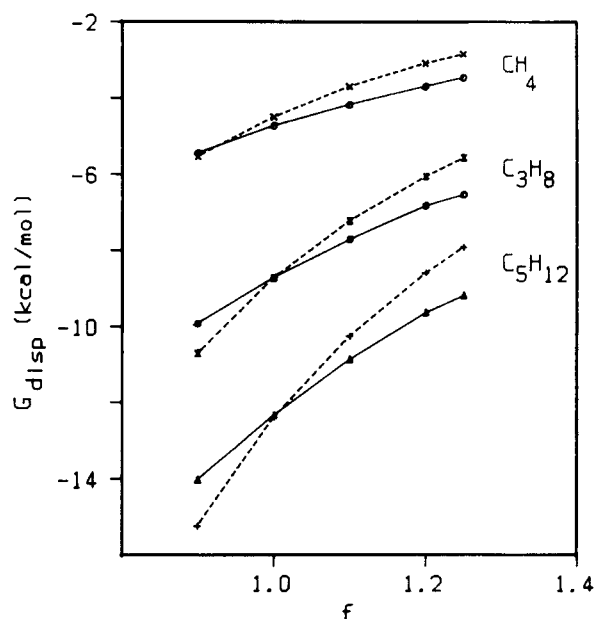
Table IX. Parameters of regression analysis: $G_{disp} = c + dTCV$.

	<i>n</i> -alkanes		<i>n</i> -alcohols		<i>n</i> -amines	
	I	II	II	III	II	III
<i>c</i>	-0.19	1.37	1.21	1.53	1.79	1.89
<i>d</i>	-0.03	-0.04	-0.04	-0.04	-0.04	-0.04
<i>s</i>	0.27	0.10	0.08	0.08	0.19	0.18
<i>r</i>	0.99823	0.99979	0.99978	0.99980	0.99888	0.99892

are compared in Tables VIII and IX for the different cavity models. A further test on the influence of the shape of the cavity may be obtained by introducing a factor f which alters the value of the R_w values used in the definition of the cavity. A multiplicative factor of this kind is often employed in the evaluation of the electrostatic contribution of the solvation energy, but it is here introduced for the limited purpose of assessing the influence of the cavity shape on G_{disp} . The results for the alkanes in water (models I and II) are graphically compared in Figure 1. A contraction or an expansion of the cavity volume produces a larger deviation of the results obtained with the two models, with respect to the canonical value $f = 1$.

Truncated Summations

The internal sum of Eq. (15) runs over all the tesseras of the molecular surface. It may be divided into partial contributions, each referred to a different sphere. For a given atom a , contributions of k elements belonging to distant spheres should be small. A

**Figure 1.** Values of G_{disp} for selected alkanes in water obtained by altering the radii defining the cavity by a multiplicative factor: $R(a) = fR_w(a)$. Continuous line: model I, interrupted line: model II (see the text for the definition of these cavity models).

truncated summation, neglecting distant contributions, should be of benefit for calculations in large molecules. In Table X we

Table X. Effect of truncation in the surface contributions: *n*-alkanes in water.

Solute	T_1	Percent	T_2	Percent	T_3	Percent	T_4	Percent	T_5	Percent	T_6	Percent	T_7	Percent
CH ₄	-4.50	100	—	—	—	—	—	—	—	—	—	—	—	—
C ₂ H ₆	-5.38	79.4	-6.77	100	—	—	—	—	—	—	—	—	—	—
C ₃ H ₈	-6.24	71.5	-8.07	92.5	-8.72	100	—	—	—	—	—	—	—	—
C ₄ H ₁₀	-7.14	67.4	-9.36	88.4	-10.42	98.3	-10.59	100	—	—	—	—	—	—
C ₅ H ₁₂	-7.91	63.8	-10.63	85.8	-12.08	97.5	-12.32	99.5	-12.38	100	—	—	—	—
C ₆ H ₁₄	-8.92	62.3	-11.98	83.7	-13.86	96.8	-14.16	98.9	-14.26	99.6	-14.31	100	—	—
C ₇ H ₁₆	-9.87	61.1	-13.23	81.9	-15.51	96.0	-15.79	97.7	-15.87	98.2	-15.91	98.5	-16.16	100
C ₈ H ₁₈	-10.72	59.6	-14.56	81.0	-17.26	96.0	-17.72	98.5	-17.83	99.2	-17.86	99.3	-17.87	99.4

consider again the *n*-alkanes in linear all-trans conformation in water, introducing truncation in the sum over *k*. In column T_1 the summation is limited, for all *a*, to tesseras belonging to its own sphere only, in column T_2 also the first neighboring spheres are considered, in column T_3 the first and second neighbors are considered, etc. The same analysis is repeated in Tables XI and XII for linear *n*-alcohols and *n*-primary amines. The data of these Tables show that approximation T_3 is sufficient for linear compounds, and that T_2 gives resonable trends. For non-linear conformations it is necessary to restate this approximation in terms of the distance between the center of the spheres. Approximation T_3 defined above corresponds to a cutoff in the *k* summation of the order of 3.50 Å. Table XIII reports averaged values for randomly selected configurations of *n*-decane with varying values of the cutoff. A cutoff of 3.50 Å gives around 95% of the whole dispersion energy, with variations confined in a range of the 1.4% of total value. In the following sections we shall not

make use of the cutoff procedure which seems however safe enough for general application.

Partition of G_{disp} over Group Contributions and Effect of Truncation in their Evaluation

The partition of G_{disp} into solute group contributions is easily evaluated by dividing the summation over *a* in Eq. (15) into group contributions. The contribution due to each group can be subjected to truncation, as examined in the previous section. Some data concerning the CH_3 group are reported in Table XIV. The first column, headed G_{disp} , reports the methyl contribution over the complete solute cavity, the following columns the per cent value for truncations T_1, T_2, T_3 defined earlier. The group contribution decreases with the increase of the size of the solute, as reasonable: in fact the addition of each CH_2 group, induces the replacement in a small, but sizeable, portion of space of the solvent, which contributes to G_{disp} , with an intramolecular group which gives no contributions. A limiting value for $G_{\text{disp}}(\text{CH}_3)$ is

Table XI. Effect of truncation in the surface contributions: *n*-alcohols in water.

Solute	T_1	Percent	T_2	Percent	T_3	Percent	T_4	Percent	T_5	Percent	T_6	Percent
CH_3OH	-4.50	79.4	-5.67	100	—	—	—	—	—	—	—	—
$\text{C}_2\text{H}_5\text{OH}$	-5.50	70.6	-6.97	89.4	-7.79	100	—	—	—	—	—	—
$\text{C}_3\text{H}_7\text{OH}$	-6.42	66.0	-8.71	89.4	-9.64	99.2	-9.71	100	—	—	—	—
$\text{C}_4\text{H}_9\text{OH}$	-7.29	63.1	-10.12	87.6	-11.30	97.8	-11.49	99.5	-11.55	100	—	—
$\text{C}_5\text{H}_{11}\text{OH}$	-7.99	60.0	-11.21	84.2	-12.91	97.0	-13.21	99.2	-13.29	99.8	-13.31	100
$\text{C}_6\text{H}_{13}\text{OH}$	-9.08	59.4	-12.60	82.4	-14.65	96.5	-15.10	98.8	-15.25	99.8	-15.27	99.9

Table XII. Effect of truncation in the surface contributions: *n*-amines in water.

Solute	T_1	Percent	T_2	Percent	T_3	Percent	T_4	Percent	T_5	Percent	T_6	Percent
CH_3NH_2	-4.87	77.9	-6.25	100	—	—	—	—	—	—	—	—
$\text{C}_2\text{H}_5\text{NH}_2$	-5.85	70.7	-7.72	93.3	-8.27	100	—	—	—	—	—	—
$\text{C}_3\text{H}_7\text{NH}_2$	-6.74	66.3	-9.02	88.8	-10.02	98.6	-10.16	100	—	—	—	—
$\text{C}_4\text{H}_9\text{NH}_2$	-7.64	63.5	-10.29	85.5	-11.73	97.5	-11.96	99.4	-12.03	100	—	—
$\text{C}_5\text{H}_{11}\text{NH}_2$	-8.26	59.5	-11.33	81.6	-13.35	96.1	-13.81	99.4	-13.87	99.8	-13.89	100
$\text{C}_6\text{H}_{13}\text{NH}_2$	-9.02	58.1	-12.44	80.1	-14.83	95.5	-15.26	98.3	-15.41	99.2	-15.44	99.4

Table XIII. Percent of G_{disp} recovered with different values of the cutoff of *R* in a set of *n*-decane conformations.

	E_1	E_2	E_3	E_4	E_5
Cutoff <i>R</i> (Å)	1.10	2.17	3.50	4.70	6.00
Mean value	48.7	79.3	94.6	98.6	99.6
Max value	56.9	80.2	95.0	99.0	99.8
Min value	43.6	78.5	93.9	98.2	99.4
Standard deviation	5.61	0.57	0.64	0.29	0.13

Table XIV. Contribution of the CH₃ group to G_{disp} and effect of truncation in its evaluation.

Solute	G_{disp} (CH ₃ , H ₂ O)	T_1 (%)	T_2 (%)	T_3 (%)	T_4 (%)	T_5 (%)	T_6 (%)
C ₂ H ₆	-3.39 ^a	79.0	100	—	—	—	—
C ₃ H ₈	-3.14	77.6	89.8	100	—	—	—
C ₄ H ₁₀	-3.10	78.7	89.9	97.3	100	—	—
C ₅ H ₁₂	-3.05	78.0	90.8	97.4	99.0	100	—
C ₆ H ₁₄	-3.09	78.9	90.6	97.3	98.6	99.7	100
C ₇ H ₁₆	-3.09	79.9	90.6	97.4	98.7	99.3	99.7
C ₈ H ₁₈	-3.08	79.2	90.9	97.7	99.0	99.6	99.8
CH ₃ OH	-3.63	86.7	100	—	—	—	—
C ₂ H ₅ OH	-3.30	79.4	89.8	100	—	—	—
C ₃ H ₇ OH	-3.12	78.1	90.0	98.6	100	—	—
C ₄ H ₉ OH	-3.10	78.9	89.9	97.7	99.3	100	—
C ₅ H ₁₁ OH	-3.09	78.9	90.6	97.0	98.6	99.6	100
C ₆ H ₁₃ OH	-3.09	78.9	90.6	97.0	98.6	99.2	99.5
CH ₃ NH ₂	-3.49	80.2	100	—	—	—	—
C ₂ H ₅ NH ₂	-3.19	78.0	91.0	100	—	—	—
C ₃ H ₇ NH ₂	-3.11	78.1	90.0	97.4	100	—	—
C ₄ H ₉ NH ₂	-3.09	78.6	90.0	97.1	98.7	100	—
C ₅ H ₁₁ NH ₂	-3.10	78.9	89.7	96.8	98.4	99.9	100
C ₆ H ₁₃ NH ₂	-3.00	79.3	91.0	97.0	98.3	99.3	99.9

^aThe values of the group contributions are given in kcal/mol.

reached when $R = n\text{-C}_5\text{H}_{11}$: $G_{\text{disp}}(\text{CH}_3) = -3.09$ kcal/mol. The effect of the truncation is similar to that analyzed for the whole molecular contribution in the preceding subsection: the T_3 approximation is sufficient, but also the T_2 may be employed in large scale calculations.

We do not report a table of numerical values for a similar analysis performed over the other two terminal groups: OH and NH₂. The trends are similar to those shown for CH₃: the limiting values are $G_{\text{disp}}(\text{OH}) = -1.86$ kcal/mol and $G_{\text{disp}}(\text{NH}_2) = -2.51$ kcal/mol. The contribution of the CH₂ group depends on the position the methylene had in the chain, which a mean limiting value is $G_{\text{disp}}(\text{CH}_2) = -2.00$ kcal/mol. The largest absolute value is that of the CH₂ group immediately near to the terminal OH, with a limiting value equal to -2.30 kcal/mol.

Changes in the Cavity Radii According to the Chemical Nature of the Components

As reported earlier, this method allows a more realistic description of the solute cavity by introducing for each type t of solvent atoms

an appropriate additive contribution $\delta_t(a)$ to the van der Waals radii for the solute atoms a : $R_w(a)$. The $\delta_t(a)$ contributions may be different for different a 's. In the preceding sections we have employed a simpler model, with a constant additive contribution $\delta_t(a)$ for all t 's and all a 's. In this section we give some examples regarding the numerical effect of the use of this feature of the method. A realistic definition of the C_t envelope—say, of the $\delta_t(a)$ contributions—requires an accurate knowledge of the whole interaction potential: when this information is lacking, approximate models can be selected, as done here, on the basis of physical plausibility. Let us consider as first example an aliphatic hydrocarbon as solvent. It is reasonable to assume that for the envelopes C_C and C_H (there are only two t types) the increment δ_t is independent from a :

$$\text{C}_C: R_C(a) = R_w(a) + \delta_C \quad (19)$$

$$\text{C}_H: R_H(a) = R_w(a) + \delta_H \quad (20)$$

For the δ_t increments we have followed the two expressions given in Table XV under the captions model A and model B. In both cases we have used the van der Waals value

Table XV. Definition of some models for the solute envelopes C_t in hydrocarbon solutions.

C_t	Model A	Model B	Model C
C _C	$R_w(a) + R_w(\text{CH}_2)$	$R_w(a) + R_w(\text{CH}_2)$	$R_w(a) + R_w(\text{C})$
C _H	$R_w(a) + R_w(\text{H})$	$R_w(a) + R_w(\text{CH}_2) - R_{\text{C-H}}$	$R_w(a) + R_w(\text{H})$

for the CH_2 group ($R_w(\text{CH}_2) = 2.0 \text{ \AA}$) for C_C and we have selected for C_H the van der Waals value for H ($R_w(\text{H}) = 1.2 \text{ \AA}$) or the difference between $R_w(\text{CH}_2)$ and the covalent distance $R_{\text{C-H}}$. In solvents like benzene, one could take into account the shape of the solvent molecules, which makes possible the contact of the solute with the peripheral H atoms or with the carbon ring; for this reason we have selected a third set of δ_i values, reported as model C in Table XV. We report in Table XVI few numerical values obtained with these cavity models: in all cases each solute group is represented by a unique sphere (model III). The difference in comparisons of the values obtained with models A and B in cyclohexane may be considered as a probe of the uncertainties related to the use of intuitive and grossly averaged quantities as are the van der Waals radii: in cyclohexane, model C is not supported by intuitive considerations, and the corresponding values may be taken as a measure of the effect of excessive variations in the cavity shape. Similar considerations may be put forward for the values related to benzene as solvent: model C seems, in this case, more supported by intuitive considerations. The definition of the C_t envelope for water as solvent is more complex, because one has to consider local effects, favoring, according to the nature of the solute chemical group of interest, a different preferential orientation of water in the immediate surroundings. The model we

have employed for water as solvent in the preceding section (called here W model, for brevity) does not seem excessively unrealistic. In the hydrophobic portions of the solute molecules the possibility of approach of the OH bond or the O lone pairs is almost equivalent, and so is justified to use an "isotropic" δ_i contribution ($\delta_\text{O}(a) = \delta_\text{H}(a)$). In the polar groups, OH and NH_2 , the isotropy of the approach is no longer acceptable, and the use of isotropic δ_i contributions represents a sort of average over the sphere of the polar group. (Note that the electric field gradient over the surface of this sphere has opposite signs in regions near the XH bond on X lone pair). For other polar groups (like ethers or carbonyls) such anisotropy is easily introduced.

The Effect of Numerical Value of the Atom-Atom Dispersion Coefficients

There are many proposals in the literature of atom-atom dispersion coefficients. Without entering, for the moment, into the discussion of what are the most suited for numerical approximations, we report in Tables XVII, XVIII, and XIX a few numerical values to show how the G_{disp} values depend from these parameters. The set of numerical values we have chosen are reported in Table XX. The calculations are performed with the approximation II (section 3.1) and the C_t models W, for water solutions, A for cyclohexane solutions, and C

Table XVI. Comparison of G_{disp} values for selected solutes in two hydrocarbon solvents computed with different models for the cavity.

Solvent solute	Cyclohexane			Benzene		
	Model A	Model B	Model C	Model A	Model B	Model C
C_3H_8	-9.02	-10.71	-10.01	-8.39	-9.41	-9.59
$\text{C}_2\text{H}_5\text{OH}$	-8.04	-9.55	-8.39	-7.46	-8.38	-8.55
$\text{C}_2\text{H}_5\text{NH}_2$	-8.60	-10.18	-9.56	-7.94	-8.93	-9.15

Table XVII. Comparison of G_{disp} values for selected solutes in water for model W of the cavity with different sets of dispersion coefficients.^a

Solute	Set 1 G_{disp}	Set 2 G_{disp}	Set 3 G_{disp}	Set 4 G_{disp}	Set 5 G_{disp}
C_3H_8	-8.72	-7.23	-8.00	-9.20	-9.38
$\text{C}_2\text{H}_5\text{OH}$	-7.79	-6.82	-7.08	-8.12	-8.61
$\text{C}_2\text{H}_5\text{NH}_2$	-8.32	-7.38	-7.81	-8.71	-8.86

^ain kcal/mol.

Table XVIII. Comparison of G_{disp} values for selected solutes in cyclohexane for model A of the cavity with different sets of dispersion coefficients.^a

Solute	Set 1 G_{disp}	Set 2 G_{disp}	Set 3 G_{disp}	Set 4 G_{disp}	Set 5 G_{disp}	Set 6 G_{disp}	Set 7 G_{disp}
C ₃ H ₈	-9.02	-7.63	-8.07	-9.38	-8.62	-9.71	-11.27
C ₂ H ₅ OH	-8.04	-7.13	-7.13	-8.26	-7.90	—	—
C ₂ H ₅ NH ₂	-8.60	-7.70	-7.86	-8.85	-8.12	-9.93	-11.05

^ain kcal/mol.**Table XIX.** Comparison of G_{disp} values for selected solutes in benzene for model C of the cavity with different sets of dispersion coefficients.^a

Solute	Set 1 G_{disp}	Set 2 G_{disp}	Set 3 G_{disp}	Set 4 G_{disp}	Set 5 G_{disp}	Set 6 G_{disp}	Set 7 G_{disp}
C ₃ H ₈	-9.59	-8.13	-7.79	-8.97	-8.79	-10.28	-11.34
C ₂ H ₅ OH	-8.55	-7.60	-6.89	-7.91	-8.06	—	—
C ₂ H ₅ NH ₂	-9.15	-8.21	-7.59	-8.47	-8.29	-10.53	-11.14

^ain kcal/mol.**Table XX.** Dispersion coefficients in a.u.

Set	Author	d_{HH}	$d_{\text{CC}}^{(6)}$	$d_{\text{NN}}^{(6)}$	$d_{\text{OO}}^{(6)}$	$d_{\text{CH}_3\text{CH}_3}^{(6)}$	$d_{\text{CH}_2\text{CH}_2}^{(6)}$
1	Huiszoon, Mulder ^a	1.8	39.1	26.2	15.3	—	—
2	derived from set 1	1.8	39.1	26.2	15.3	105.64	79.86
3	Kang, Jhon ⁴¹	2.55	20.74	21.54	10.20	—	—
4	Kitaygorodski ^{34b}	2.97	24.03	16.71	11.34	—	—
5	Mirsky ^{37c}	2.11	30.61	18.83	18.86	—	—
6	Williams, ³⁵ Govers ³⁶	1.98	41.29	55.25	—	—	—
7	Huiszoon, Mulder ^{38, 39d}	2.91	36.66	37.80	—	—	—

^aImproved set of values, communicated by W. A. Sokalski.^bValues taken from Claverie et al.^{27, 28}^cValues quoted by Gavezzotti.⁴⁰^dCoefficients obtained from studies on azabenzene compounds.

for benzene solutions. The range of values for a given system is relatively large: in some cases this range reaches the 40% of the mean value for the set of dispersion coefficients we have employed. Some regularities are however evident: in all solvent the dispersion energies are ordered in this way: C₃H₈ > C₂H₅NH₂ > C₂H₅OH and for each solute the ordering of the solvents is the following: benzene > cyclohexane > water.

CONCLUSIONS

In this article we have presented a simple numerical method to compute dispersion contributions to the solvation energy. The exposition has been centered on the flexibility of the method, able to be adapted to different realizations of the model for the

system, and on the effects that such modifications, or the selection of the input parameters, have on the final values. The model has been purposely kept to a low level of "realism."

In particular an analysis has not been attempted of the results obtainable making use of realistic solute-solvent pair correlation function derived from experiment or from computer solvent simulations. Such analysis will be done in a forthcoming article. No attention has been paid to the "correctness" of the final values. The dispersion energy contributions is not a physical observable which can be singled out from experimental data, and assessments on the "correctness" of the results must consider all the components of the solvation energy. It is a more complex task that will be attempted in another occasion.

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