Positive and negative domains of vertex-angle space for three-body contributions of several lower order dispersion multipoles

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Positive and negative domains of vertex-angle space of the spherical harmonics for the three-body contributions of five lower order dispersion multipoles have been determined and are shown in figures. Procedures, which use the figures to determine the sign of the three-body contribution for bodies which form a triangle with specified vertex angles, are given. No calculation is required.

1. Introduction

In the interpretation of the dispersion component of the interaction energy, it is useful to know the sign of any omitted nonadditive contributions. This paper considers the three-body multipolar dispersion contribution for five of the lowest order spherical harmonics. Suppose the three bodies form a triangle with specified vertex angles. For two of the five contributions, one determines whether the contribution vanishes or is positive (or negative) for an arbitrary triangle by locating one point in its figure. For the other three contributions, one can determine whether the contribution is positive or is negative in a useful fraction of all triangles by simply locating three points in its figure. The five figures used show the complete set of nodal curves which divide the space of two of the three vertex angles into domains in which the contribution is positive and domains in which it is negative. The results are valid for spherical atoms and are reasonable approximations for molecules of the regular tetrahedral point group T_d and the regular octahedral point group O_h.

† It is with deep sorrow that I report that my colleague, Dr. David Belford, passed away before this work had been completed.

2. Methods used to determine the nodal curves and the signs of the domains

Axilrod and Teller [1] and Muto [2] derived the equation for the leading term in the multipolar expansion for the three-body dispersion contribution for spherical atoms and approximately spherically molecules. Their result for the leading long-range three-body dispersion contribution, U^3, in the third perturbation order has been extended to higher order multipoles by Bell [3]. He derived general equations, which he first simplified by an appropriate choice of coordinate frame and then gave explicit equations for three additional lower order multipoles in the following convenient form. Let

$o(k)$: the order of the kth spherical harmonic, $k = 1, 2, 3$; (1a)

$\theta(k)$: the vertex angle of the kth spherical harmonic, $k = 1, 2, 3$; (1b)

R_{hj}: the distance between the expansion centers of the hth and jth spherical harmonics. (1c)

Then for a given choice of the interacting species,

$$U^3(o(k), \theta(k), R_{hj}) = Z[o(k)]\, W[o(k), \theta(k)] \,.$$

$$R_{12}{}^{-o(1)-o(2)-1} R_{13}{}^{-o(1)-o(3)-1} R_{23}{}^{-o(2)-o(3)-1} \,; \tag{2a}$$

$Z[o(k)]$: a function solely of the multipole orders and the choice of the interacting species; (2b)

$W[o(k), \theta(k)]$: a function solely of the multipole orders and the three vertex angles. (2c)

Doran and Zucker [4] derived an explicit equation for an additional multipole contribution and verified Bell's equation for the dipole-dipole-quadrupole contribution, which disagreed with an earlier equation.

Since the sign of U^3 is determined by the sign of $W[o(k), \theta(k)]$ and the three vertex angles, $\theta(k)$, of the spherical harmonics are dependent, two were chosen as independent variables, $[(\chi, \phi), \chi + \phi \leqslant 180°]$. (The choices of χ and ϕ are given in section 3.1.) For each set of spherical harmonic orders, $\{o(k)\}$, trigonometric identities were used to transform $W[o(k), \theta(k)]$ into a function of (χ, ϕ) which had the form

$$W[o(k), \chi, \phi] = A + B \sin\phi \,, \tag{3}$$

where A and B have general forms specified in appendix A.

Since each $W[o(k), \chi, \phi]$ is an analytic function of (χ, ϕ), its zeros must lie on continuous curves which divide the (χ, ϕ) space into positive and negative domains.

Appendix A gives the procedure used to determine sets of roots (χ_0, ϕ_0) on these nodal curves. The procedure replaces the computationally intensive determination of a large number of roots of transcendental equations with the more efficient determination of the roots of a polynomial.

The signs of $W[o(k), \chi, \phi]$ in the domains bounded by the nodal curves whose points are solutions to the equations

$$W[o(k), \chi, \phi] = 0 \tag{4}$$

were determined in the following ways. (a) The first partial derivatives of $W[o(k), \chi, \phi]$ were calculated at a set of points on each nodal curve. The local linear Taylor series approximation at each point gave a unique, consistent assignment of the signs. (b) The signs of $W[o(k), \chi, \phi]$ determined in (a) were verified by calculating $W[o(k), \chi, \phi]$ for test points in each domain.

3. Results

Points on the nodal curves and the signs in the domains were determined for each of the three lowest total spherical harmonic orders

$$o = o(1) + o(2) + o(3) = 3, 4, 5 \tag{5}$$

and the one of order $o = 6$, for which Bell [3] had derived eq. (2): $o = 3$, triple dipole; $o = 4$, dipole, dipole-quadrupole; $o = 5$, dipole-quadrupole-quadrupole and dipole-dipole-octupole; $o = 6$, triple quadrupole.

3.1. CHOICES ADOPTED FOR χ AND ϕ

For the contributions of total orders 4 and 5 two of the $o(k)$ are the same and one is distinct. In this case $W[o(k), \theta(k)]$ is invariant under a permutation of the m and n such that $o(m) = o(n)$. Then,

$$\phi \equiv \text{the vertex angle for the distinct spherical harmonic order}; \tag{6a}$$

$$\chi \equiv \theta(m) \quad \text{or} \quad \theta(n). \tag{6b}$$

For the triple dipole and triple quadrupole contributions in which all three spherical harmonic orders, $o(k)$, are identical, $W[o(k), \theta(k)]$ is invariant under any permutation of the k. Therefore, for these contributions,

$$\chi = \theta(m), \quad \phi = \theta(n), \quad \text{any } m \text{ and any } n. \tag{6c}$$

3.2. INTERPRETATION OF THE FIGURES

Figures 1–5 show the continuous curves drawn through the solutions (χ_0, ϕ_0) to eq. (4), which are the complete set of nodal curves for each of the five different

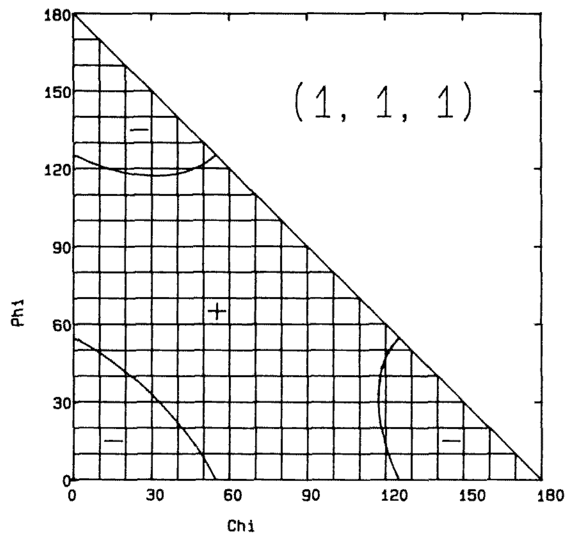

Fig. 1. Positive and negative domains of (χ, ϕ) space for the three-body triple dipole (spherical harmonic orders (1,1,1)) contribution are identified by (+) and (−). The angles χ and ϕ are defined by eq. (6c). The curves are the nodal curves.

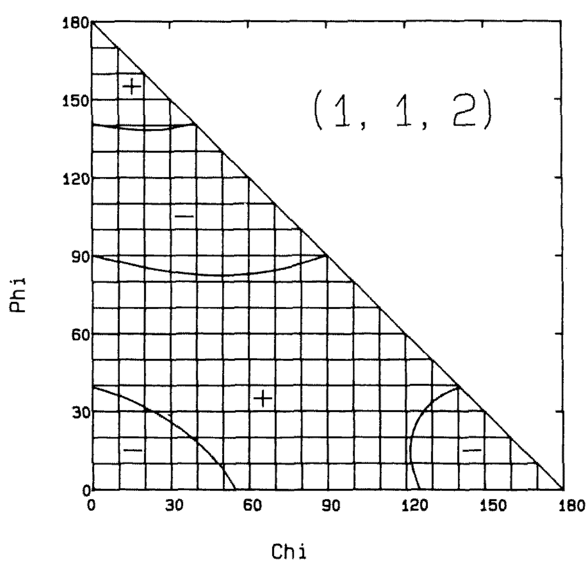

Fig. 2. Positive and negative domains of (χ, ϕ) space for the three-body dipole-dipole-quadrupole (spherical harmonic orders (1,1,2)) contribution are identified by (+) and (−). The angles χ and ϕ are defined by eqs. (6a, b). The curves are the nodal curves.

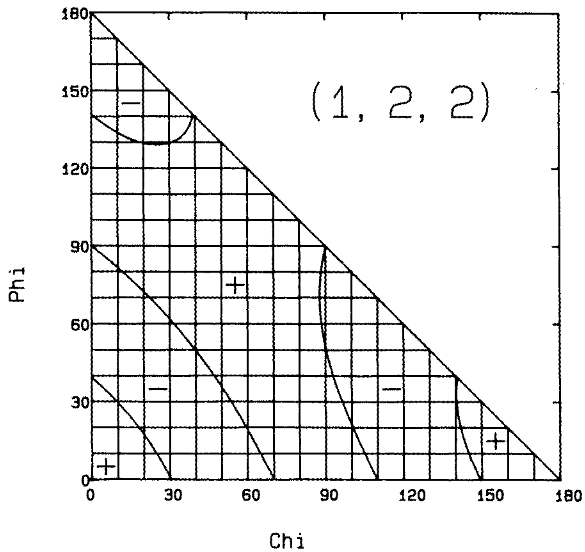

Fig. 3. Positive and negative domains of (χ, ϕ) space for the three-body dipole-quadrupole-quadrupole (spherical harmonic orders (1,2,2)) contribution are identified by (+) and (−). The angles χ and ϕ are defined by eqs. (6a, b). The curves are the nodal curves.

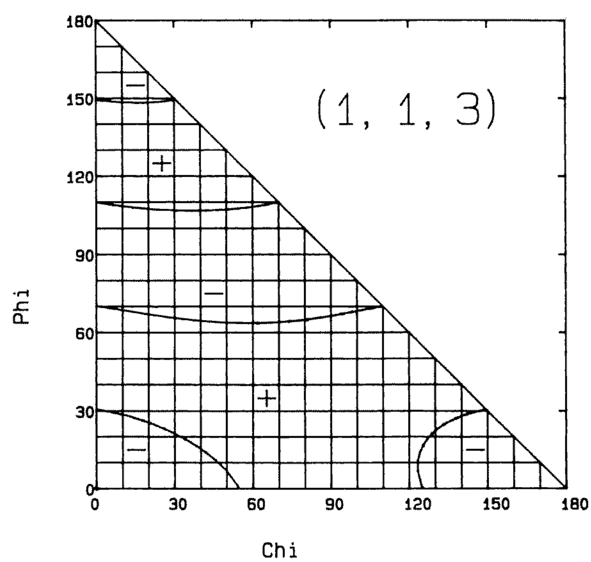

Fig. 4. Positive and negative domains of (χ, ϕ) space for the three-body dipole-dipole-octupole (spherical harmonic orders (1,1,3)) contribution are identified by (+) and (−). The angles χ and ϕ are defined by eqs. (6a, b). The curves are the nodal curves.

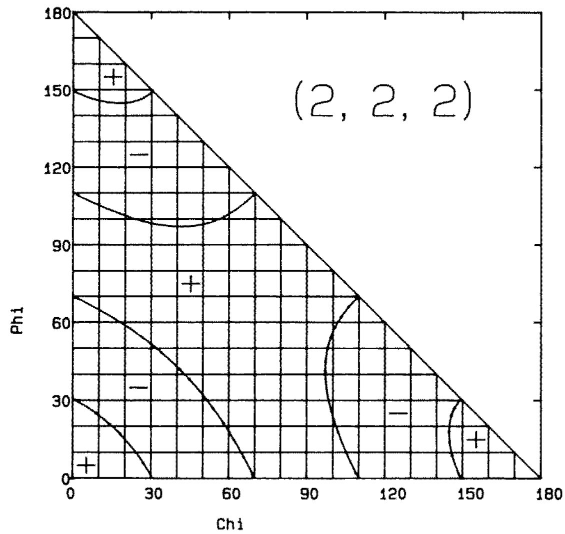

Fig. 5. Positive and negative domains of (χ, ϕ) space for the three-body triple quadrupole (spherical harmonic orders (2,2,2)) contribution are identified by (+) and (−). The angles χ and ϕ are defined by eq. (6c). The curves are the nodal curves.

multipole contributions. These nodal curves divide the (χ, ϕ) space into domains. Domains in which $W[o(k), \chi, \phi]$ is negative are designated (−) and domains in which $W[o(k), \chi, \phi]$ is positive are designated (+). Section 3.5 shows how these figures in (χ, ϕ) space are used to determine the sign of each contribution for three interacting bodies which form a triangle with specified vertex angles.

Figure 6 shows the domains of (χ, ϕ) space for the interactions of both total orders 3 and 4: [(1, 1, 1), (1, 1, 2)]. Domains in which both $W[o(k), \chi, \phi]$ are positive are designated (+), domains in which both are negative are designated (−) and domains in which one is positive and the other is negative are designated (?). ϕ is the vertex angle for the spherical harmonic order 2 in the (1,1,2) interaction and any of the three equivalent vertex angles in the (1,1,1) interaction. Each curve shown is a nodal curve in (χ, ϕ) space for one of the interactions. Figure 7 does the same for the two interactions of total order 5: [((1,2,2), (1,1,3)]. ϕ is the vertex angle for spherical harmonic order 1 in the (1,2,2) interaction and 3 in the (1,1,3) interaction. Section 3.5 also shows how each of these figures is used to determine a sign common to *both* combinations when the interacting bodies form a triangle with specified vertex angles.

3.3. SYMMETRY RELATIONS

Appendix B gives simple proofs that characteristics of the nodal curves shown in the figures are direct consequences of symmetries of $W[o(k), \theta(k)]$ of eq. (2) for the multipole interactions studied. These symmetries also give identities which

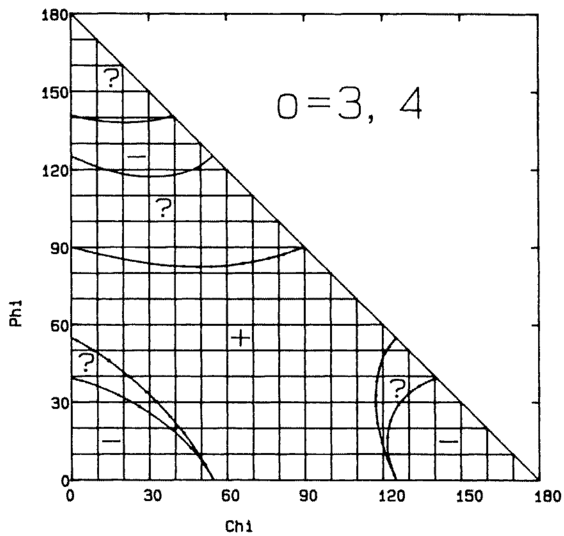

Fig. 6. *The three-body contributions of both total spherical harmonic orders, 3 and 4 (spherical harmonic orders (1,1,1) and (1,1,2)).* Domains of (χ, ϕ) space in which the contributions of both orders are positive are identified by (+) and domains in which the contributions of both are negative are identified by (−). Domains in which one is positive and the other is negative are identified by (?). The angles χ and ϕ are defined by eqs. (6a, b).

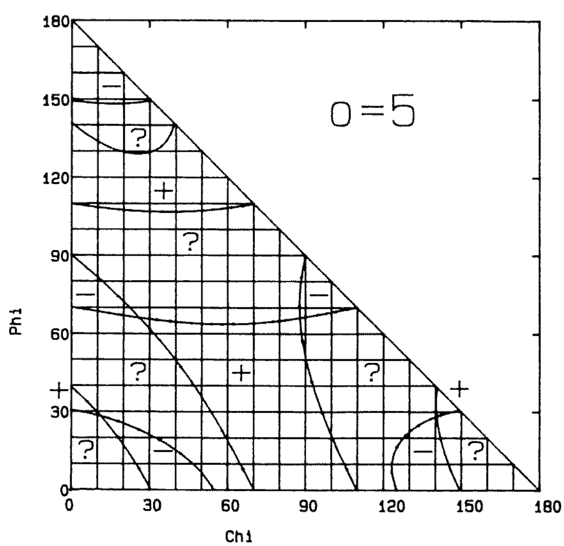

Fig. 7. *The three-body contributions of both total spherical harmonic order 5 (spherical harmonic orders (1,2,2) and (1,1,3)).* Domains of (χ, ϕ) space in which the contributions of both orders are positive are identified by (+) and domains in which the contributions of both are negative are identified by (−). Domains in which one is positive and the other is negative are identified by (?). The angles χ and ϕ are defined by eqs. (6a, b).

were used to generate additional points on the nodal curves from the points determined according to appendix A.

3.4. SPECIAL SOLUTIONS WHICH TEST THE CORRECTNESS OF THE NODAL CURVES

3.4.1. Isosceles triangle geometries

Consider a nodal curve, $\phi(\chi)$, in any of the figures 1–5 in which ϕ spans an interval $[\phi_{\min}, \phi_{\max}]$, where $0 < \phi_{\min}$. Then χ spans the interval $[0, 180° - \phi_{\max}]$. The symmetry relation for all five figures given by appendix B implies that at the minimum, (χ_m, ϕ_m), of $\phi(\chi)$, the species lie at the corners of an isosceles triangle with $(\chi_m, \phi_m) = ([180° - \phi_m]/2, \phi_{\min})$. Table 1 gives the roots ϕ_m calculated with the special equations for isosceles triangle geometries.

The independent determination of these special solutions points gave a very close check on the correctness our nodal points obtained using appendix A. For each $\langle \chi_m, \phi_m \rangle$ there were two roots (χ_L, ϕ') and (χ_R, ϕ') from our programs and one of the symmetry relations such that: (i) $\chi_L < \chi_m < \chi_R$; (ii) $0 < \phi' - \phi_m \leqslant 0.02°$.

3.4.2. Limit points

The limit points for which either χ or ϕ approached 0° or their sum approached 180° are given in table 2. The fact that these limit points, which were independently calculated, and the roots determined by our general programs lie on the same plots of the curves gave additional approximate checks on our programs.

Another figure, which shows the sub-domains in which the U^3 (as a function of (χ, ϕ)) for each of the five contributions share a common positive or negative sign, is available on request.

3.5. USE OF THE FIGURES TO DETERMINE THE SIGN OF U^3 FOR THREE BODIES WHICH FORM AN ARBITRARY TRIANGLE

Suppose the bodies form a triangle with vertex angles

$$(\theta_1, \theta_2, \theta_3) . \tag{7}$$

Table 1
ϕ_m is the value of ϕ in degrees at the minimum $\langle \chi_m, \phi_m \rangle$ of a curve. At the minimum the species lie at the corners of an isosceles triangle.

Spherical harmonic orders	ϕ_m		
(1,1,1)	117.22		
(1,1,2)	82.36	138.12	
(1,2,2)	128.97		
(1,1,3)	63.62	106.77	148.25
(2,2,2)	97.02	144.79	

Table 2
The angles χ_L and ϕ_L in degrees for limit points $\langle \chi_L, 0\rangle$ and $\langle 0, \phi_L\rangle$.

Spherical harmonic orders	χ_L		ϕ_L	
(1,1,1)	54.74	125.26	54.74	125.26
(1,1,2)	54.74	125.26	39.23	90.00
			140.77	
(1,2,2)	30.56	70.12	39.23	90.00
	109.88	149.44	140.77	
(1,1,3)	54.74	125.26	30.56	70.12
			109.88	149.44
(2,2,2)	30.56	70.12	30.56	70.12
	109.88	149.44	109.88	149.44

Consider first the procedure for the use of figs. 1 and 5 in which the three spherical harmonic orders are the same. Since $W[o(k), \theta(k)]$ of eq. (2) is invariant under *any* permutation of the k, choose arbitrarily one of the six possible pairs, $(\chi = \theta_i, \phi = \theta_j)$, and locate the point on the figure. Then if $(\chi = \phi_i, \phi = \theta_j)$ lies on one of the nodal curves of $Wo(k), \chi, \phi]$ shown, U^3 for the triangle vanishes. If the point lies in a domain designated "+" ("−"), U^3 is positive (negative). For example, the (2,2,2) contribution to U^3 for the triangle $(123°, 37°, 20°)$ is negative since one of the possible choices, $(\chi, \phi) = (123°, 37°)$, lies in a domain in fig. 5 designated (−). Thus, this procedure determines whether U^3 vanishes for the triangle, and if not determines its sign.

Consider next the procedure for the use of figs. 2, 3 and 4 in which one spherical harmonic order is distinct. Figure 3 for the (1,2,2) interaction will be used as an example. Recall that eq. (6a) defines ϕ as vertex angle for the distinct spherical harmonic order, in this case 1. Therefore, U^3 for the three interacting bodies is the sum

$$U^3 = f \sum_j W[o(k), \chi_j, \phi_j], \quad \phi_j = \theta_j, \quad j = 1, 2, 3\,; \tag{8a}$$

$$f\text{: a positive function specified by eq. (2)}. \tag{8b}$$

By symmetry eq. (B.2) of appendix B, χ_j can be *either* of the other two angles,

$$[\chi_1 = \theta_2 \text{ or } \theta_3; \chi_2 = \theta_1 \text{ or } \theta_3; \chi_3 = \theta_1 \text{ or } \theta_2]\,. \tag{8c}$$

The jth term in the sum will vanish if (χ_j, θ_j) lies on one of the nodal curves shown, will be positive if it lies in a domain designated "+" and negative if it lies in a domain designated "−". Therefore, one must locate three (χ_j, ϕ_j) of eq. (8) in the figure. At most one of the three can lie on a nodal curve. Therefore, the sum of the three terms is negative if each (χ_j, ϕ_j) is either a point on a nodal curve or in a domain designated "−" and the sum is positive if each is either a point on a nodal curve or in a domain designated "+". For example, the (1,2,2) contribution to U^3 is negative for any triangle with $(\theta_1, \theta_2, \theta_3) = (134°, 36°, 10°)$ since in fig. 3 each of the three $(\chi_j, \phi_j)[(10°, 134°), (134°, 36°)$ and $(36°, 10°)]$ lies in a domain designated "−". Similarly, the (1,2,2) contribution to U^3 is positive for any triangle with $(\theta_1, \theta_2, \theta_3) = (30°, 70°, 80°)$ since each of the three $(\chi_j, \phi_j)[(70°, 30°), (80°, 70°)$ and $(70°, 80°)]$ lies in a domain designated "+". If at least one point is in a "+" domain and at least one in a "−" domain, the figure cannot be used to determine the sign of the sum. The simple procedure of locating three points determines the sign of U^3 for the interactions of figs. 2–4 in [14%, 23%, 14%] of all triangles. (Since two angles determine the third, $A_D \equiv$ [area of domains in (θ_1, θ_2) space of U^3] was determined for each figure. The percentage for each figure $= 100 \cdot \{A_D/[\text{total area}]\}$).

The procedure for figs. 2–4 is also used for fig. 6. One must locate three (χ_j, ϕ_j) of eq. (8) in the figure. Then *both* U^3 for the (1,1,1) and U^3 for the (1,1,2) interactions are negative if each (χ_j, ϕ_j) is either a point on a nodal curve or in a domain designated "−" and both are positive if each is either a point on a nodal curve or in a domain designated "+". In 14% of all triangles one can determine that *both* U^3 are positive or *both* are negative by simply locating three points in the figure. The same procedure is also used for fig. 7. However, the fraction of all triangles for which the procedure shows that U^3 for the (1,2,2) and U^3 for the (1,1,3) contributions are *both* positive or are *both* negative is much smaller.

4. Comparisons with earlier work

In agreement with fig. 1, Axilrod and Teller [1] reported that both the equilateral and right triangle configurations are positive and, as is obvious from their equation, the collinear configuration is negative. Midzuno and Kihara [5] reported that the interaction was repulsive whenever the largest of the angles $[\theta_1, \theta_2$ and $\theta_3] < 117°$ (our value: 117.221°) and attractive whenever the largest was $> 126°$ (our value: 125.26°). Our isosceles triangle geometry for the triple dipole contribution agrees with that reported by Bruch et al. [6]. They also made qualitative comments about the contributions of several higher order multipoles in isosceles triangle configurations with a vertex angle in the 110–120° range. The latter cannot be directly compared with our results.

O'Shea and Meath [7] have studied the effect of charge overlap on the accuracy of the triple dipole equation and have discussed the use of the triple dipole equation to represent the total three-body contribution [8]. We are unaware of any study of the effect of charge overlap on the accuracy of the higher three-body dispersion multipole contributions. However, both Murrell and Shaw [9] and Kreek and Meath [10] have studied the effect of charge overlap on the higher order two-body dispersion multipoles.

5. Summary

The sign of each three-body multipole dispersion contribution is determined by the vertex angles of the triangle. The positive and negative domains of two vertex angle space have been determined for five of the lowest spherical harmonic orders. When all spherical harmonic orders are the same, one determines that the contribution from three bodies which form a triangle with arbitrary vertex angles vanishes or its sign by locating one point in its figure. When one of the spherical harmonic orders is distinct, one determines the sign of the contribution in a useful fraction of all triangles by locating 3 points in its figure. Qualitative characteristics of the nodal curves and relations between them have been shown to be simple consequences of the symmetry of the multipole interactions.

For those who would like figures which can be more accurately read, an ACII file of lists of points on the curves accurate to 0.01° is available on request.

Acknowledgements

It is a pleasure to thank Dr. Mihaly Mezei of the Mount Sinai School of Medicine both for his noticing some apparently common domains on preliminary figures and his suggestion that figures be added showing positive and negative domains common to two multipole contributions. We also thank him for his preparation of all figures from the point lists.

Appendix A

THE DETERMINATION OF POINTS ON THE CURVES ON WHICH U^3 AS A FUNCTION OF (χ, ϕ) VANISHES

$w[o(k), \chi, \phi]$ has the general form

$$A + B\sin\phi; \tag{A.1a}$$

where *either*

$$\begin{aligned} &A = \text{a sum of terms } c_n \cos^{2n}\phi, \\ &B = \text{a single term or a sum of terms } d_n \cos^{2n+1}\phi, \\ &c_n \text{ and } d_n \text{ are function of trigonometric functions of } \chi, \quad n \geqslant 0; \end{aligned} \tag{A.1b}$$

or

$$\begin{aligned} &B = \text{a sum of terms } c_n \cos^{2n}\phi, \\ &A = \text{a single term or a sum of terms } d_n \cos^{2n+1}\phi, \\ &c_n \text{ and } d_n \text{ are functions of trigonometric functions of } \chi, \quad n \geqslant 0. \end{aligned} \tag{A.1c}$$

Each root of $W[o(k), \chi, \phi]$ is also a root of $W_M[o(k), \chi, \phi] \equiv A^2 - B^2 \sin^2\phi = A^2 - B^2(1 - \cos^2\phi)$. Furthermore, W_M has the form of the polynomial equation (A.2):

$$W_M[o(k),\chi,\phi] = \sum_j C_j[o(k),\chi]\,Y^j, \quad 0 \leqslant j \leqslant M\,; \tag{A.2a}$$

$$Y = \cos^2\phi\,; \tag{A.2b}$$

$C_j[o(k),\chi)$: a coefficient, which for each set of orders $\{o(k)\}$ is an explicit function of trigometric functions of χ; (A.2c)

M: the order of the polynomial in Y, determined by $\{o(k)\}$. (A.2d)

This form was used in the following efficient determination of a set of roots of W_M. For each 4° step of χ, the coefficients C_j were computed and the roots (χ, Y) of W_M were determined. Any root which was not consistent with eq. (A.2b), $Y = \cos^2\phi$, was rejected.

Since W_M has roots (χ_0, ϕ_0) which are not roots of $W[o(k),\chi,\phi)$, only those roots of W_M for which the absolute value of $W[o(k),\chi_0,\phi_0] < [\{1.1 \times 10^{-7}\}\cdot$ {the maximum absolute value of one of the terms in the summation}] were accepted as roots of $W[o(k),\chi,\phi]$.

Appendix B

SYMMETRY RELATIONS AND CHARACTERISTICS OF THE NODAL CURVES

A symmetry relation for all five figures

For each of the five interactions, at least wo of the spherical harmonic orders $o(k)$ are the same. Let their indices be denoted by $k = m$ and $k = n$. Then $W[o(k),\theta(k)]$ of eq. (2) is invariant under a permutation of m and n. When one of the orders $o(p)$ is distinct, eq. (6a) defines ϕ as its vertex angle, $\theta(p)$. Therefore, for each figure,

$$W[o(k),\chi = \theta(m),\phi = \theta(p)] = W[o(k),\chi = \theta(n),\phi = \theta(p)]\,. \tag{B.1}$$

Therefore

$$W[o(k),\chi_a,\phi_a] = W[o(k),\chi_b,\phi_b] \tag{B.2a}$$

whenever

$$\chi_b = 180° - (\chi_a + \phi_a), \quad \phi_b = \phi_a\,. \tag{B.2b}$$

Thus, whenever $\langle\chi_a,\phi_a\rangle$ is a root of eq. (4), $\langle\chi_b,\phi_b\rangle$ is also a root. This equation was used in supplementing the lists of nodal points for all 5 figures.

Two symmetry relations valid for figs. 1 and 5 only

For figs. 1 and 5 all orders $o(k)$ are the same. In this case: $W[o(k),\theta(k)]$ of eq.

(2) is invariant under a permutation of *any* pair of the three indices $k = r, s, t$. Consider first a fixed choice of χ:

$$\chi = \theta(t)\,. \tag{B.3}$$

Then,

$$W[o(k), \chi = \theta(t), \phi = \theta(r)] = W[o(k), \chi = \theta(t), \phi = \theta(s)]\,. \tag{B.4}$$

Therefore

$$W[o(k), \chi_a, \phi_a] = W[o(k), \chi_c, \phi_c] \tag{B.5a}$$

whenever

$$\chi_c = \chi_a, \quad \phi_c = 180° - (\chi_a + \phi_a)\,. \tag{B.5b}$$

Thus whenever $\langle \chi_a, \phi_a \rangle$ is a root of eq. (4), $\langle \chi_c, \phi_c \rangle$ is also a root. Second, W is invariant under a permutation of the choices for both χ and ϕ:

$$W[o(k), \chi = \theta(r), \phi = \theta(s)] = W[o(k), \chi = \theta(s), \phi = \theta(r)]\,. \tag{B.6}$$

Therefore, whenever $\langle \chi = \theta(r), \phi = \theta(s) \rangle$ is a root of eq. (4), then $\langle \chi = \theta(s), \phi = \theta(r) \rangle$ is also a root. Equations (B.5) and (B.6) were also used in supplementing the list of points for figs. 1 and 5.

Characteristics of the nodal curves

Consider a nodal curve of section 3.4.1 with a minimum which corresponds to an isosceles triangle geometry. Such a curve in Figs. 1 and 5, in which all spherical harmonic orders are the same, implies the existence of two additional curves. The symmetry equation (B.5) requires another curve A in which both χ and ϕ span the same interval, $[0, 180° - \phi_{\max}]$. The symmetry equation (B.6) requires a third curve B in which the roles of χ and ϕ are interchanged. In this curve, χ spans the interval $[\phi_{\min}, \phi_{\max}]$ and ϕ spans the same interval as it does in curve A. This curve is a function, $\chi(\phi)$, which has a minimum at $\chi = \phi_{\min}$ and $\phi = ([180° - \phi_{\min}]/2$. Clearly, a curve with an isosceles triangle point in figs. 2, 3 and 4 for which only two of the multipole orders are the same has no corresponding curves A and B.

Although figs. 2, 3 and 4, in which only two of the three orders are the same, also have curves in which ϕ spans an interval $[0, \phi_{\mathrm{L}}]$ and χ spans an interval $[0, \chi_{\mathrm{L}}]$, χ_{L} and ϕ_{L} are different. Symmetry equation (B.2) requires another curve in which ϕ spans the same interval, $[0, \phi_{\mathrm{L}}]$. As in figs. 1 and 5, this curve is a function $\chi(\phi)$ with a minimum, $(\chi_{\min}, \phi_{\min})$. However, in these figures, the minimum cannot correspond to an isosceles triangle geometry.

References

[1] B.M. Axilrod and E. Teller, J. Chem. Phys. 11 (1943) 299.

[2] Y. Muto, Proc. Phys. Math. Soc. Jpn. 17 (1943) 629.

[3] R.J. Bell, J. Phys. B3 (1970) 751.
[4] M.B. Doran and I.J. Zucker, J. Phys. C4 (1971) 307.
[5] Y. Midzuno and T. Kihara, J. Phys. Soc. Jpn. 11 (1956) 1045.
[6] L.W. Bruch, O. Navarro and A. Flores, J. Chem. Phys. 67 (1977) 2371.
[7] S.F. O'Shea and W.J. Meath, Mol. Phys. 28 (1974) 1431.
[8] S.F. O'Shea and W.J. Meath, Mol. Phys. 31 (1976) 515.
[9] J.N. Murrell and G. Shaw, J. Chem. Phys. 49 (1968) 4731.
[10] H. Kreek and W.J. Meath, J. Chem. Phys. 50 (1969) 2289.