

# THE INTERACTION ENERGY OF AN ION PAIR WITH OVERLAPPING HYDRATION SHELLS

## II.\* A SPHEROIDAL CAVITY MODEL

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### *Summary*

The energy of interaction of two monovalent ions of opposite charge with overlapping hydration shells and in an aqueous medium is discussed in terms of a spheroidal cavity model. Some of the calculations carried out in an earlier paper by Levine and Rosenthal (1966) are shown to be inadequate and an improved model is tested for consistency with the "truncated spheres model" proposed in Part I. The calculations suggest that this new model can be adapted to an examination of the water molecules in the first hydration shells of an ion pair. Only calculations for the  $K^+$  and  $F^-$  ions are included.

### I. INTRODUCTION

In Part I (pp. 571–85 of the present issue) the interaction energy of an ion pair in an aqueous medium is discussed in terms of a "truncated spheres model" embedded in a dielectric continuum that represents the aqueous medium. However, although this model may be mathematically satisfactory it is unlikely to represent the "true" physical situation because the hydration shells of the ions tend to repel, particularly at small separations. There is, therefore, a considerable distortion of the cavity shape, which should be accounted for with an improved model. Now it appears (Levine and Rosenthal 1966) that it is difficult to choose a spheroidal cavity in such a way that both the interaction energy and the force between the ions is continuous at an ion separation equal to the diameter of an isolated ion complex. Levine and Rosenthal were unable to effect such a matching when the cavity is empty because the interaction energy of the two ions, which is defined as the difference between the free energy associated with the two ions at the given separation and that at infinite separation, is a very small difference and is extremely sensitive to changes in cavity shape and cavity volume. On the other hand, when the cavity contains both point charges and a system of poles and multipoles situated in empty cavities (or the multipoles replaced by a dielectric medium) continuity in the energy and force is obtained for various geometries in either of two ways: (1) by setting the volume of the cavity equal to a linear function of the separation and keeping the position of the ionic charges fixed relative to the ends of the major axis of the spheroid, or (2) by varying the position of the two charges relative to the ends of the major axis and keeping the volume fixed. Clearly, some combination of these two possibilities

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is better but any future work on such lines requires the use of a discrete model representing the ions and their attached water molecules. Before attempting such a complicated analysis it is important to see if a refined model based on the spheroidal cavity can meet with more success.

A failing of the spheroidal cavity model of Levine and Rosenthal (1966) that is not pointed out by them stems from the fact that the field intensity at the ion centres (and hence the induced multipole moments) exhibits a discontinuity at contact separation of at least two orders of magnitude. The reason for such an abrupt change is made clear in Part I. It is with this fact in mind that a variation of the spheroidal model is suggested, namely, that matching of the interaction energy and the force between the ions should be carried out at a smaller separation, say 90% of the diameter of a single ion complex. In that case the discontinuity in the field intensity at the ion centres is very much reduced and the redistribution of the water molecules, originally in a tetrahedral configuration (at infinite separation), is kept to a minimum. The possible success of this model suggests that a spheroidal cavity may be useful in studying the behaviour of the attached water molecules and, in particular, it may be possible to determine the ionic separation at which, on average, the coordination number per ion changes. Such a change is suggested in the work of Eigen and Tamm (1962).

Some characteristics of the spheroidal model have already been investigated by Westheimer and Kirkwood (1938, 1939), Hill (1944, 1956), Buckingham (1953), Linderstrøm-Lang (1953), Buckley and Maryott (1954), and Tanford (1957), to mention but a few. None of these authors were concerned with the same type of problem but each found the model sufficiently accurate for their purposes. The numerical work in the present paper is based on the data in Part I.

## II. POTENTIAL PROBLEM FOR SPHEROIDAL CAVITY

To begin we shall consider a cavity model whose boundary is an ellipsoid of revolution. Some of the characteristics of this spheroidal model have already been investigated by Levine and Rosenthal (1966; subsequently referred to as L.R.) in which the water molecules in the coordination shells are represented by induced dipoles and quadrupoles placed at the centre of each ion. In the present discussion it is found convenient to use confocal elliptical coordinates  $(\xi, \eta, \phi)$ ; thus, if  $\rho_1$  and  $\rho_2$  are the distances of a typical point P from the two foci, whose distance apart is  $2a$ , then  $\xi = (\rho_1 + \rho_2)/2a$ ,  $\eta = (\rho_1 - \rho_2)/2a$ , and  $\phi$  is the angle by which the typical point has been rotated past a fixed plane through the major axis. Since we have chosen an ellipsoid of revolution to represent the boundary and we confine all the charges to lie on the major axis between the two foci, the model is axially symmetrical and the angle  $\phi$  does not enter the formulation explicitly. In this coordinate system the boundary of the ellipsoidal cavity will be defined by  $\xi = \xi_0 = 1/E$ , where  $E$  is the eccentricity of the spheroid and the ion centres are symmetrically placed between the foci  $f_1$  and  $f_2$  at a distance  $R$  apart, as shown in Figure 1. If the spheroid is treated as a uniform medium of dielectric constant  $\epsilon'$  embedded in an aqueous medium of dielectric constant  $\epsilon$  then the potential at a point  $r(\xi, \eta)$  outside the spheroid

has the form

$$\psi_0 = \frac{1}{\epsilon} \sum_k \frac{e_k}{|\mathbf{r} - \mathbf{r}_k|} + \sum_{n=0}^{\infty} A_n Q_n(\xi) P_n(\eta), \quad (1)$$

where  $e_k$  is the set of charges placed on the major axis,  $P_n$  and  $Q_n$  represent the Legendre functions of order  $n$  of the first and second kind respectively, and the  $A_n$  are constants to be determined from the boundary conditions. Similarly, the potential inside the spheroid may be written in the form

$$\psi_1 = \frac{1}{\epsilon'} \sum_k \frac{e_k}{|\mathbf{r} - \mathbf{r}_k|} + \sum_{n=0}^{\infty} B_n P_n(\xi) P_n(\eta). \quad (2)$$

At this stage we shall replace the actual charge distribution inside the cavity by point charges  $+e$  and  $-e$  at positions  $O_1$  and  $O_2$ , and the molecules inside the ion complex by dipoles  $\mu$  and quadrupoles  $\Theta$  also situated at these points and having directions in the appropriate sense along  $O_1 O_2$ . In order to take account of the

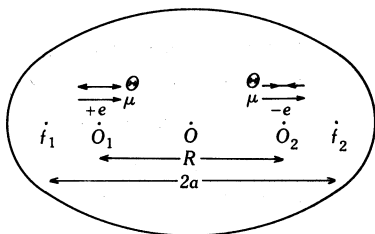


Fig. 1.—Model of a spheroidal cavity with foci at  $f_1$  and  $f_2$  which is taken to represent overlapping hydration shells;  $\mu$  and  $\Theta$  are the induced dipole and quadrupole moments respectively.

changes with ion separation in the induced dipole and quadrupole moments at each ion centre under the influence of the reaction field, it seems sufficient for the present to assume that these moments are proportional to the reaction field and the reaction field gradient respectively. Thus, at the ion centre  $O_1$  we have the relations

$$\mu = -a \partial \psi_R / \partial z, \quad \Theta = -\gamma \partial^2 \psi_R / \partial z^2, \quad (3)$$

where the reaction field  $\psi_R$  is that part of the potential  $\psi_1$ , given in (2), which excludes the poles of various orders situated at  $z = -\frac{1}{2}R$  and  $a$  and  $\gamma$  are the dipole and quadrupole polarizabilities respectively. Making use of this and the boundary conditions appropriate to the problem; namely

$$\psi_0 = \psi_1, \quad \epsilon \partial \psi_0 / \partial \xi = \epsilon' \partial \psi_1 / \partial \xi \quad \text{at} \quad \xi = 1/E, \quad -1 \leq \eta \leq 1, \quad (4)$$

we find that

$$B_n = (\beta_n/a)(1/\epsilon - 1/\epsilon')C_n, \quad (5)$$

where

$$C_n = (2n+1)Q_n(E^{-1})/P_n(E^{-1})(1-D_n), \quad (6)$$

$$D_n = \frac{\epsilon' E^{-1} - P_{n-1}(E^{-1})/P_n(E^{-1})}{\epsilon E^{-1} - Q_{n-1}(E^{-1})/Q_n(E^{-1})}, \quad (7)$$

and

$$\beta_n = \sum_k e_k P_n(\eta_k), \quad (8)$$

because the point charges  $e_k$  are assumed to lie on the line joining the foci ( $\xi = 1$ ) at the positions given by  $\eta = \eta_k$ . It follows that

$$\begin{aligned} \mu' \left\{ -1 + \frac{a'}{4\epsilon' z^3} - 2a' \left( \frac{a_0}{a} \right)^3 \left( \frac{1}{\epsilon'} - \frac{1}{\epsilon} \right) \sum' C_n P_n^2 \right\} + \Theta' \left\{ \frac{3a'}{16\epsilon' z^4} + 2a' \left( \frac{a_0}{a} \right)^4 \left( \frac{1}{\epsilon'} - \frac{1}{\epsilon} \right) \sum' C_n P_n P_n^* \right\} \\ = -a' \left\{ \frac{1}{4\epsilon' z^2} + 2 \left( \frac{a_0}{a} \right)^2 \left( \frac{1}{\epsilon'} - \frac{1}{\epsilon} \right) \sum' C_n P_n P_n^* \right\}, \end{aligned} \quad (9)$$

$$\begin{aligned} 2\gamma'\mu' \left\{ -\frac{3}{16\epsilon' z^4} - \left( \frac{a_0}{a} \right)^4 \left( \frac{1}{\epsilon'} - \frac{1}{\epsilon} \right) \sum' C_n P_n P_n^* \right\} + \Theta' \left\{ 1 - \frac{3\gamma'}{8\epsilon' z^5} + 2\gamma' \left( \frac{a_0}{a} \right)^5 \left( \frac{1}{\epsilon'} - \frac{1}{\epsilon} \right) \sum' C_n P_n^2 \right\} \\ = \gamma' \left\{ \frac{1}{4\epsilon' z^3} - 2 \left( \frac{a_0}{a} \right)^3 \left( \frac{1}{\epsilon'} - \frac{1}{\epsilon} \right) \sum' C_n P_n P_n^* \right\}, \end{aligned} \quad (10)$$

where  $P_n = P_n(R/2a)$ ,  $P_n^* = P_n^*(R/2a)$ ,  $P_n^* = P_n^*(R/2a)$ , and we have introduced the dimensionless quantities

$$\mu' = \mu/ea_0, \quad \Theta' = \Theta/ea_0^2, \quad a' = a/a_0^3, \quad \gamma' = \gamma/a_0^5, \quad z = R/2a_0; \quad (11)$$

$a_0$  is the radius of the spherical ions corresponding to infinite separation and  $\sum'$  means that the summation is taken over the odd values of  $n$ .

As in Part I the interaction energy can be obtained by using the Güntelberg-Muller charging process. Thus

$$V(R) = \frac{1}{2}e\{\psi_1(1, -R/2a) - \psi_1(1, R/2a)\} + (e^2/a_0)(1/\epsilon' - 1/\epsilon), \quad (12)$$

where the last term on the right-hand side is minus the Born energy of the ion complexes, i.e. the interaction energy corresponding to infinite separation. From L.R. it follows that

$$V(R) = V_e(R) + V_\mu(R) + V_\Theta(R), \quad (13)$$

with

$$V_e(R) = -\frac{e^2}{\epsilon R} \left\{ \frac{\epsilon}{\epsilon'} + \frac{2R}{a} \left( \frac{\epsilon}{\epsilon'} - 1 \right) \sum' C_n P_n^2 - \frac{R}{a_0} \left( \frac{\epsilon}{\epsilon'} - 1 \right) \right\}, \quad (14)$$

$$V_\mu(R) = -\frac{e^2}{\epsilon R} \left\{ \frac{\epsilon}{\epsilon'} \left( \frac{\mu'}{z} + \frac{\mu'^2}{2z^2} \right) - 4 \left( \frac{a_0}{a} \right)^2 \left( \frac{\epsilon}{\epsilon'} - 1 \right) \mu' z \sum' C_n P_n P_n^* \right\}, \quad (15)$$

and

$$V_\Theta(R) = -\frac{e^2}{\epsilon R} \left\{ \frac{\epsilon}{\epsilon'} \left( \frac{\Theta'}{2z^2} + \frac{3\Theta'^2}{4z^4} \right) + 4 \left( \frac{a_0}{a} \right)^3 \left( \frac{\epsilon}{\epsilon'} - 1 \right) \Theta' z \sum' C_n P_n P_n^* \right\}. \quad (16)$$

It is now important to choose a suitable geometry for the spheroid. Let  $2a_1$  and  $2b_1$  be the lengths of the major and minor axes of the spheroid respectively and  $ga_0$  denote the distance from the centre of each ion to the nearer end of the major axis. Then, if the volume of the spheroid is  $f$  times the sum of the volumes of the two hydration shells at infinite separation

$$2fa_0^3 = a_1^3(1 + E^2), \quad \text{with} \quad a = a_1 E. \quad (17)$$

A knowledge of  $f$  and  $g$  then leads to a complete specification of the spheroid at the given separation.

Already it is shown in L.R. the difficulty of matching both the interaction energy and the force between the ions with the two-sphere model at contact separation. Thus, continuity in the energy could be obtained by choosing a large volume for the spheroid and by keeping the positions of the ion centres fixed relative to the ends of the major axis. Continuity in the force was obtained in two ways: (1) by allowing the positions of the ion charges to remain fixed relative to the ends of the major axis and varying the volume linearly with the separation, and (2) by keeping the volume fixed and varying the positions of the ion charges linearly with the separation. In the first case we set

$$f = f(R/2a_0) = f(1) - \lambda_f(1 - R/2a_0), \quad (18)$$

while in the second case

$$g = g(R/2a_0) = g(1) + \lambda_g(1 - R/2a_0), \quad (19)$$

where  $\lambda_f$  and  $\lambda_g$  are constants. It is interesting to note that continuity in the force could be obtained for  $\epsilon' > 1$  either by decreasing the volume or increasing the distance from the ends of the major axis with decrease in separation; however, for  $\epsilon' = 1$  the volume has to be increased or the distance of the ion charges from the ends of the major axis has to be increased with decreasing separation. It is clear that the induced multipole moments of the charge distribution in the cavity are very important and may account for this curious behaviour. To show their effect we have matched the spheroid with the two spheres at contact separation.

Here we fix  $g$ , allow the volume to vary with separation, and neglect the quadrupole moment, since this will be sufficient to show the essential characteristics of the matching procedure. Thus, Figure 2(a) shows the variation in effective dielectric constant  $\epsilon_{\text{eff}}$  with separation when  $\epsilon' = 1$  and the induced dipole moment is taken into account. It is seen that matching is effected with  $g = 0.936$ ,  $f(1) = 1.35$ , and  $\lambda_f = -0.8$ . In Figure 2(b), the induced multipole moments are replaced by a dielectric medium with  $\epsilon' = 5$  and this time  $g = 1.007$ ,  $f(1) = 1.25$ , and  $\lambda_f = +0.6$ . Finally, if we separate the "electronic" from the "orientation" polarizability, introduce a dielectric medium with  $\epsilon' = 2.5$ , and use half the dipole polarizability, as was done in Part I, then matching is obtained for  $g = 0.942$ ,  $f = 1.20$ , and  $\lambda_f = 0.4$ , as shown in Figure 2(c). These results are to be compared with the truncated spheres model discussed in Part I. By way of example such a comparison is shown in Figure 3. It becomes clear that the effective dielectric constant decreases more quickly with decreasing separation for the truncated spheres model (curve C) than for the spheroidal model (curves A and B).

A fact that emerges is that the induced dipole moment at contact separation is very much larger than the value one would have expected from the two-spheres model, being about 100-fold for the case  $\epsilon' = 1$  and 30-fold for the case  $\epsilon' = 2.5$ . Actually, Tanford (1957) pointed out the difficulty of positioning the ion charges, for in his calculations he shows that a movement of the charges by as little as 1 Å can alter the interaction energy threefold. It is not surprising therefore that it is so difficult to match the induced dipole moment as well as the energy and force at contact separation, for there is an abrupt change in cavity shape in going from the

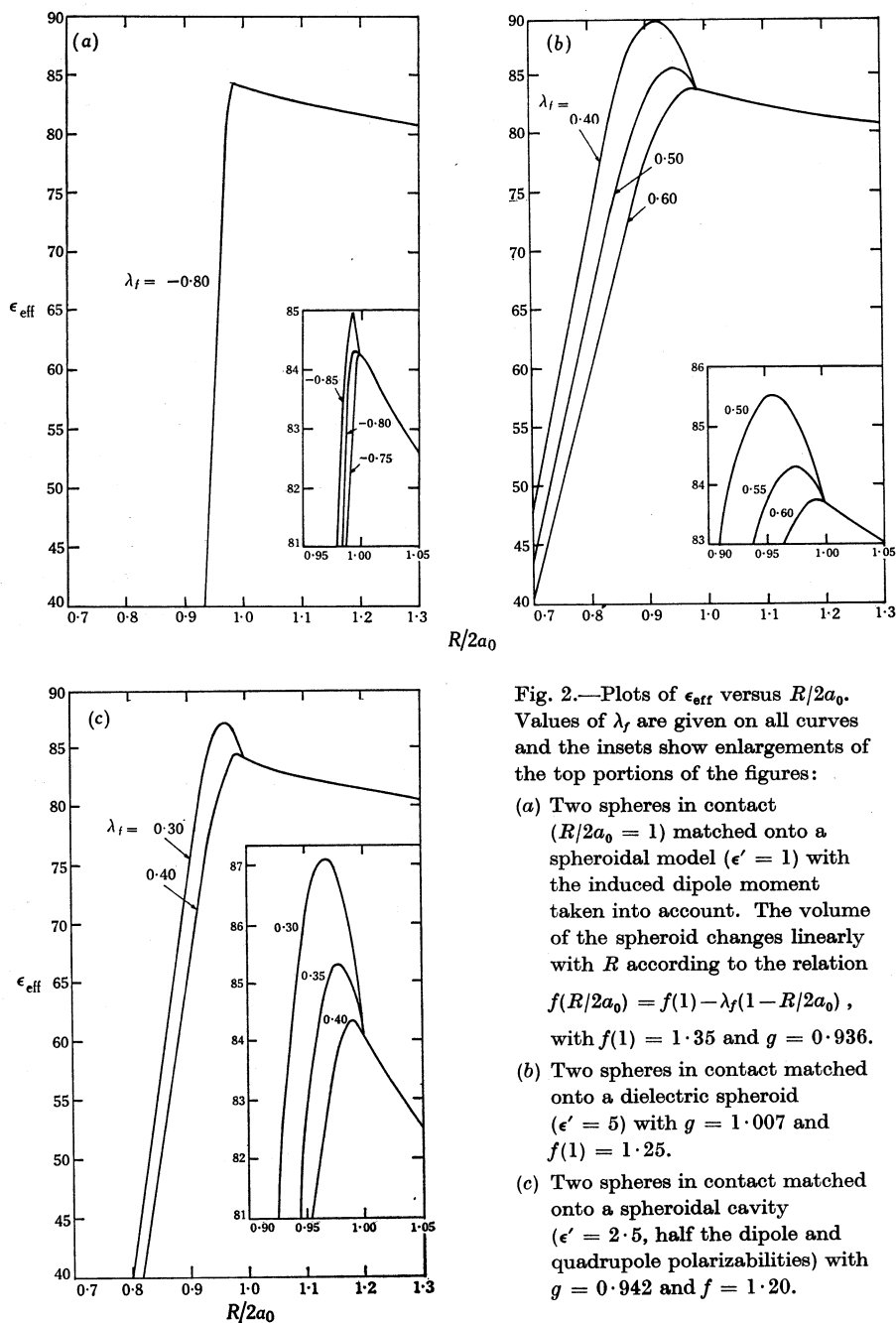


Fig. 2.—Plots of  $\epsilon_{\text{eff}}$  versus  $R/2a_0$ . Values of  $\lambda_f$  are given on all curves and the insets show enlargements of the top portions of the figures:

- (a) Two spheres in contact ( $R/2a_0 = 1$ ) matched onto a spheroidal model ( $\epsilon' = 1$ ) with the induced dipole moment taken into account. The volume of the spheroid changes linearly with  $R$  according to the relation  $f(R/2a_0) = f(1) - \lambda_f(1 - R/2a_0)$ , with  $f(1) = 1.35$  and  $g = 0.936$ .
- (b) Two spheres in contact matched onto a dielectric spheroid ( $\epsilon' = 5$ ) with  $g = 1.007$  and  $f(1) = 1.25$ .
- (c) Two spheres in contact matched onto a spheroidal cavity ( $\epsilon' = 2.5$ , half the dipole and quadrupole polarizabilities) with  $g = 0.942$  and  $f = 1.20$ .

one model to the other. This difficulty does not arise in the truncated spheres model. Nevertheless, it is not known which is the better model to represent the physical situation. A further point worth examining is whether or not the assumption that  $|\beta|$  is small (that is,  $|(r_1 + r_w)^2 E/e| \ll 1$ ) remains valid at small separation where there is a strong field, and hence whether the water dipoles point away from the line joining the centre of the water molecule to its ion.

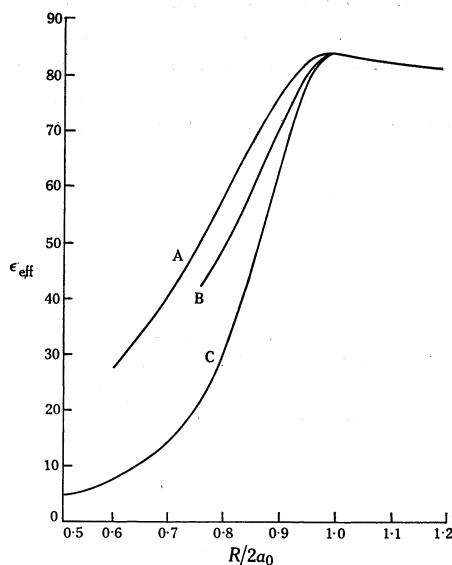


Fig. 3.—Comparison of two dielectric spheroid models ( $\epsilon' = 5$ ) with truncated spheres model matched at contact:

A, spheroidal model,  $g = 1.007$ ,

$$f(R/2a_0) = 1.25 - 0.6(1 - R/2a_0);$$

B, spheroidal model,  $f = 1.25$ ,

$$g(R/2a_0) = 1.007 + 1.3(1 - R/2a_0);$$

C, truncated spheres model,  $f = 1$ .

TABLE 1

COMPARISON OF INDUCED DIPOLE MOMENTS ( $\mu$ ) AND FIELD INTENSITY ( $E$ ) AT THE ION CENTRES FOR TWO-SPHERES AND SPHEROIDAL CAVITY MODELS AT CONTACT SEPARATION

$\epsilon'$	Two-spheres Model			Spheroidal Model				
	$\epsilon_{\text{eff}}$	$\mu$ (debye)	$E \times 10^{-6}$ (e.s.u.)	$f(1)$	$g(1)$	$\lambda_f$	$\mu$ (debye)	$E \times 10^{-6}$ (e.s.u.)
1	84.23	0.0332	0.0022	1.35	0.936	-0.8	3.5633	0.2352
5	83.78	—	0.0015	1.25	1.007	0.6	—	0.0913
2.5	83.95	0.0133	0.0018	1.20	0.942	0.4	0.7751	0.0498

Now an inspection of Table 1 shows that this criterion is not satisfied at contact separation and so we expect the transition from the two-spheres to the spheroidal cavity model to be unsatisfactory in taking account of the water molecules in the first hydration shell. A possible alternative is to match the spheroid onto the truncated spheres model at some smaller separation  $R/2a_0 = 0.9$ , say, for then the change in cavity shape is not so pronounced. Some preliminary calculations are now carried out on the dielectric cavity model  $\epsilon' = 5$  in order to ascertain whether such a matching could meet with more success.

We know from L.R. that the force between the ions can be made continuous by varying the factors  $f$  and/or  $g$  in accordance with (18) and (19). It is therefore sufficient, in the first stage of the matching procedure, to make the interaction energy continuous and to find a spheroidal shape for which the electric field intensity at the ion centres is also continuous, at least, if this is possible. Figure 4 shows the  $f$  versus  $g$  relation, which allows matching in the energy at  $R/2a_0 = 0.9$ .

It is seen that the smallest possible volume factor  $f = 1.13$  gives the best result, for then the field intensity at the ion centres changes by a factor of about  $8/5$  during the transition. This is certainly much better than the factor found by matching at contact separation. The assumption that  $|\beta| \ll 1$  is then valid and so there is some hope of using this model to study the redistribution of the water molecules in the

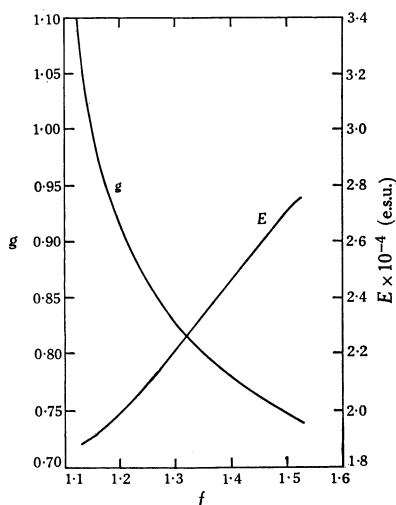


Fig. 4.—Relation between the parameters  $f$  and  $g$  and the field intensity  $E$  at the ion centres, which allows matching in the energy at  $R/2a_0 = 0.9$  ( $\epsilon' = 5$ ).

first hydration shells associated with their overlap. However, the field intensity between the two ions increases with decreasing separation and a stage is reached where the water molecules begin to interlock and where it is no longer possible to represent the charge distribution of the two ion complexes by a set of multipoles placed at the two ion centres. Perhaps a better approach is to examine an arrangement of water molecules *in vacuo* at close proximity and to find out what is the effect of surrounding these molecules with an aqueous medium. Such an approach has been used by Eley and Evans (1938) and Buckingham (1957) with a more recent development by Coulson and Eisenberg (1966). A discussion of this model has been developed by the author and will be presented in a subsequent paper.

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