

Interactions in Polar Media. I. Interparticle Interaction Energy

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(Received 15 November 1962)

Using permanent plus induced charge distributions on particles a Hartree method is used to compute the polar contribution to the interparticle interaction energy. Each particle may be a single molecule or a collection of molecules, a whole electrode or an entire medium for example. The total interparticle interaction energy is taken to be the sum of this polar term and of an interparticle electron correlation term. The second of these includes effects due to interparticle London dispersion and exchange repulsion forces. A symmetry property associated with a quantum mechanical operator characterizing the induced charge distribution is obtained in a compact way using a projection operator. The polar term is also calculated from classical electrostatics and shown to be the same as the one above. The present work is a generalization of earlier treatments in which the particles were single molecules interacting via permanent and induced dipoles.

An application of this work is the more general formulation of theories associated with polar interactions in condensed phases, such as the theory of electron transfer rates in solution and at electrodes, and the theory of electronic spectral shifts and band broadening of polar solutes in polar media.

INTRODUCTION

IN theoretical analyses of dielectric properties of condensed phases each molecule is usually treated as having a permanent dipole plus an induced dipole proportional to the reaction field acting on it.¹⁻³ In many calculations, this neglect of higher permanent and induced multipoles is both convenient and, as a

first approximation, correct. However, for purposes of establishing certain general properties of various phenomena it introduces assumptions which are not only unnecessary but which also lead to an unduly complex notation. For example, on the basis of this dipole approximation one can deduce some formal relations involving the effects of polar solvent-solute interactions on electronic spectra, on electron transfer rates in solution, and on rates of electrochemical electron transfers.⁴ However, they can also, be derived—in fact, more simply—from a more general model of polar interactions.⁵

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¹ See, for example, reviews: H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, London, 1950); C. F. H. Böttcher, *Theory of Electric Polarization* (Elsevier Publishing Company, New York, 1952); W. F. Brown, Jr., *Encyclopedia of Physics* edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 17.

² M. Mandel and P. Mazur, *Physica* 24, 116 (1958); cf. W. F. Brown, Jr., *ibid.* 24, 695 (1959).

³ Permanent multipoles have been included by L. Jansen, *Phys. Rev.* 110, 661 (1958).

⁴ R. A. Marcus, *Discussions Faraday Soc.* 29, 21 (1960) and unpublished work.

⁵ R. A. Marcus, *J. Chem. Phys.* (to be submitted).

In the present paper, a more general model for polar interactions in condensed media is described. It can be shown that a number idealized models of molecules, or of an entire medium, or of an electrode also satisfy the same formal equations. Thus, when theories of these phenomena are based on the above model a variety of more specific ones are automatically included as well. For this reason, use of the model has permitted the development of a unified theory for electron transfer rates in solution and at electrodes.⁵

INTERPARTICLE INTERACTION ENERGY

Usually, the intermolecular interaction energy of any configuration of the nuclei in a macroscopic system is taken to be the sum of London dispersion, exchange repulsion and classical permanent and induced-dipole electrostatic terms. For certain formal calculations such detailed assumptions are not needed. Rather, we may consider the macrosystem to be composed of particles, each particle having a specified set of nuclei in a fixed configuration, which is later permitted to vary. Each particle may, for example, be a molecule or any collection of molecules (a whole electrode, for example). The total electronic energy of the system at any specified nuclear configuration is the sum of the electronic energies of the isolated particles, each having a specified configuration, and of the interparticle interaction energy. It is desired to calculate this interparticle term, i.e., to calculate the work required to bring the particles together from infinity.

As discussed later, we assume that the interparticle interaction energy is the sum of a polar term and an interparticle electron-correlation term. (Among the contributions to the second would be those arising from interparticle London dispersion and exchange repulsion interactions.) We define this polar term to be the interaction energy calculated when electronic wavefunction of the macrosystem is assumed to be the best product of antisymmetrized many-electron wavefunctions, one for each particle. As shown later, a polar term so defined is then equal to the classical electrostatic interaction energy of one-electron charge densities on the particles. The best such wavefunction is the one which minimizes the energy. That is, we shall employ a Hartree-type treatment in which the component wavefunctions are many-electron ones rather than the usual one-electron functions of the atomic Hartree method.

Let X be the electronic wavefunction of the system and X_i the antisymmetrized electronic wavefunction of particle i . Let each X_i be normalized to unity.

$$X = \prod_i X_i. \quad (1)$$

When the interparticle interaction is removed, each X_i reduces to the exact wavefunction X_i^0 for the isolated i particle. In case the eigenspaces Ω_i and Ω_i^0 to which X_i and X_i^0 respectively belong are degenerate, a pre-

cise definition of X_i^0 is given later. Let H_i^0 be the Hamiltonian for an isolated i and let E_i^0 be the corresponding electronic energy:

$$H_i^0 X_i^0 = E_i^0 X_i^0. \quad (2)$$

Let H_{ij} be the coulombic interaction of the electrons and nuclei of i with those of j . (H_{ij} is the sum of the pertinent $1/r$ terms). The Hamiltonian of the entire system H is therefore

$$H = \sum_i H_i^0 + \frac{1}{2} \sum_{i \neq j} \sum_j H_{ij}. \quad (3)$$

We shall use the symbol $(\ , \)$ to denote the pertinent inner product, e.g., (X, HX) is $\int X^* HX d\tau$, where one integrates over all electron coordinates τ of the entire system. $(X_i, V_i X_i)$ is $\int X_i^* V_i X_i d\tau_i$, integration being over all electron coordinates τ_i of particle i . $(X_i X_j, v_{ij} X_i X_j)$ is $\int X_i^* X_j^* V_{ij} X_i X_j d\tau_i d\tau_j$, etc.

Minimizing (X, HX) with respect to variations in each X_i , subject to constancy of (X, X) , X_i is found in a standard way to be the solution of (4). The total energy $E = (X, HX)/(X, X)$, is found to be given by (6), when (3) to (5) are used.

$$(H_i^0 + V_i - E_i) X_i = 0, \quad (4)$$

where E_i is a Lagrangian multiplier, and V_i is the sum of coulombic attraction terms of the electrons of particle i with the nuclei of all j , $\sum_j v_{ij}$, and of v_{ij} , the internuclear and interelectron repulsion of i and j , averaged over the electronic distribution of all $j \neq i$, and of $\sum_j v_{ij}$, the Coulombic attraction of the nuclei of i with electrons of all $j \neq i$, averaged over the electronic distribution of the j 's.

$$V_i = \sum_j v_{ij} + \sum_j (X_j, [v_{ij} + v_{ji}] X_j), \quad (5)$$

$$E = \sum_i E_i - \frac{1}{2} \sum_{i \neq j} \sum_j (X_i, X_j, v_{ij} X_i X_j) - \sum_{i \neq j} \sum_j (X_i, v_{ij} X_j). \quad (6)$$

where we have normalized X , i.e., have set $(X, X) = 1$. E^{pol} , the polar contribution to the interparticle interaction energy is given by (7):

$$E^{\text{pol}} = E - \sum_i E_i^0. \quad (7)$$

We wish to obtain an expression for E^{pol} in terms of charge densities. If particle i has N electrons (coordinates $\mathbf{r}_1, \dots, \mathbf{r}_N$) and nuclei $a, b, \dots$ (coordinates $\mathbf{r}_a, \mathbf{r}_b, \dots$ and charges $Z_{ae}, Z_{be}, \dots$), then the total charge density of particle i , $\rho_i(\mathbf{r})$, is the sum of electronic and nuclear terms $\rho_i^e(\mathbf{r})$ and $\rho_i^n(\mathbf{r})$:

$$\begin{aligned} \rho_i(\mathbf{r}) = N e \int \dots \int X_i^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \\ \times (\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N \\ + X_i \sum_a Z_{ae} \delta(\mathbf{r} - \mathbf{r}_a) = \rho_i^e(\mathbf{r}) + \rho_i^n(\mathbf{r}), \end{aligned} \quad (8)$$

where δ is the Dirac δ function. N and a should bear a subscript i , but we omit it for brevity. The charge density on the isolated particle i is

$$\rho_i^0(\mathbf{r}) = Ne \times \int \dots \int \frac{X_i^{0*}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) X_i^0(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N}{(X_i^0, X_i^0)} + \sum_a Z_a e \delta(\mathbf{r} - \mathbf{r}_a). \quad (9)$$

The induced charge density ρ_i^{in} is the difference:

$$\rho_i = \rho_i^0 + \rho_i^{\text{in}}. \quad (10)$$

Equation (5) for V_i can be written in terms of these ρ_i 's:

$$V_i(\mathbf{r}_1 \dots \mathbf{r}_N) = e \sum_{m=1}^N \Phi_i(\mathbf{r}_m) + \sum_j [v_{ij}^n + (X_{ij}, v_{ij} X_j)], \quad (11)$$

where

$$\Phi_i(\mathbf{r}) = \sum_{j \neq i} \int \frac{\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (12)$$

and v_{ij}^n is the internuclear repulsion between particles i and j . To express E^{p01} in terms of the ρ 's we first introduce a parameter λ into Eq. (4):

$$(H_i^0 + \lambda V_i - E_i^\lambda) X_i^\lambda = 0. \quad (13)$$

Application of the Hellman-Feynmann theorem⁶ to (13) yields

$$\partial E_i^\lambda / \partial \lambda = (X_i^\lambda, V_i X_i^\lambda), \quad (14)$$

since $\partial(\lambda V_i) / \partial \lambda$ equals V_i . Integrating from 0 to 1 we find

$$E_i = E_i^0 + \int_{\lambda=0}^1 (X_i^\lambda, V_i X_i^\lambda) d\lambda. \quad (15)$$

Introducing (8) and (11) into (15), and noting that ρ_i^n is independent of λ one obtains (16) after some manipulation:

$$E_i = E_i^0 + \int_{\lambda=0}^1 \int \rho_i^\lambda \Phi_i d\mathbf{r} d\lambda. \quad (16)$$

Similarly, when (8) is introduced into the last two terms of (6) they yield

$$-\frac{1}{2} \sum_{i \neq j} \sum_j \iint \frac{\rho_i(\mathbf{r}) \rho_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|},$$

i.e.,

$$-\frac{1}{2} \sum_i \int \rho_i \Phi_i d\mathbf{r},$$

in virtue of (12). Combining this result with (6), (7), and (16) we obtain

$$E^{p01} = \sum_i \iint \rho_i^\lambda \Phi_i d\mathbf{r} d\lambda - \frac{1}{2} \sum_i \int \rho_i \Phi_i d\mathbf{r}. \quad (17)$$

Noting that ρ_i^λ equals $\rho_i^{\text{in}\lambda} + \rho_i^0$ (only $\rho_i^{\text{in}\lambda}$ depends on λ) and that $\frac{1}{2}$ equals

$$\int_0^1 \lambda d\lambda,$$

Eq. (17) can be written in the final form:

$$E^{p01} = \frac{1}{2} \sum_i \int \rho_i^0 \Phi_i d\mathbf{r} + \sum_i \int_{\lambda=0}^1 \int (\rho_i^{\text{in}\lambda} - \lambda \rho_i^{\text{in}}) \Phi_i d\mathbf{r} d\lambda, \quad (18)$$

where Φ_i is given by (12).

When ρ_i^{in} is linear in Φ_i , i.e., when the electronic response of i is linearly dependent on the perturbing potential field, $\rho_i^{\text{in}\lambda}$ equals $\lambda \rho_i^{\text{in}}$ and the second integral vanishes:

$$E^{p01} = \frac{1}{2} \sum_i \int \rho_i^0 \Phi_i d\mathbf{r}. \quad (19)$$

This assumption of linear response is usually made in the more specific models.

To complete the equations of this section, an equation is needed relating ρ_i^{in} to Φ_i . It is obtained in a compact way via projection operators:

Let P_i^0 be the operator which projects functions of the electron coordinates of particle i onto the eigenspace Ω_i^0 corresponding to E_i^0 . Let the eigenspace Ω_i corresponding to E_i be spanned by functions $X_{i\alpha}$, the dimension of Ω_i being equal to the degeneracy of Ω_i . The functions $X_{i\alpha}^0$ are then defined by (20), and the operator P_i^0 can be written as in (21)⁷:

$$P_i^0 X_{i\alpha} = X_{i\alpha}^0, \quad (20)$$

$$P_i^0 = \sum_{\alpha} (X_{i\alpha}, \quad) X_{i\alpha}^0 = \sum_{\alpha} P_{i\alpha}^0, \quad (21)$$

$$P_{i\alpha}^0 = (\bar{X}_{i\alpha}^0, \quad) X_{i\alpha}^0, \quad (22)$$

where the functions $\bar{X}_{i\alpha}^0$ are biorthogonal to $X_{i\alpha}^0$:

$$(\bar{X}_{i\alpha}^0, X_{i\beta}^0) = \delta_{\alpha\beta}. \quad (23)$$

We normalize $X_{i\alpha}$ and adjust $X_{i\alpha}^0$ so as to satisfy (24):

$$(X_{i\alpha}, X_{i\alpha}) = 1, \quad (X_{i\alpha}^0, X_{i\alpha}) = 1, \quad (24)$$

i.e., $X_{i\alpha}^0$ is not normalized. We shall focus attention on one particular $X_{i\alpha}$ and its $X_{i\alpha}^0$, and omit the α in the following notation (except in $P_{i\alpha}^0$ to avoid ambiguity). From the inner product of (4) with this $X_{i\alpha}^0$ and from the Hermitian nature of H_i^0 , with the aid of Eqs. (2) and (24), one obtains (25), and from (4) and (25), one obtains Eq. (26):

$$E_i = E_i^0 + (X_{i\alpha}^0, V_i X_{i\alpha}), \quad (25)$$

$$(E_i^0 - H_i^0) X_{i\alpha} = [V_i - (X_{i\alpha}^0, V_i X_{i\alpha})] X_{i\alpha}. \quad (26)$$

⁶ H. Hellmann, *Einführung in die Quantenchemie* (F. Deuticke, Leipzig, 1937); R. P. Feynmann, Phys. Rev. 56, 340 (1939).

⁷ The projection operator P_i^0 corresponds to one used by C. Bloch for a different purpose [Nucl. Phys. 6, 329 (1958)]. His P_0 , $|\alpha\rangle$, $|\alpha\rangle_0$, and $|\bar{\alpha}\rangle_0$ correspond to our $P_{i\alpha}^0$, $X_{i\alpha}$, $X_{i\alpha}^0$, and $\bar{X}_{i\alpha}^0$, respectively. His Fig. 1 gives an excellent picture of these vectors and of this operator.

From the definition of $P_{i\alpha}^0$, the rhs of (25) can be written as $(1-P_{i\alpha}^0)V_iX_i$. Noting⁸ that

$$(1-P_i^0)(1-P_{i\alpha}^0)$$

equals $1-P_i^0$, then applying $1-P_i^0$ and $(E_i^0-H_i^0)^{-1}$ to (26) (an order dictated by the fact that the inverse of $E_i^0-H_i^0$ exists only on the orthogonal complement of Ω_i^0), one obtains (27) for X_i :

$$X_i - X_i^0 = B_i V_i X_i, \quad (27)$$

where we have used the idempotent property of the projection operator $1-P_i^0$ and where B_i is a Hermitian operator^{9,10}

$$B_i = (E_i^0 - H_i^0)^{-1}(1 - P_i^0) \quad (28)$$

One could solve Eq. (27) formally for X_i in terms of V_i and X_i^0 , so obtaining an expression for ρ_i^{in} when (8) to (10) are used. When ρ_i^{in} is assumed to be linear in Φ_i , the corresponding approximation in (27) is obtained by replacing X_i on the rhs by X_i^0 , as may be shown by an iteration procedure. Thereby,

$$X_i = X_i^0 + B_i V_i X_i^0 + O[V_i^2], \quad (29)$$

where O denotes "order of."

To this same approximation, the induced many-electron probability density p_i^{in} , given by (30), can be written as (31):

$$p_i^{\text{in}} = X_i^* X_i - X_i^{0*} X_i^0 / (X_i^0, X_i^0) \quad (30)$$

$$= 2 \operatorname{Re} X_i^{0*} (X_i - X_i^0) + O[V_i^2], \quad (31)$$

where Re denotes "real part of" and where we have used the fact that terms quadratic in $X_i - X_i^0$ are at least quadratic in V_i , because of (29). From (29) and (31), and neglecting $O[V_i^2]$, we find

$$p_i^{\text{in}} = 2 \operatorname{Re} X_i^{0*} B_i V_i X_i^0, \quad (32)$$

ρ_i^{in} is obtained by multiplying p_i^{in} by Ne and integrating over the coordinates of all electrons but one.

⁸ It equals $1 - P_i^0 - P_{i\alpha}^0 + P_i^0 P_{i\alpha}^0$. But from (21) to (23) $P_i^0 P_{i\alpha}^0$ equals $P_{i\alpha}^0$.

⁹ Using the idempotency of $1 - P_i^0$ and its commutativity with $(E_i^0 - H_i^0)^{-1}$, we have

$$B_i = (E_i^0 - H_i^0)^{-1}(1 - P_i^0)^2 = (1 - P_i^0)(E_i^0 - H_i^0)^{-1}(1 - P_i^0)$$

The commutativity followed from the fact that both operators are functions of H_i^0 in an operational calculus.¹⁰ Since B_i is seen to be a symmetrical product of factors, each of which is Hermitian, it is Hermitian.

In the chemical literature the operator B_i normally appears as an infinite sum (and integral when part of the spectrum of eigenvalues is continuous), which one can find by solving any equation $(E_i^0 - H_i^0)W = Z(Z \perp \Omega_i^0)$ for W by expanding W in a complete set of eigenfunctions of H_i^0 . The answer for W can then be equated to $W = (E_i^0 - H_i^0)^{-1}(1 - P_i^0)Z$ and B_i can be obtained thereby.

¹⁰ cf. A. E. Taylor, *Introduction to Functional Analysis* (John Wiley & Sons, Inc., New York, 1958), p. 287 for discussion of a calculus of operators and for this commutativity property.

Introducing (11), we obtain

$$\rho_i^{\text{in}}(\mathbf{r}_1) = 2Ne \operatorname{Re} \int X_i^{0*}(\mathbf{r}_1, \dots, \mathbf{r}_N) B_i \times \sum_{m=1}^N \Phi_i(\mathbf{r}_m) X_i^0(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (33)$$

since the last sum in (11) is independent of the electronic coordinates of i and since $(1 - P_i^0)X_i^0$ vanishes. Thus, ρ_i^{in} is linearly dependent on Φ_i via a linear operator, which we call A_i , namely

$$\rho_i^{\text{in}}(\mathbf{r}) = A_i(\mathbf{r}, \mathbf{r}') \Phi_i(\mathbf{r}'). \quad (34)$$

A_i is shown in the next section to be a symmetric operator when it acts on the space of potentials, Φ_i . Equations (10), (12), (19), (34), and this symmetry property represent the essence of the present formalism. It is shown elsewhere that various more idealized models of the particles also satisfy these equations, once A_i is properly chosen. It is perhaps worthwhile to emphasize that Eqs. (10), (12), (19), and (34) apply even if there are only several "particles," all but one of these being individual molecules, and the last being the remainder of the macrosystem. Use of this particular case is made elsewhere.

SYMMETRY PROPERTY OF A_i

We wish to show that A_i has the property

$$\int \Phi_{i1} A_i \Phi_{i2} d\mathbf{r} = \int \Phi_{i2} A_i \Phi_{i1} d\mathbf{r}, \quad (35)$$

where 1 and 2 denote two macroscopic systems differing in corresponding ρ_i^0 's but not in the position of their nuclei nor in corresponding A_i 's. Equation (35) can be rewritten as

$$\int \Phi_{i1} \rho_{i2}^{\text{in}} d\mathbf{r} = \int \Phi_{i2} \rho_{i1}^{\text{in}} d\mathbf{r}. \quad (36)$$

If a molecule i is to have the same A_i in the two systems, then p_i^{in} of Eq. (32) should depend only on V_i . That is, we have from (32)

$$p_i^{\text{in}} = 2 \operatorname{Re} X_i^{0*} B_i V_i X_i^0, \quad (37)$$

where the X_i^0 is to be taken as the same for both systems 1 and 2.

Since B_i is Hermitian we have:

$$\operatorname{Re}(V_{i1} X_i^0, B_i V_{i2} X_i^0) = \operatorname{Re}(V_{i2} X_i^0, B_i V_{i1} X_i^0). \quad (38)$$

Using (11), (37), and noting that the second term on the rhs of (11) is independent of the electron coordinates of i and that p_i^{in} vanishes when integrated alone over those coordinates, (36) then follows from (38).

Equation (36) can also be used to derive an equation which will be extensively used elsewhere. Summing (36) over i and using (12); one finds by subtraction of

a term common to both sides

$$\sum_{i \neq j} \sum_j \iint \frac{\rho_{i1}^{\text{in}}(\mathbf{r}) \rho_{j2}^{\text{in}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|},$$

addition of

$$\sum_{i \neq j} \sum_j \iint \frac{\rho_{i1}^0(\mathbf{r}) \rho_{j2}^0(\mathbf{r}') d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}$$

to both sides, and use of (12) that

$$\sum_i \int \rho_{i1}^0 \Phi_{i2} d\mathbf{r} = \sum_i \int \rho_{i2}^0 \Phi_{i1} d\mathbf{r}. \quad (39)$$

REMARKS ON APPLICATION TO ELECTRODE SYSTEMS AND ON IDEALIZED MODELS

It will be shown in Part II that when any of the particles is treated as a dielectric continuum having a specified nuclear configuration, Eqs. (10), (12), (19), and (34) are still formally satisfied. The appropriate A_i is then expressible in terms of certain electrostatic properties. In the standard electrostatic calculations on electrode systems, i.e., on electrode-ion-solvent interactions, the electrode is treated as a dielectric continuum of infinite dielectric constant. Accordingly, this classical treatment of polar interactions between electrodes and particles in solution is also automatically included in any treatment based on the above four equations. Alternatively, these equations are also valid for more general models for the electrode in which A_i is obtained quantum-mechanically from (33).

Another special case of Eqs. (10), (12), (19), and (34), occurs when each particle is a molecule and when only its dipolar contributions to ρ_i^0 and ρ_i^{in} are considered. This case is obtained by expanding ρ_i^0 and, in (33), Φ_i in a Taylor's series and retaining the initial term in each case. The corresponding values of ρ_i^0 and A_i can be written as

$$\rho_i^0(\mathbf{r}) = -\nabla_r \delta(\mathbf{r} - \mathbf{r}_i^0) \cdot \mathbf{u}_i, \quad (40)$$

$$A_i(\mathbf{r}, \mathbf{r}') = \nabla_r \delta(\mathbf{r} - \mathbf{r}_i^0) \cdot \alpha_i \nabla_{r'} \int d\mathbf{r}'' \delta(\mathbf{r}' - \mathbf{r}_i^0), \quad (41)$$

where $\mathbf{r}_i^0$ is the center of charge, not necessarily assumed to be the same for the permanent and induced terms, $\mathbf{u}_i$ is the dipole moment, α_i the polarizability tensor (or scalar). The subscript to ∇ indicates the variable to be differentiated. It is understood that a $\Phi_i(\mathbf{r}')$ is to be placed on the right of both sides of Eq. (41).

RELATED APPROACHES TO THE INTERMOLECULAR ENERGY

A comparatively recently derived expression for the polar term in the intermolecular energy has been given by Mandel and Mazur,¹¹ as well as by Brown,¹² who

based their arguments on classical electrostatics and considered permanent and induced point dipoles. As they have pointed out, many earlier expressions for this term were either incomplete or wrong. Their expression is obtained from Eqs. (10), (12), (19), and (34), upon introducing the dipole approximation embodied in Eqs. (40) and (41).

Another calculation of the polar contribution to the intermolecular potential energy as well as other terms was based on solving the Schrödinger equation using third-order Rayleigh-Schrödinger perturbation theory and neglecting electron exchange.¹³ To this order, a portion of the polar term was obtained, with the additional modification that the polarizability operator was affected by the London dispersion forces. This coupling term was used in partial explanation of minor deviations from the Clausius-Mosotti equation applied to nonpolar gases.¹⁴ Similarly, exchange effects also modify the polarizability.¹⁵ However, it appears that the polarizability calculated from refractive index data on very dilute gases differs relatively slightly from that calculated from similar data on condensed phases of the same substance, and such coupling terms have been disregarded in the present paper.¹⁶ The Rayleigh-Schrödinger perturbation theory as just used is appropriate for dilute gases but not for condensed phases, where it becomes unwieldy because of many-body interactions. In each order of perturbation a variety of contributions occur, varying in importance, and the theory does not separate them.

One treatment more suited to these many-body interactions might be one analogous to that used for intramolecular interactions: a Hartree-Fock treatment for interactions followed by a method introducing electron correlation. In a more general but formal analysis McWeeny has used a wavefunction which is an antisymmetrized product of antisymmetrized many-electron wavefunctions of each molecule.¹⁷ (A special case of this is a Hartree-Fock product.) Such a product contained only electron correlation between electrons of like spin. Configuration interaction was then used

¹³ L. Jansen and P. Mazur, *Physica* **21**, 193 (1955) and reference 3.

¹⁴ P. Mazur and L. Jansen, *Physica* **21**, 208 (1955).

¹⁵ For example, see C. A. Ten Seldam and S. R. de Groot, *Physica* **18**, 905, 910 (1952), who regarded the electrons as being confined to a box.

¹⁶ For example, C. P. Smyth, *Dielectric Behavior and Structure* McGraw-Hill Book Company, Inc., New York, 1955) for data on gaseous and solid benzene ($4\pi\alpha/3 = 26.6$ and $26.7-28.5$, respectively.); cf. F. G. Keyes and J. G. Kirkwood, *Phys. Rev.* **36**, 754 (1930), for data on gaseous and liquid CO_2 ($4\pi\alpha/3 = 7.49$ at 10 atm and 7.81, respectively); cf. C. P. Smyth, E. W. Engel, and E. B. Wilson, Jr., *J. Am. Chem. Soc.* **51**, 1736 (1929), who found additivity of molar refraction in liquid media. The latter reference also refers to data of Lorentz and others on gases and liquids, which are found to have the same α , within 1-3% when this α is obtained from the Lorentz-Lorenz expression. Strictly speaking, this expression is appropriate to cubic crystals, and α_{solid} should be determined from the data on crystals by an equation derived for the pertinent crystal type and then compared with α_{gas} .

¹⁷ R. McWeeny, *Proc. Roy. Soc. (London)* **A253**, 242 (1959).

¹¹ M. Mandel and P. Mazur, *Physica* **24**, 116 (1958).

¹² W. F. Brown, Jr., *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956, Vol. 17, p. 1; *Physica* **24**, 695 (1958)).

to introduce additional correlation, including that of the London dispersion type. To terms second order in the configuration interaction, the intermolecular potential energy was the sum of a term arising from a single configuration plus a correlation term. The same remarks apply to the interparticle potential energy, merely by choosing the wavefunction to be an antisymmetrized product of wavefunctions for each particle, and then adding the other antisymmetrized products of particle wavefunctions. The Hartree expression discussed earlier is an approximation to a portion of the single configuration term, and is what we have called the polar contribution.

COMPARISON WITH THE ELECTROSTATIC CALCULATION

A consequence of the Hartree approximation of the preceding section and of the corresponding absence of electron correlation was that the equations for E^{pol} could be expressed in terms of one-electron charge densities and their properties. Accordingly, one might anticipate perhaps that Eq. (18) can be obtained from purely electrostatic considerations, although the values of both ρ_i^0 and ρ_i^{in} themselves can only be determined quantum mechanically. This conjecture turns out to be true.

To calculate E^{pol} from electrostatics we use a method rather similar to that used previously for the dipolar case on a macroscale,¹⁸ applied now to the present multipolar problem on a microscopic scale. (Another way of obtaining the same result, more directly but less illustratively, is given in Part II). The electrostatic energy of interaction between the particles can be regarded as the sum of:

(i) interaction of the permanent charge distributions,

$$\frac{1}{2} \sum_{i \neq j} \sum_j \iint \frac{\rho_i^0(\mathbf{r}) \rho_j^0(\mathbf{r}') d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}.$$

The $\frac{1}{2}$ avoids double counting.

(ii) interaction of the permanent and induced charge distributions,

$$\sum_{i \neq j} \sum_j \iint \frac{\rho_i^0(\mathbf{r}) \rho_j^{\text{in}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}.$$

(iii) interaction of the induced charge distributions,

$$\frac{1}{2} \sum_{i \neq j} \sum_j \iint \frac{\rho_i^{\text{in}}(\mathbf{r}) \rho_j^{\text{in}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}.$$

(iv) energy stored in the induced charge distributions,

$$\sum_i \int_{\lambda=0}^1 \int (\rho_i^{\text{in}\lambda} - \rho_i^{\text{in}}) \Phi_i d\mathbf{r} d\lambda,$$

where λ is a parameter and where $\rho_i^{\text{in}\lambda}$ depends on

$\lambda \Phi_i$ via the same operator that ρ_i^{in} depends on Φ_i . The operator need not be linear. The energy stored in i is computed as follows: Consider particle i under the influence of an external potential field $V^\lambda = \lambda V$. The work done when V^λ is increased from 0 to V is

$$\int_{\lambda=0}^1 \int (\rho_i^{\text{in}\lambda} + \rho_i^0) dV^\lambda d\mathbf{r}, \quad \text{i.e.,} \quad \int_{\lambda=0}^1 \int (\rho_i^{\text{in}\lambda} + \rho_i^0) V d\mathbf{r} d\lambda.$$

To obtain the energy "stored" one must subtract the interaction energy of the final ρ_i with V , $\int (\rho_i^{\text{in}} + \rho_i^0) V d\mathbf{r}$. Multiplying the latter by

$$\int_{\lambda=0}^1 d\lambda,$$

term (iv) is obtained.

Adding (i) to (iv) we have

$$\begin{aligned} E^{\text{pol}} &= \frac{1}{2} \sum_{i \neq j} \sum_j \iint \frac{\rho_i(\mathbf{r}) \rho_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \\ &\quad + \sum_i \iint \rho_i^{\text{in}\lambda} \Phi_i d\mathbf{r} d\lambda - \sum_i \int \rho_i^{\text{in}} \Phi_i d\mathbf{r} \\ &= \frac{1}{2} \sum_i \int \rho_i^0 \Phi_i d\mathbf{r} + \sum_i \int \rho_i^{\text{in}\lambda} \Phi_i d\mathbf{r} d\lambda - \sum_i \iint \rho_i^{\text{in}} \Phi_i d\mathbf{r}, \quad (42) \end{aligned}$$

where we have used Eq. (12). Comparison of Eqs. (18) and (42) for E^{pol} shows that they are indeed identical, since $\int_0^1 \lambda d\lambda$ equals $\frac{1}{2}$.

Parenthetically, it may further be noted that terms (i) to (iv) have their quantum-mechanical counterparts.

Taking the inner product of (4) with X_i , we find

$$E_i = (X_i, H_i^0 X_i) + (X_i, V_i X_i). \quad (43)$$

E^{pol} is then obtained from (6), (7), and (43):

$$\begin{aligned} E^{\text{pol}} &= \sum_i [(X_i, H_i^0 X_i) - E_i^0 + (X_i, V_i X_i)] \\ &\quad - \frac{1}{2} \sum_{i \neq j} \sum_j (X_i X_j, v_{ij} X_i X_j) - \sum_{i \neq j} \sum_j (X_j, v_{ij} X_i). \quad (44) \end{aligned}$$

The term $(X_i, H_i^0 X_i)$ is the energy "stored in i ." That is, it is the energy stored in i is isolated, E_i^0 , plus the additional amount stored due to the perturbation. Thus, term (iv) is $\sum_i [(X_i, H_i^0 X_i) - E_i^0]$. The remaining terms in (44) are Coulombic ones and are easily shown to be the sum of (i) to (iii).

ACKNOWLEDGMENT

This research was supported by the Alfred P. Sloan Foundation and the National Science Foundation. A portion of it was performed at the Courant Institute of Mathematical Sciences, New York University, under the tenure of a National Science Foundation Senior Post-Doctoral Fellowship.

¹⁸ R. A. Marcus, J. Chem. Phys. 24, 979 (1956).