Dispersion contribution to two-atom interaction energy: multipole interactions

D D Richardson

Research School of Physical Sciences, The Australian National University, Canberra, ACT 2600, Australia

Abstract. This paper gives a theory of non-retarded dispersion interaction energy of molecules with charge distributions on them that readily allows inclusion of higher-order multipole interactions. The two-particle dispersion energy for a pair of harmonic oscillators is evaluated for dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions. It also is found that the dispersion energy remains finite for all separations between the oscillators, supporting the earlier result of Mahanty and Ninham for dipole–dipole interactions with distributed dipole moments.

1. Introduction

Several papers have recently appeared concerned with calculating particle self-energies and the interaction energy between systems of two or more finite-sized particles (Mahanty and Ninham 1973, 1975, Mahanty 1974, Mahanty and Richardson 1975). These papers are all based on the notion that the presence of other atoms near an atom perturbs the electronic charge density surrounding it, setting up a polarization density in the atom, which in turn produces an electromagnetic field to perturb the surrounding atoms. The change in the overall electromagnetic field modes is responsible for the dispersion interaction energy between the atoms.

One important aspect of these calculations is the evaluation of the dispersion energy between pairs of neutral atoms or molecules. Such energies are of importance in the calculation of the properties of rare gas liquids, for example. Mahanty and Ninham (1975) have indicated that the two-particle dispersion energy for the dipole–dipole interaction does not diverge at zero separation if the finite size of the molecules is taken into account.

In this paper is presented a more rigorous theory of dispersion energy than has previously been made based on the field mode theory of Mahanty and Ninham (1973, 1975). The non-retarded limit, only, is considered here and we ignore the effect of permanent multipoles. The present theory readily lends itself to inclusion of higher-order multipole interactions than dipole–dipole and we present a two-particle dispersion energy calculation which incorporates dipole–quadrupole and quadrupole–quadrupole interactions as well.

This paper is arranged as follows: in § 2 we present the theory which will enable us to include higher-order multipoles in the dispersion interaction. At the end of the section we discuss the relation between the present expression for dispersion energy and the more usual result from time-independent perturbation on the Coulomb potential. In

§ 3 we present the dipole–dipole, dipole–quadrupole and quadrupole–quadrupole results for a pair of interacting harmonic oscillators and discuss some features of the results.

2. Atom pair dispersion interaction energy

Historically, the dispersion interaction between two molecules was evaluated using perturbation theory on the Coulomb interaction between the constituent electrons and nuclei. In recent literature it has been demonstrated that an equivalent formulation of the problem can be made in terms of the effect of the molecules on the electromagnetic field. The dispersion interaction between two atoms can be shown to arise from changes in the electromagnetic field modes and hence the zero-point energy associated with them, due to the presence of the two atoms having a finite separation. Fluctuations in the charge density associated with the electron cloud surrounding each atom lead to the existence of instantaneous multipoles on the atom (assumed to have no permanent multipole moment and spherical charge distribution in the ground state). The fields from these multipoles polarize the other atom and lead to some collective behaviour of the pair, giving the dispersion interaction. In the past the calculations of the force involved have been made by assuming the multipoles are point multipoles located at the centre of each atom, fixed relative to the other. In the present work, by treating the charge density of each atom directly, we are able to obtain a form factor from the formalism which describes each multipole as having a finite size. The calculation avoids the use of time-independent perturbation theory on the Coulomb potential, but finds an expression for the electric field modes around the atoms by means of the atomic charge densities, which are written in a multipole expansion.

The present calculation is summarized as follows: the potential at any point due to the atomic charge densities of both atoms is found by solving Poisson's equation assuming each atomic charge density to be independent of the other. The resultant potential is used to perturb each atom's charge density using time-dependent perturbation theory. An expression for the electric field at any point is obtained in terms of these perturbed charge densities. The charge densities are then expanded in a multipole expansion which is linear in the field at each atom and derivatives of the field. By evaluating the electric field at each atom, and finding its derivatives at each atom, one is able to obtain an infinite-dimension secular determinant which may be evaluated by truncating the multipole expansion to any desired order, to give the change in the modes of the field which cause the dispersion interaction. These modes are used to obtain an expression to order e^4 (e = electronic charge) for the dispersion interaction energy.

We now give the details of the calculation.

Consider two neutral atoms, with no permanent multipoles in their ground states, at positions $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$, with respective atomic charge densities $\rho(\boldsymbol{r} - \boldsymbol{R}_1; \omega)$ and $\rho(\boldsymbol{r} - \boldsymbol{R}_2; \omega)$. The non-retarded field equation for the atom pair is Poisson's equation

$$\nabla_r^2 \phi(\boldsymbol{r}; \omega) = -4\pi \sum_{j=1}^{2} \rho(\boldsymbol{r} - \boldsymbol{R}_j; \omega) \tag{1}$$

which has solution

$$\phi(\boldsymbol{r}; \omega) = -4\pi \sum_{j=1}^{2} \int G(\boldsymbol{r} - \boldsymbol{r}'; \omega) \rho(\boldsymbol{r}' - \boldsymbol{R}_j; \omega) \, \mathrm{d}^3 r' \tag{2}$$

where $G(r; \omega)$ is the scalar Green function

$$G(r; \omega) = -\frac{1}{(2\pi)^3} \int \frac{e^{ik.r}}{k^2} \, d^3k. \tag{3}$$

The electric field is the gradient of the scalar potential, equation (2),

$$\mathscr{E}(r; \omega) = 4\pi \sum_{j=1}^{2} \int \nabla_r G(r - r'; \omega) \rho(r' - R_j; \omega) \, d^3r'. \tag{4}$$

We must now obtain a secular equation to determine the altered field modes which result from the perturbation of one atomic charge cloud by the other. To do this we express the charge density on the right-hand side of equation (4) by a time-dependent perturbation series in which all terms are linear in the electric field or its derivatives. The charge density of either atom is perturbed by the time-dependent perturbation which represents the change in electromagnetic field due to the presence of the other atom:

$$H_1 = \left(\int \rho(r) \phi(r) \, d^3r \right) f(t) \tag{5}$$

where $f(t)$ is a real function of time. For a single-electron atom this reduces to $e\phi(r)f(t)$ where e is the electronic charge, as the contribution from the nucleus to the integral is zero. Details of the calculation, for the one-electron atom, of the first-order perturbation on the charge density are given in appendix 1. To first order the charge density may be written

$$\rho(r; \omega) = \rho_{00}(r) + \rho_1(r; \omega) \, e^{i\omega t} \tag{6}$$

where, for the one-electron atom,

$$\rho_1(r; \omega) = -\frac{e^2}{\hbar} \sum_n \frac{\langle 0|\delta(u-r)|n\rangle \langle n|\phi(u)|0\rangle}{\omega_{0n} - \omega} + \frac{\langle n|\delta(u-r)|0\rangle \langle 0|\phi(u)|n\rangle}{\omega_{0n} + \omega} \tag{7}$$

and u is the integration variable for evaluation of the matrix elements, $\omega_{0n} = (E_0 - E_n)/\hbar$ and the sum is over all the unperturbed electronic states of the individual atom. The zeroth-order term $\rho_{00}(r)$ is the unperturbed charge density of the atom, which for electrons localized close to the nucleus is zero.

The scalar potential $\phi(u)$ appearing in the matrix elements of the perturbed charge density, equation (7), is a solution of Laplace's equation (the homogeneous part of equation (1)) and may be written as a multipole expansion (Podolsky and Kunz 1969) about the centre of each atom, in the form

$$\phi(u) = \phi_0(R_i) + u \cdot \nabla_r \phi(r) \bigg|_{r=R_i} + \frac{1}{2} u_i u_j \frac{\partial^2}{\partial x_i \partial x_j} \phi(r) \bigg|_{r=R_i} + \ldots \tag{8}$$

The $\phi_0(R_i)$ term of the expansion can be shown because of its spherical symmetry to give zero contribution to the perturbed charge density, equation (7). The electric field, equation (4), may thus be written as a multipole expansion in the field at the atom centres, since $\mathscr{E}(R_i) = \nabla_r \phi(r)|_{r=R_i}$, etc.

The secular determinant is now found by using equation (4) to evaluate $\mathscr{E}(R_i)$, $\nabla_r \mathscr{E}(r)|_{r=R_i}$, etc and each of these quantities may be written as an expansion of all the field components and its derivatives, making use of the multipole expansion. In fact, the determinant obtained by elimination of the field and its derivatives is of infinite dimension. To evaluate the dispersion energy the multipole series is truncated to whatever order is desired. We illustrate, by treating only the dipole term of the multipole

expansion, how terms of the secular determinant may be obtained. Then the electric field, equation (4), at $r = R_i$ is written

$$\mathscr{E}(R_j; \omega) = -\frac{4\pi e^2}{(2\pi)^3 \hbar} \sum_{j=1}^{2} \int \frac{ik}{k^2} e^{ik\cdot(R_i - R_j)}$$

$$\times \sum_n \left(\frac{\langle 0|e^{-ik\cdot u}|n\rangle \langle n|u|0\rangle}{\omega_{0n} - \omega} + \frac{n|e^{-ik\cdot u}|0\rangle \langle 0|u|n\rangle}{\omega_{0n} + \omega} \right) d^3k \cdot \mathscr{E}(R_j) \tag{9}$$

$$= -4\pi \sum_{j=1}^{2} \mathscr{G}_{11}(R_i - R_j; \omega) \cdot \mathscr{E}(R_j) \tag{10}$$

where we have performed the integral over r' in equation (4). $\mathscr{G}_{11}(r; \omega)$ is a 3×3 dyadic Green function, which shows several interesting features. Note the presence of the matrix element $\langle 0|e^{-ik\cdot u}|n\rangle$. This matrix element represents a form factor and gives to each multipole, represented by the matrix element multiplied with it, a finite-size value. For the more common case where point multipoles are assumed, $e^{-ik\cdot u}$ is replaced by the first-order term $-ik \cdot u$. Under these circumstances the Green function becomes of the form

$$\mathscr{G}_{11}(r; \omega) = -\frac{\alpha(\omega)}{(2\pi)^3} \sum_{j=1}^{2} \int \frac{kk}{k^2} e^{ik\cdot(r - R_j)} d^3k = \alpha(\omega) \cdot \nabla_r \nabla_r G(r) \tag{11}$$

where $G(r)$ is given in equation (3), and $\alpha(\omega)$ is a polarizability tensor.

As shown below, this expression applies to the time-independent perturbation calculations (eg Margenau and Kestner 1971, Meath 1972) and allows a rigorous definition of the polarizability $\alpha(\omega)$. The form of polarizability chosen by Mahanty and Ninham (1975) is based on the concept of a finite multipole size, but in that paper no attempt was made to show the k-dependence of the polarizability in any rigorous sense, as has been done here. It is the use of a finite-sized multipole which leads to a finite energy (shown to quadrupole order in the next section) as the atoms are brought to coincidence ($R = R_1 - R_2 = 0$) and this result gives twice the zero-point energy of a single atom, represented here by the case when $R_i = R_j$ in equation (10).

In describing the finite-sized property of the dipole we have assumed that other multipoles are similarly of finite size. In fact, it is readily shown that the matrix element $\langle 0|e^{-ik\cdot u}|n\rangle$ appears in all terms of the expression for $\mathscr{E}(R_i; \omega)$, ie if we do not truncate the multipole expansion at the dipole term. We may generalize equation (10) in the form of an expansion in the electric field and its derivatives, making use of the multipole expansion, equation (8), giving

$$\mathscr{E}(R_i; \omega) = -4\pi \sum_{j=1}^{2} \left(\mathscr{G}_{11}(R_i - R_j; \omega) + \mathscr{G}_{12}(R_i, R_j; \omega) \cdot \frac{\partial}{\partial x} \mathscr{E}(r) \Big|_{r=R_j} \right.$$

$$\left. + \mathscr{G}_{13}(R_i, R_j; \omega) \cdot \frac{\partial}{\partial y} \mathscr{E}(r) \Big|_{r=R_j} + \mathscr{G}_{14}(R_i, R_j; \omega) \cdot \frac{\partial}{\partial z} \mathscr{E}(r) \Big|_{r=R_j} + \ldots \right) \tag{12}$$

where the first term gives the dipole term as in equation (9) and $\mathscr{G}_{12}$ has $\langle 0|u|n\rangle$ of $\mathscr{G}_{11}$ replaced by $\langle 0|uu_x|n\rangle$, etc.

In a similar manner, $\nabla_r \mathscr{E}(r; \omega)|_{r=R_i}$ and the higher-order terms are obtained by taking the gradient evaluated at $r = R_i$ of the right-hand side of equation (12). When written in matrix form, we thus obtain an infinite-dimension secular equation

$$|I + 4\pi \mathscr{G}_2| = 0 \tag{13}$$

where $\mathscr{G}_2$ is a dyadic Green function which has 3×3 submatrices given by $\mathscr{G}_{11}$ of equation (10), $\mathscr{G}_{12} \ldots, \mathscr{G}_{1n} \ldots$ of equation (12), $\mathscr{G}_{21} = \nabla_r \mathscr{G}_{11}(r - R_i)|_{r = R_i}$ etc.

Following Mahanty and Ninham (1975) the dispersion energy of the atom pair can be defined as the change in the zero-point energy of the electromagnetic field due to the two atoms, which is given by

$$E_2 = -\frac{\hbar}{4\pi i} \oint d\omega \ln\left(\frac{|\mathbf{I} + 4\pi\mathscr{G}_2|}{\prod_{j=1}^{2} |\mathbf{I} + 4\pi\mathscr{G}(R_j, R_j; \omega)|}\right) \tag{14}$$

where the denominator represents the sum of self-energies of the individual atoms, the Green functions $\mathscr{G}(R_j, R_j; \omega)$ being given by the submatrices of $\mathscr{G}_2$ with $R_i = R_j$, and the contour is taken over the positive real axis.

Making use of the expansion

$$\ln(\mathbf{I} + \lambda\mathbf{S}) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \lambda^n \operatorname{Tr}(\mathbf{S}^n) \tag{15}$$

the two-particle dispersion energy to leading order (ie to order e^4 in electronic charge) is

$$E_2(R) = \frac{4\pi\hbar}{i} \oint d\omega \operatorname{Tr}(\mathscr{G}_2(R_1, R_2; \omega)\mathscr{G}_2(R_2, R_1; \omega)). \tag{16}$$

The present derivation of the two-atom dispersion energy differs considerably from the more usual method which makes use of time-independent perturbation theory on the Coulomb potential to second order (see, for example, Margenau and Kestner 1971, chap 2). We shall complete this section with a discussion of the relation between the two results.

For a system of two neutral single-electron atoms, with no permanent multipoles, and with centre at R_i, $i = 1, 2$, so $R = R_1 - R_2$ as above, and electrons at u_1 and u_2 respectively, the Coulomb potential is given by the multipole expansion (Podolsky and Kunz 1969)

$$U(R) = \sum_{m,n} U_{mn} \tag{17}$$

where

$$U_{mn} = \frac{1}{m!} \frac{1}{n!} e^2 (u_1 . \nabla_{R_1})^m (u_2 . \nabla_{R_2})^n \frac{1}{R} \tag{17a}$$

and e is electronic charge. The factor $1/R$ may be written as the Green function, equation (3), above.

Performing time-independent perturbation on the potential, equation (17), with unperturbed wavefunctions taken as Heitler–London wavefunctions formed from the product of single-atom wavefunctions, it can be shown that the first non zero term is the second-order term, which is written as the dispersion energy

$$\Delta E = \sum_{\lambda} \frac{|V_{0\lambda}|^2}{E_0 - E_\lambda} \tag{18}$$

where the excited state $|\lambda\rangle = |n_1\rangle|n_2\rangle$ in terms of single-atom states, and

$$E_0 - E_\lambda = (E_0^{(1)} - E_{n_1}) + (E_0^{(2)} - E_{n_2})$$

for single-atom ground and excited states $E_0^{(1)}$, $E_0^{(2)}$ and E_{n_1}, E_{n_2}. The matrix element

$V_{0\lambda}$ is given by

$$V_{0\lambda} = \sum_{m,n} \langle 00| U_{mn} |n_1 n_2 \rangle. \tag{19}$$

We now consider only the dipole–dipole term ($m = n = 1$) of the multipole expansion, equation (17). As only the electron coordinates u_1 and u_2 operate on the atomic wavefunctions, we may write

$$
\begin{aligned}
V_{0\lambda} &= 4\pi \langle 00| e^2 (u_1 . \nabla_{R_1})(u_2 . \nabla_{R_2}) G(R_1 - R_2) |n_1 n_2 \rangle \\
&= 4\pi e^2 \langle 0|u_1|n_1 \rangle . \nabla_{R_1} \nabla_{R_2} G(R_1 - R_2) . \langle 0|u_2|n_2 \rangle.
\end{aligned} \tag{20}
$$

The sum over λ is now taken as separate sums over each single-electron atom states.

The Green function for our present calculation, for the point dipole case, is given from equation (11) as

$$\mathcal{G}_{11}(R;\omega) = -\frac{1}{(2\pi)^3} \frac{e^2}{\hbar} \int \frac{kk}{k^2} e^{ik.(R_1 - R_2)} d^3 k \sum_n \left(\langle 0|u|n \rangle \langle n|u|0 \rangle \frac{2\omega_{0n}}{\omega_{0n}^2 - \omega^2} \right). \tag{21}$$

We require the trace of the product of the Green function, equation (21), for evaluation of the dispersion energy. The latter may then be written from equation (16) as

$$E_2 = \frac{4\pi\hbar}{i} \oint d\omega \sum_{n_1,n_2} \sum_{ijkl} \left(\frac{2\omega_{0n_1} u_i^1 u_l^1}{\omega_{0n_1}^2 - \omega^2} G_{ji} G_{lk} \frac{2\omega_{0n_2} u_j^2 u_k^2}{\omega_{0n_2}^2 - \omega^2} \right) \tag{22}$$

where u_i^1 is the ith component of the matrix element $\langle 0|u|n_1 \rangle$ and G_{ji} is the ijth component of $\nabla_R \nabla_R G(R)$ and the factor $e^2/\hbar$ is included in G_{ji} (see equation (10)).

On the other hand, the dispersion energy from time-independent perturbation theory is given from equation (20) and equation (18) as

$$\Delta E = \sum_{n_1,n_2} \sum_{ijkl} \frac{u_i^1 u_k^1 G_{ij} G_{kl} u_j^2 u_l^2}{\omega_{0n_1} + \omega_{0n_2}} \tag{23}$$

where the symbols have the same meaning as for equation (22) and $e^2/\hbar$ has been included in the Green function. We now make use of a frequency-dependent representation for equation (23) (see Margenau and Kestner 1971, p 58) to write

$$
\begin{aligned}
\Delta E &= \frac{(4\pi)^2}{\pi} \int_0^\infty \sum_{n_1,n_2} \sum_{ijkl} \frac{\omega_{0n_1} u_i^1 u_k^1}{\omega_{0n_1}^2 + \xi^2} G_{ij} G_{kl} \frac{\omega_{0n_2} u_j^2 u_l^2}{\omega_{0n_2}^2 + \xi^2} d\xi \\
&= \frac{4\pi\hbar}{i} \oint d\omega \sum_{n_1,n_2} \sum_{ijkl} \left(\frac{2\omega_{0n_1} u_i^1 u_k^1}{\omega_{0n_1}^2 - \omega^2} G_{ij} G_{kl} \frac{2\omega_{0n_2} u_j^2 u_l^2}{\omega_{0n_2}^2 - \omega^2} \right)
\end{aligned} \tag{24}
$$

where the contour in the last integral encloses the positive real axis. The equivalence with equation (22) found from the present method is immediately obvious. It should be noted that equation (22) is obtained from the use of $-ik . u$ for $e^{-ik.u}$ which is the same as assuming the dipoles in the system are point dipoles.

Hence for point dipoles the results of the two methods are identical. The use of a finite-sized dipole (and higher-order multipoles) leads to a lack of divergence of the dispersion energy as the separation (R) between atoms goes to zero, as noted earlier. The present method is shown in the next section to yield the same R dependence for dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions in the large-R limit, as the time-independent calculation (see, eg, Margenau and Kestner 1971, Meath 1972). From the equivalence of equations (22) and (24), this is to be expected.

The present method has much wider applicability than the time-independent perturbation method, however. Apart from the ability to introduce finite multipole size in a consistent manner, when the theory is extended to the retarded-field case the dipole–dipole term yields the Casimir–Polder results for large R, a result which cannot be obtained from the original form of the time-independent perturbation approach dealing with the Coulomb interaction terms.

3. Examples and discussion

In this section we present a very simple example to illustrate the features of the present calculation. Although no attempt is made to rigorously describe any real physical system, a scheme for calculation is suggested which may be applied to atoms with excited states well separated from the ground state.

The main difficulty in estimating the dispersion energy E_2 from equation (16) is the evaluation of the Green functions occurring in equation (12) which involves the sum over the (unperturbed) excited states $|n\rangle$ of each atom (see equation (9) for the dipole term, for example). One must also make a choice of suitable atomic wavefunctions, but this problem will not be discussed in the present work.

An important aspect of the sum over single-atom states emerges when the part in large parentheses of equation (9) (and similar terms for higher orders) becomes separable into space and time parts. The sum may then be written in the form $\alpha(\omega)\mathbf{f}(\mathbf{k})$ which allows one to represent the polarizability $\alpha(\omega)$ and the form factor $\mathbf{f}(\mathbf{k})$ phenomenologically to fit experimental observation of the dispersion force. Such a model has wide applications; for example, in the study of the interaction of a macroscopic particle with a dielectric slab and other interactions with macroscopic objects. Mahanty (1974) and Mahanty and Ninham (1973, 1975) have made use of such a model where $\alpha(\omega)$ is taken as scalar and the form factor $\mathbf{f}(\mathbf{k})$ is made isotropic, with a Gaussian distribution.

Several approaches to evaluation of the sum over atomic states like that in equation (9) are possible. Dalgarno (1963) has presented a general scheme for evaluation of the sum. A simpler method, suggested by Dalgarno (1961) is to approximate the sum by taking a single excited state and replacing the sum over n by only one term, depending on the dominant optical transition for the system of interest. We will make use of another method in which it is assumed the excited states may be described by a single effective excited state so, eg, ω_{0n} in equation (9) is replaced by an effective frequency $\bar{\omega}$. Use is then made of the completeness of single-atom excited state wavefunctions to write

$$\sum_n |n\rangle\langle n| = 1. \tag{25}$$

Then one simply has to make a choice of suitable ground state wavefunctions for each atom.

In what follows we present results of a calculation of dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interaction contributions to dispersion energy E_2 for 'atoms' with a 1s ground state described by an harmonic oscillator wavefunction (Morse and Feshbach 1953)

$$\psi_{001}(r) = \frac{1}{(4\pi^{3/2}a^3)^{1/2}} e^{-r^2/2a^2} \tag{26}$$

where $a = (\hbar/m\omega)^{1/2}$ represents the 'size' of the oscillator.

We truncate the multipole series, equation (8), at the quadrupole term and evaluation of the Green functions of the electric field, equation (12), up to $\mathscr{G}_{14}$, and derivatives of these, enables the evaluation of the trace in equation (16) for the two-atom dispersion energy. For the wavefunction of equation (26) as the ground state and making use of the assumption of an effective excited state represented by $\bar{\omega}$, so equation (25) may be used, we obtain the dipole–dipole (DD), quadrupole–dipole and dipole–quadrupole (DQ), and quadrupole–quadrupole (QQ) two-atom dispersion energies as follows:

$$E_2(\mathrm{DD}) = -\frac{3\hbar}{\pi}\left(\frac{e^4 a_1^2 a_2^2}{16\hbar^2}I(\bar{\omega})\right)R^{-6}F_6(R) \tag{27}$$

$$E_2(\mathrm{DQ}) = -\frac{3\hbar}{\pi}\left(\frac{e^4 a_1^2 a_2^2}{16\hbar^2}I(\bar{\omega})\right)a_1 a_2 R^{-8}F_8(R) \tag{28}$$

$$E_2(\mathrm{QQ}) = -\frac{3\hbar}{\pi}\left(\frac{e^4 a_1^2 a_2^2}{16\hbar^2}I(\bar{\omega})\right)a_1^2 a_2^2 R^{-10}F_{10}(R) \tag{29}$$

where a_1 and a_2 are the 'sizes' of atoms 1 and 2 respectively, $R = |\mathbf{R}_1 - \mathbf{R}_2|$ and $I(\bar{\omega})$ is an integral over frequency,

$$I(\bar{\omega}) = -\frac{1}{i}\oint \mathrm{d}\omega\left(\frac{2\bar{\omega}}{\bar{\omega}^2 - \omega^2}\right)^2 = \frac{2\pi}{\bar{\omega}}. \tag{30}$$

The functions $F_6(R)$, $F_8(R)$ and $F_{10}(R)$ are given by

$$F_6(R) = \frac{1}{3}\prod_{j=1}^{2}\left[\mathrm{erf}\left(\frac{R}{a_j}\right) - \frac{2}{\sqrt{\pi}}\frac{R}{a_j}\mathrm{e}^{-R^2/a_j^2}\right]$$
$$+ \frac{2}{3}\prod_{j=1}^{2}\left[\frac{2}{\sqrt{\pi}}\left(\frac{R^3}{a_j^3} + \frac{R}{a_j}\right)\mathrm{e}^{-R^2/a_j^2} - \mathrm{erf}\left(\frac{R}{a_j}\right)\right] \tag{31}$$

$$F_8(R) = \frac{1}{4}\prod_{j=1}^{2}\left[3\,\mathrm{erf}\left(\frac{R}{a_j}\right) - \frac{2}{\sqrt{\pi}}\left(\frac{2R^3}{a_j^3} + \frac{3R}{a_j}\right)\mathrm{e}^{-R^2/a_j^2}\right]$$
$$+ \frac{1}{6}\prod_{j=1}^{2}\left[\frac{2}{\sqrt{\pi}}\left(\frac{2R^5}{a_j^5} + \frac{2R^3}{a_j^3} + \frac{3R}{a_j}\right)\mathrm{e}^{-R^2/a_j^2} - 3\,\mathrm{erf}\left(\frac{R}{a_j}\right)\right] \tag{32}$$

$$F_{10}(R) = \frac{1}{3}\prod_{j=1}^{2}\left[3\,\mathrm{erf}\left(\frac{R}{a_j}\right) - \frac{2}{\sqrt{\pi}}\left(\frac{2R^3}{a_j^3} + \frac{3R}{a_j}\right)\mathrm{e}^{-R^2/a_j^2}\right]$$
$$+ \frac{5}{6}\prod_{j=1}^{2}\left[\frac{2}{\sqrt{\pi}}\left(\frac{R^5}{a_j^5} + \frac{2R^3}{a_j^3} + \frac{3R}{a_j}\right)\mathrm{e}^{-R^2/a_j^2} - 3\,\mathrm{erf}\left(\frac{R}{a_j}\right)\right]$$
$$+ \frac{1}{3}\prod_{j=1}^{2}\left[3\,\mathrm{erf}\left(\frac{R}{a_j}\right) - \frac{1}{\sqrt{\pi}}\left(\frac{2R^7}{a_j^7} + \frac{R^5}{a_j^5} + \frac{4R^3}{a_j^3} + \frac{6R}{a_j}\right)\mathrm{e}^{-R^2/a_j^2}\right]. \tag{33}$$

Note from equations (27)–(30) that the frequency dependence of all terms is identical and independent of the term of the multipole expansion, under the assumptions we have made. It will also be remarked that the function $F_6(R)$, equation (31), is identical with that of Mahanty and Ninham (1975) and we may infer that the polarizability tensor chosen by them corresponds to the assumptions we have made. As these authors have

found for the dipole–dipole interaction, we conclude that the simple R^{-6}, R^{-8}, R^{-10} dependence of the respective multipole interactions is modified for $R \simeq a$ by the functions $F_6(R)$, $F_8(R)$ and $F_{10}(R)$.

For the limit of small R,

$$F_6(R) \rightarrow \frac{8}{4\pi} \left(\frac{R^2}{a_1 a_2} \right)^3 \tag{34}$$

as found by Mahanty and Ninham (1975) and

$$F_8(R) \rightarrow 0, \qquad F_{10}(R) \rightarrow \frac{332}{300\pi} \frac{R^{10}}{a_1^5 a_2^5}.$$

Thus we have demonstrated the assertion made in § 2 that the effect of the form factor $e^{-i\mathbf{k}\cdot\mathbf{u}}$ in equation (10) is to remove the divergence at the origin, although this region is of little physical interest as exchange and monopole forces will dominate. For large R, however, we find $F_6(R) \rightarrow 1$, giving the London result, $F_8(R) \rightarrow \frac{15}{4}$ and $F_{10}(R) \rightarrow \frac{27}{2}$. The latter two values, from a calculation of time-independent perturbation theory including all states of the harmonic oscillator, are 5 for $F_8(R)$ and 30·625 for $F_{10}(R)$ (Margenau and Kestner 1971). Thus the contribution of higher-order terms of the multipole expansion is reduced under our approximation which uses equation (25). It is expected from the discussion at the end of the last section, when carried over to higher-order multipoles, that if the sum over single-atom states $|n\rangle$ were performed exactly, the correspondence with the perturbation calculation would be much closer. Our assumption of a single effective excited state is not very good for a harmonic oscillator where the separation between the energies of states of different principal quantum number is equal. The method will apply best to atoms where the excited states are close together relative to their separation from the ground state.

In figure 1 we have plotted for $a_1 = a_2 = a$, curves of $(a^6/R^6)F_6(R)$, $(a^8/R^8)F_8(R)$ and $(a^{10}/R^{10})F_{10}(R)$ against R/a. For comparison the curve of a^6/R^6 against R/a is also drawn. The energy scale is in arbitrary units. The figure illustrates the points made earlier about non-divergence as $R \rightarrow 0$ and shows the asymptotic limit of $(a^6/R^6)F_6(R)$ giving the London result a^6/R^6. Note the minimum in the DQ curve at $0.72(R/a)$, though in this region, as stated above, other forces will dominate. For $R \simeq 3a$ the asymptotic result for the dipole–dipole interaction, equation (34), is good to about 0.5%.

4. Conclusion

In this paper we have presented a more rigorous theory of dispersion interaction energy by the direct calculation of electric field modes than previously given (Mahanty and Ninham 1973, 1975, Mahanty 1974). The theory given is only applicable to situations of non-retarded electromagnetic fields, although extension to the retarded situation is possible. Some results for a two-particle harmonic oscillator model are presented to illustrate the theory, taking advantage of the ease with which higher-order multipoles than dipoles may be included in the expression for the dispersion energy to find results for dipole–quadrupole and quadrupole–quadrupole interactions, as well as the dipole–dipole interaction. It is found that the dipole–dipole result, for the simple example used, has the same functional form for dispersion energy as Mahanty and Ninham (1975). It is also found that the dipole–quadrupole and quadrupole–quadrupole interactions
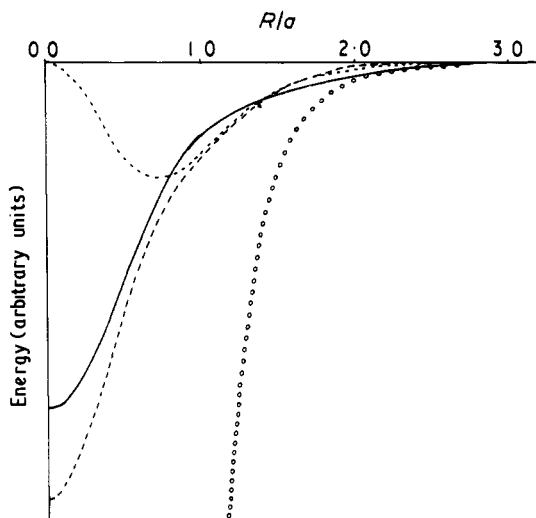
R/a

Figure 1. Plots of multipole contributions to the dispersion energy of two harmonic oscillators, as a function of R/a where R is the separation between oscillators and a the 'size' of the oscillator. The energy scale is in arbitrary units. The curves are as follows: full curve, dipole–dipole $a^6 R^{-6} F_6(R)$; dotted curve, dipole–quadrupole $a^8 R^{-8} F_8(R)$; broken curve, quadrupole–quadrupole $a^{10} R^{-10} F_{10}(R)$; open circles, London result (dipole–dipole) $a^6 R^{-6}$.

leave the dispersion energy finite as the separation between atoms (R) goes to zero, as was found for the dipole–dipole case earlier (Mahanty and Ninham 1975). The removal of the divergence as R goes to zero is the result of the multipoles having a finite size. For large separation R, the R dependence of the dispersion energy agrees with the point multipole results.

For the present theory, use of quantum theory to calculate the dispersion energy has been avoided, unlike the perturbation approach as used, for example, by Meath (1972), and perturbation theory has only been applied to the charge density of the atoms as a result of a scalar potential perturbation. The present calculation is thus a semi-classical formulation of the dispersion energy.

In appendix 2 is presented a brief discussion of the use of a vector potential in the non-retarded case, and it is shown that in this limit the result is equivalent to that used in this paper. To treat the retarded-field problem, the choice of gauge becomes important. It is most convenient to choose the Lorentz gauge and work with a vector potential. Then equation (A.11) for the wave equation is modified to include time dependence of the vector potential and so the Green function (A.14) is also altered. Other relations will also differ to include retardation, and the form of the perturbation used in appendix 1 will be described in terms of a vector potential. In principle, the theory is solvable on similar lines to the present work. It has been solved for the special case of a separable polarizability by Mahanty and Ninham (1975).

Appendix 1. Perturbation calculation of charge density

For computational convenience we consider a time-dependent Hamiltonian which perturbs each atom in the system via the scalar potential $\phi(r)$ as

$$\mathscr{H}_1 = e\phi(r)\,e^{i\omega t}. \tag{A.1}$$

The physical response will be given as the real part of the response due to $\mathscr{H}_1$. In equation (A.1), e is the electronic charge and ω the frequency of the field. The unperturbed state equation is defined as

$$\mathscr{H}_0 u_n = E_n u_n.$$

The perturbed wavefunctions are expanded in the unperturbed ones

$$\psi(r, t) = \sum_n a_n(t)u_n(r)\,e^{-i\omega_n t} \tag{A.2}$$

where $\omega_n = E_n/\hbar$. Putting (A.2) in the time-dependent Schrödinger equation we obtain

$$\dot{a}_n(t) = \frac{e}{i\hbar}\sum_n \langle n|\phi|m\rangle\,e^{i\omega t}\,e^{-i\omega_{mn}t}a_m(t). \tag{A.3}$$

We assume that in zeroth order

$$a_0(t) = 1$$
$$a_n(t) = 0, \qquad n \neq 0.$$

Then, in first order

$$a_n(t) = \frac{e}{i\hbar}\langle n|\phi|0\rangle \int_{-\infty}^{t} e^{i\omega t}\,e^{-i\omega_{0n}t}\,dt \tag{A.4}$$

and

$$\psi(r, t) = u_0(r)\,e^{i\omega_0 t} + \frac{e}{i\hbar}\sum_n \langle n|\phi|0\rangle \int_{-\infty}^{t} e^{i\omega\tau}\,e^{-i\omega_{0n}\tau}\,d\tau\,u_n(r)\,e^{-i\omega_n t}. \tag{A.5}$$

For an observable B the expectation value is, to first order,

$$\langle B\rangle = \langle \psi|B|\psi\rangle$$

$$= B_{00} + \frac{e}{i\hbar}\sum_n \left(\langle 0|B|n\rangle\langle n|\phi|0\rangle \int_{-\infty}^{t} e^{i\omega\tau}\,e^{-i\omega_{0n}\tau}\,d\tau\,e^{i\omega_{0n}t} \right.$$

$$\left. - \langle 0|\phi|n\rangle\langle n|B|0\rangle \int_{-\infty}^{t} e^{i\omega\tau}\,e^{i\omega_{0n}\tau}\,d\tau\,e^{-i\omega_{0n}t} \right)$$

$$= B_{00} + \int_{-\infty}^{\infty} e^{i\omega\tau}G(t-\tau)\,d\tau \tag{A.6}$$

where

$$G(t-\tau) = \theta(t-\tau)\frac{e}{i\hbar}\sum_n (\langle 0|B|n\rangle\langle n|\phi|0\rangle\,e^{i\omega_{0n}(t-\tau)} - \langle n|B|0\rangle\langle 0|\phi|n\rangle\,e^{-i\omega_{0n}(t-\tau)}) \tag{A.7}$$

and $\theta(\tau)$ is a step function which is unity for $\tau > 0$ and zero otherwise. Now the change in the expectation value of B due to the perturbation is

$$\delta\langle B\rangle = \int_{-\infty}^{\infty} e^{i\omega\tau}G(t-\tau)\,d\tau = e^{i\omega t}G(\omega) \tag{A.8}$$

where the Fourier transform $G(\omega)$ of $G(t)$ is

$$G(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} G(t) \, dt = \frac{e}{\hbar} \sum_n \left(\frac{\langle 0|B|n \rangle \langle n|\phi|0 \rangle}{\omega_{0n} - \omega} + \frac{\langle n|B|0 \rangle \langle 0|\phi|n \rangle}{\omega_{0n} + \omega} \right) \quad \text{(A.9)}$$

which is obtained by completing the time integral and using equation (A.7).

For the application in this paper we are interested in summing over all frequencies, which we do in equation (14), and hence it is sufficient to consider $\delta \langle B \rangle$ as given by equation (A.8), rather than the real part of this.

If we associate the operator B with the charge density, we may associate it with the operator $e\delta(r - r')$. From (A.8), then, the first-order change in the charge density will have time dependence $e^{i\omega t}$ and from Poisson's equation the first-order change in ϕ, $\phi_1(r, \omega)$ in equation (A.23) will also have $e^{i\omega t}$ time dependence. The perturbation result for the charge density is given from (A.9) in equation (A.20).

The current density $J(r - r')$ may be associated with the operator (Bohm 1969) $(\hbar e/2mi)(\delta(r - r')\nabla_{r'} + \nabla_{r'}.\delta(r - r'))$ so the first-order change in current density from (A.9) is

$$J(r) = \frac{e \, e^{i\omega t}}{2m \, \hbar} \sum_n \left(\frac{u_0^*(r)\nabla_r u_n(r) \langle n|\phi|0 \rangle}{\omega_{0n} - \omega} + \frac{u_n^*(r)\nabla_r u_0(r) \langle 0|\phi|n \rangle}{\omega_{0n} + \omega} \right). \quad \text{(A.10)}$$

The perturbation $-eu$ assumed by Mahanty and Ninham (1973) is a correct representation of the polarization only to first order. In fact, the polarization may be expanded in a series of which $-eu$ is the first term (de Groot and Suttorp 1972). The present treatment is equivalent to treating the full series.

Appendix 2

In this appendix is presented a brief analysis of the use of the vector potential to obtain the electric field around an atom pair to enable closer comparison with the earlier work of Mahanty and Ninham (1973, 1975). We will show that use of the vector potential leads to an identical result with the above scalar potential calculation, as it should in the non-retarded limit.

The vector potential wave equation in this limit is

$$\nabla_r^2 A(r, \omega) = -\frac{4\pi}{c} J(r, \omega) \quad \text{(A.11)}$$

for speed of light c, and J the current density of the system. For the two-particle case $J(r, \omega)$ should be replaced by

$$\sum_{j=1}^{2} J(r - R_j; \omega)$$

in (A.11), and the procedure may be carried through as for the single-atom example given here.

The aim of this appendix is to demonstrate that in the non-retarded limit, use of the vector potential equation (A.11) is equivalent to use of the scalar potential equation (1). We may show this by means of the continuity equation

$$\nabla . J + \frac{1}{c} \frac{\partial \rho}{\partial t} = 0 \quad \text{(A.12)}$$

which we use to demonstrate the validity of the Lorentz condition

$$\nabla \cdot A + \frac{1}{c}\frac{\partial \phi}{\partial t} = 0. \tag{A.13}$$

From equation (A.11) the vector potential is given as

$$A(r) = -\frac{4\pi}{c(2\pi)^3}\int \frac{e^{ik\cdot(r-r')}}{k^2}J(r')\,d^3r'. \tag{A.14}$$

After integration by parts we find

$$\nabla \cdot A = -\frac{4\pi}{c(2\pi)^3}\int \frac{e^{ik\cdot(r-r')}}{k^2}(\nabla_{r'}\cdot J(r'))\,d^3r'. \tag{A.15}$$

Now from quantum mechanics the divergence of current density in terms of the system wavefunction ψ is

$$\nabla \cdot J = \frac{\hbar}{2mi}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*) = \frac{\partial}{\partial t}(\psi^*\psi) \tag{A.16}$$

from Schrödinger's equation.

Hence

$$\nabla \cdot A = -\frac{4\pi}{c(2\pi)^3}\int \frac{e^{ik\cdot(r-r')}}{k^2}\frac{\partial \rho(r')}{\partial t}\,d^3r' \tag{A.17}$$

where the charge density

$$\rho(r') = \psi^*(r')\psi(r'). \tag{A.18}$$

We have already shown that from Poisson's equation the scalar potential is

$$\phi(r,\omega) = \frac{4\pi}{(2\pi)^3}\int \frac{e^{ik\cdot(r-r')}}{k^2}\rho(r')\,d^3r' \tag{A.19}$$

for a single particle.

Hence from equation (A.17)

$$\nabla \cdot A = -\frac{1}{c}\frac{\partial \phi}{\partial t}$$

and the Lorentz condition is satisfied.

Making use of appendix 1, equation (A.8), the charge density is given by

$$\rho(r,\omega) = \rho_{00}(r) - \frac{e^2}{\hbar}e^{i\omega t}$$

$$\times \sum_n \left(\frac{\langle 0|\delta(u-r)|n\rangle \langle n|\phi(u)|0\rangle}{\omega_{0n}-\omega} + \frac{\langle n|\delta(u-r)|0\rangle \langle 0|\phi(u)|n\rangle}{\omega_{0n}+\omega} \right) \tag{A.20}$$

to first order, then

$$\dot{\rho}(r) = i\omega\rho_1(r)$$

where $\rho_1(r)$ is the second term of equation (A.20). It may also be shown that

$$\phi(r;\omega) = \frac{4\pi}{(2\pi)^3}\int \frac{e^{ik\cdot(r-r')}}{k^2}(\rho_{00}(r') + e^{i\omega t}\rho_1(r';\omega))\,d^3r' = \phi_0(r) + \phi_1(r;\omega)\,e^{i\omega t}$$

so

$$\dot{\phi}(r, \omega) = i\omega\phi_1(r, \omega).$$

Now the electric field is given as

$$\mathscr{E} = -\nabla\phi - \frac{1}{c}\frac{\partial A}{\partial t}. \tag{A.21}$$

We may eliminate ϕ from equation (A.21) using the Lorentz condition equation (A.13),

$$\mathscr{E} = \frac{ic}{\omega}\nabla(\nabla . A) - \frac{1}{c}\frac{\partial A}{\partial t} - \nabla\phi_0$$

which becomes, in the non-retarded limit

$$\mathscr{E} = -\nabla\phi_0 - \frac{ic}{\omega}\nabla(\nabla . A). \tag{A.22}$$

This result is identical with the more usual result

$$\mathscr{E} = -\nabla\phi_1 - \nabla\phi_0. \tag{A.23}$$

In the work presented in this paper we are interested only in the change in the electric field from its unperturbed value of $-\nabla\phi_0$ so we drop this term from equations (A.22) and (A.23).

Hence use of a vector potential wave equation leads to the same electric field as for a scalar potential wave equation, in the non-retarded limit. For the retarded-field case a scalar potential theory is inadequate and it is necessary to use the procedure outlined in this section, with equation (A.11) modified to include the time dependence of A which will now be significant. Other relations are accordingly modified.

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