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INTERACTION DIPOLE BETWEEN RARE-GAS ATOMS^{*}

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INTRODUCTION

The dipole moment function, $\mu(R)$, is by definition the electric dipole moment of two atoms A and B at a distance R apart, and is independent of coordinate origin if the system A + B is electrically neutral. The dipole moments of stable heteronuclear diatomic molecules are important properties which have been extensively studied experimentally and theoretically, usually in the vicinity of the equilibrium bond distance. Of course a dipole moment can exist due to the interaction of any two dissimilar atoms even in S-states, whether they bind or not, and in particular between different kinds of rare-gas atoms.

It is useful theoretically to distinguish two sources of the interaction dipole: (a) inter-electron correlation of the kind which leads to the attractive dispersion forces, dominant at long-range and varying as R^{-7} ; (b) electron exchange, which becomes important when the electron clouds of the atoms overlap, and leads to the repulsive forces between closed-shell atoms, which vary exponentially with R.

It was first pointed out by A.D. Buckingham¹ in 1957 that the long-range dispersion dipole (neglecting retardation effects) can be expanded as a multipole series in $1/R$ and for

S-states begins with a term in R^{-7} :

$$\mu(R) \sim \frac{D_7}{R^7} + \frac{D_9}{R^9} + \dots \quad (1)$$

Buckingham carried out simple approximate calculations of D_7 and of the exchange dipole for the interaction of hydrogen and helium atoms. The conclusions were that the contributions to the interaction dipole from dispersion and exchange were both small at the collision diameter ($\sigma \approx 5.5$ Bohr), of the order of 10^{-3} Debye, and of opposite sign (dispersion : $^{+-}$ HHe).

The first observation of collision-induced absorption spectra was made by Kiss and Welch² in 1959 with rare-gas mixtures in the infrared. The spectra are due to the rapidly changing interaction dipole when two dissimilar rare-gas atoms collide. The complete absorption bands for helium-argon and neon-argon were first seen in the far infrared by Bosomworth and Gush³, but for helium-neon the absorption was too weak to be observed. These experiments led to a lot of theoretical work concerned with developing an adequate theory of the absorption⁴⁻⁶ and with calculating the interaction dipole-moment function⁷.

Matcha and Nesbet⁷ computed the dipole moments of the rare-gas diatoms HeNe, HeAr and NeAr as given by the

molecular Hartree-Fock approximation. Hartree-Fock computations of the dipole moments of bound diatomic molecules in the vicinity of the equilibrium distance are in very good agreement with experiment⁸. However, since the Hartree-Fock approximation does not describe the correlation effects involving two or more electrons, it can only account for the interaction dipole due to exchange and the subsequent distortion of the atomic orbitals. Furthermore, the computer programmes⁹ used were designed for calculations in the bonding region, and in the intermediate range corresponding to the conventional collision diameters (about 5 Bohrs) severe numerical cancellation occurred. For this reason the calculations were carried out from $R = 2$ Bohrs outwards, to provide a more reliable extrapolation to the distances of importance in the collision-induced absorption experiments. It was discovered that the computed dipole-moments could all be fitted by single exponentials of the form

$$\mu_{HF}(R) \approx B \exp(-R/\rho) \quad (2)$$

over the range considered.

The culmination of the theoretical work on the collision-induced absorption spectra at present is the

model-free calculation of the line shape of the helium-argon absorption by McQuarrie and Bernstein¹⁰. They use a Lennard-Jones (12,6) interatomic potential with parameters deduced from molecular beam scattering experiments and the calculated Hartree-Fock dipole moment function of Matcha and Nesbet⁷. The only assumption made is that the classical electromagnetic theory of Levine and Birnbaum⁶ is adequate to describe the absorption. The calculated results reproduce the experimental line shape³ fairly well, but only after the dipole-moment function is modified slightly to give a better fit.

In a recent paper Levine¹¹ shows that if one assumes the exponential form (2) for the dipole-moment function, then it is possible to obtain a reliable value of the range parameter ρ from two moments of the experimental absorption spectrum. It is then possible, by assuming an interatomic potential, to also obtain an experimental value for the constant B in (2). Levine shows that the dipole-moment function for helium-argon deduced in this way from experiment is larger than Matcha and Nesbet's calculated function, and claims that the difference lies outside the experimental errors of the first, or the numerical errors of the second.

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Levine goes on to suggest that the discrepancy is due to the neglect of the electron correlation effects responsible for the dispersion dipole. By means of a semi-classical treatment based on the Drude model, he derives an approximate expression for the coefficient D_7 in (1), and estimates the values of D_7 for HeNe, HeAr and NeAr. In particular, the dispersion dipole he calculates for HeAr is of the same order of magnitude as the Hartree-Fock overlap dipole at the collision diameter.

In view of the current interest and uncertainty in the interaction dipole between pairs of closed shell atoms in thermal collision, it seems worthwhile attempting to develop a rough but reliable theory appropriate to the long and intermediate ranges involved. It will be assumed, by analogy with recent work on the interatomic potentials for such atoms¹², that the dispersion and overlap contributions are additive and that cross terms can be neglected. The dispersion contribution will be approximated by the first term of (1), involving the coefficient D_7 . The object of the first part of the paper is to develop the theory of D_7 by expressing it in terms of properties of the individual atoms, by analogy with the modern theory of the van der Waals coefficients¹³ C_6 , etc. This was attempted recently by Gersten¹⁴, but

he inadvertently annihilated the two terms which are actually dominant. The expression for D_7 in terms of frequency-dependent atomic properties lends itself more easily to fruitful approximations.

The object of the second part of the paper is to develop a simple perturbation approach to the exchange dipole given by the Hartree-Fock approximation. The idea is to try and avoid the severe numerical cancellation of a full-scale calculation in the intermediate range, by assuming the overlap is small.

DISPERSION DIPOLE

For a system of two atoms A and B at a fixed distance R apart, the interaction dipole is directed along the internuclear axis, which we shall take to be the z-axis in the direction A to B. The dipole moment function $\mu(R)$ is therefore the expectation value of the z-component, μ_0 , of the dipole moment operator for the state Ψ of the system,

$$\mu(R) = \langle \Psi | \mu_0 | \Psi \rangle / \langle \Psi | \Psi \rangle. \quad (3)$$

The wavefunction Ψ satisfies the Schrödinger equation

$$H\Psi = E\Psi, \quad (4)$$

where H is the Hamiltonian of the diatom system AB, and E is the energy. In the following treatment we shall neglect all relativistic and electromagnetic retardation effects, so that H is simply the spin-free Hamiltonian,
Perturbation Theory

The Hamiltonian can be written in the perturbation form

$$H = H_0 + V \quad (5)$$

where $H_0 = H_A + H_B$ is the Hamiltonian for the non-interacting atoms A and B. If atom A consists of charges e_i^a (actually N_a electrons, $-e$, and a nucleus $Z_a e$) at positions r_i^a with respect to the nucleus of A as origin, and atom B of charges e_j^b at positions r_j^b , with respect to the nucleus of B, and $\underline{R}$ is the vector from A to B, then the electrostatic interaction energy is

$$V = \sum_i^A \sum_j^B \frac{e_i^a e_j^b}{|\underline{R} + \underline{r}_j^b - \underline{r}_i^a|} \quad (6)$$

If the charge distributions of A and B do not overlap, then V may be written as the multipole expansion^{15,16}

$$V = \sum_{n=1}^{\infty} \frac{V_n}{R^n} \quad (7)$$

where

$$V_{nm} = \sum_{l=0}^n (-1)^l \sum_m \binom{n}{l+m}^{\frac{1}{2}} \binom{n}{l-m}^{\frac{1}{2}} M_{n-l}^m(A) M_l^{-m}(B), \quad (8)$$

and the irreducible multipole moments of A and B are defined by

$$M_l^m = \sqrt{\frac{4\pi}{2l+1}} \sum_i e_i r_i^l Y_l^m(\hat{r}_i) \quad (9)$$

The definition (9) is chosen to accord with the conventional definitions of the moments; for example:

$$\text{charge} \quad e = M_0^0 = \sum_i e_i, \quad (10)$$

$$\text{dipole} \quad \mu_z = \mu_0 = M_1^0 = \sum_i e_i r_i \cos \theta_i, \quad (11)$$

$$\text{quadrupole} \quad Q_{zz} = Q_0 = M_2^0 = \sum_i e_i r_i^2 P_2(\cos \theta_i). \quad (12)$$

(Note that the polar angles θ_i^a, θ_j^b are both defined with respect to the z-axis AB as polar axis.) Since atoms A and B are electrically neutral, $V_1 = V_2 = 0$, and the multipole series (7) begins

$$V = \frac{V_3}{R^3} + \frac{V_4}{R^4} + \dots, \quad (13)$$

where V_3 is the dipole-dipole interaction term and V_4 is the dipole-quadrupole interaction term.

Provided that the overlap between atoms A and B can be neglected, so that the effects of electron exchange are negligible, we can apply Rayleigh-Schrödinger perturbation theory in a well-known manner¹⁷. The unperturbed wavefunction Ψ_0 is simply the product of the normalized

wavefunctions A_0 and B_0 for the separate atoms in their ground S-states,

$$\Psi_0 = A_0 B_0 \equiv |0\rangle. \quad (14)$$

The wavefunction Ψ through second-order in V is given by¹⁸

$$\Psi = (1 + R_0 V + R_0 V' R_0 V + \dots) \Psi_0, \quad (15)$$

where $V' = V - E^{(1)} = V$, since the first-order energy $E^{(1)} = \langle 0|V|0\rangle$ vanishes identically for atoms in S-states.

The reduced resolvent R_0 (or modified Green's operator) for the ground state can be defined by

$$R_0 = \sum_K' \frac{|K\rangle\langle K|}{E_0 - E_K}, \quad (16)$$

where K specifies a state of the unperturbed system $A + B$, and the primed sum is over all discrete and continuum states excluding the ground state ($K = 0$).

The dipole moment of a neutral system is independent of the origin of coordinates in the dipole moment operator, and it follows that

$$\mu_0 = \mu_0^a + \mu_0^b \quad (17)$$

where, in atomic units,

$$\mu_o^a = - \sum_{i=1}^{N_a} z_i^a, \quad \mu_o^b = - \sum_{j=1}^{N_b} z_j^b. \quad (18)$$

When (15) is substituted into equation (3) for the dipole moment, it is obvious that the first term

$$\langle 0 | \mu_o | 0 \rangle = \langle A_o | \mu_o^a | A_o \rangle + \langle B_o | \mu_o^b | B_o \rangle \quad (19)$$

vanishes, since neither atom has a permanent dipole, nor indeed any non-vanishing multipole moment. Furthermore, μ_o is a one-electron operator, and V a two-electron operator (product-type), and this leads to the result that $\langle 0 | \mu_o R_o V | 0 \rangle = 0$. Thus the first non-vanishing terms are of second-order in V , and arise from

$$\mu(R) = \frac{\langle 0 | \mu_o R_o V R_o V + V R_o V R_o \mu_o + V R_o \mu_o R_o V | 0 \rangle + \dots}{1 + \langle 0 | V R_o^2 V | 0 \rangle + \dots} \quad (20)$$

If the multipole series (13) is substituted into (20), then since a 2^l -pole has the parity of l , it follows that the first two non-vanishing terms are given by

$$\mu(R) = \frac{D_2}{R^2} + \frac{D_4}{R^4} + \dots, \quad (21)$$

where the coefficient D_7 is given by

$$D_7 = 2 \langle 0 | \mu_0 R_0 V_3 R_0 V_4 + \mu_0 R_0 V_4 R_0 V_3 + V_3 R_0 \mu_0 R_0 V_4 | 0 \rangle; \quad (22)$$

we have assumed that all quantities are real.

Reduction of D_7

According to (8), the dipole-dipole term V_3 can be written

$$V_3 = - (2\mu_0^a \mu_0^b + \mu_+^a \mu_-^b + \mu_-^a \mu_+^b), \quad (23)$$

where $\mu_{\pm} = M_1^{\pm 1}$ given by (9). The dipole-quadrupole term V_4 can be written

$$V_4 = V_4^{ab} - V_4^{ba}, \quad (24)$$

where

$$V_4^{ab} = 3\mu_0^a \Theta_0^b + \sqrt{3}(\mu_+^a \Theta_-^b + \mu_-^a \Theta_+^b), \quad (25)$$

and $\Theta_{\pm} = M_2^{\pm 1}$ given by (9). By introducing (17) and (24), and using parity arguments, D_7 can be reduced first of all to

$$\begin{aligned}
D_7 = 2 & \langle 0 | \mu_0^b R_0 V_3 R_0 V_4^{ab} - \mu_0^a R_0 V_3 R_0 V_4^{ba} \\
& + \mu_0^b R_0 V_4^{ab} R_0 V_3 - \mu_0^a R_0 V_4^{ba} R_0 V_3 \\
& + V_3 R_0 \mu_0^b R_0 V_4^{ab} - V_3 R_0 \mu_0^a R_0 V_4^{ba} | 0 \rangle. \quad (26)
\end{aligned}$$

The next step is to substitute (23) and (25) into (26).

The only terms which survive are those for which the sum $\Sigma m = 0$ for the azimuthal indices. For example, the first term in (26) becomes

$$\begin{aligned}
\langle 0 | \mu_0^b R_0 V_3 R_0 V_4^{ab} | 0 \rangle = & - \langle 0 | 6 \mu_0^b R_0 \mu_0^a \mu_0^b R_0 \mu_0^a \oplus_0^b \\
& + 2\sqrt{3} \mu_0^b R_0 \mu_+^a \mu_-^b R_0 \mu_-^a \oplus_+^b | 0 \rangle. \quad (27)
\end{aligned}$$

A simple application of the Wigner-Eckart theorem now leads to

$$\langle 0 | \mu_0^b R_0 V_3 R_0 V_4^{ab} | 0 \rangle = -9 \langle 0 | \mu_0^b R_0 \mu_0^a \mu_0^b R_0 \mu_0^a \oplus_0^b | 0 \rangle, \quad (28)$$

and for D_7 as a whole,

$$\begin{aligned}
D_7 = 18 & \langle 0 | \mu^a R_0 \mu^a \mu^b R_0 \mu^b \oplus^a + \\
& + \mu^a R_0 \mu^b \oplus^a R_0 \mu^a \mu^b + \mu^a \mu^b R_0 \mu^a R_0 \mu^b \oplus^a \\
& - (\text{ditto } ba) | 0 \rangle, \quad (29)
\end{aligned}$$

where we have dropped the suffix 0 on μ and θ , which from now on will refer to the z and zz components.

The next stage in the reduction is to analyze the two-atom resolvent R_0 , given by (16). The states K of the combined system $A + B$ can be specified by the states k and l of the separate atoms A and B . Thus

$$|K\rangle = |A_k\rangle |B_l\rangle, \quad (30)$$

and (16) can be written

$$\begin{aligned} R_0 &= \sum_{k=1} \sum_{l=1} \frac{|A_k B_l\rangle \langle A_k B_l|}{E_0^A + E_0^B - E_k^A - E_l^B}, \\ &= R_0^A |B_0\rangle \langle B_0| + R_0^B |A_0\rangle \langle A_0| + R_0^{AB}, \end{aligned} \quad (31)$$

where

$$R_0^A = \sum_k' \frac{|A_k\rangle \langle A_k|}{E_0^A - E_k^A}, \quad (32)$$

and the prime on the sum indicates that the ground state $k = 0$ is omitted; similarly for B. The first two terms in (31) clearly represent single-atom excitations. The last term describes simultaneous electron excitations in A and B, and is defined by

$$R_0^{AB} = \sum_k' \sum_l' \frac{|A_k B_l\rangle \langle A_k B_l|}{E_0^A + E_0^B - E_k^A - E_l^B} \quad (33)$$

By making use of the identity¹⁹

$$\frac{1}{a+b} = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \cdot \frac{a}{a^2 + \omega^2} \cdot \frac{b}{b^2 + \omega^2} \quad (a, b > 0), \quad (34)$$

it is possible to write (33) in the form

$$R_0^{AB} = - \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} R_0^A(\omega) R_0^B(\omega), \quad (35)$$

where

$$R_0^A(\omega) = - \sum_k' \frac{(E_k^A - E_0^A) |A_k\rangle \langle A_k|}{(E_k^A - E_0^A)^2 + \omega^2}, \quad (36)$$

and similarly for B. (Note the sign in (35). This form is only possible provided that $E_k > E_0$ for all k ; that is, for the ground state.) It follows immediately from (36) that

$$R_0^A(\omega) |A_0\rangle = 0, \quad R_0^B(\omega) |B_0\rangle = 0 \quad (37)$$

for all ω , and since $R_0^A \equiv R_0^A(0)$, we have

$$R_0^A |A_0\rangle = 0, \quad R_0^B |B_0\rangle = 0, \quad R_0^{AB} |A_0\rangle = 0, \quad R_0^{AB} |B_0\rangle = 0. \quad (38)$$

However, note that from (31)

$$R_0 |A_0\rangle = R_0^B |A_0\rangle \neq 0; \quad (39)$$

Gersten¹⁴ apparently failed to notice these single-atom terms.

Returning to equation (29) for D_7 , on substituting for R_0 from (31) many terms drop out because of (37) and (38), or because $\langle 0|\mu|0\rangle = 0$ and $\langle 0|0|0\rangle = 0$ for both atoms. The result is

$$\begin{aligned}
 D_7 = 18 & \left[\langle A_0 | \mu^a R_0^A \mu^a \langle B_0 | \mu^b R_0^{AB} \mu^b | B_0 \rangle \otimes^a | A_0 \rangle \right. \\
 & + \langle A_0 | \mu^a R_0^A \otimes^a \langle B_0 | \mu^b R_0^{AB} \mu^b | B_0 \rangle \mu^a | A_0 \rangle \\
 & + \langle B_0 | \mu^b \langle A_0 | \mu^a R_0^{AB} \mu^a R_0^{AB} \otimes^a | A_0 \rangle \mu^b | B_0 \rangle \\
 & \left. - (\text{dito } ba) \right]. \quad (40)
 \end{aligned}$$

Note that the first two terms in brackets involve one single and one double resolvent, and thus have a different structure from the third term, which involves two double resolvents (and may therefore be expected to be smaller). By inserting the integral (35) for R_0^{AB} in (40), we obtain

$$D_7 = D_7^I + D_7^{II}, \quad (41)$$

where

$$D_7^I = 18 \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \left[\langle 0 | \mu R_0(\omega) \mu | 0 \rangle_A \right. \quad (42)$$

$$\times \langle 0 | \mu R_0 \otimes R_0(\omega) \mu + \mu R_0 \mu R_0(\omega) \otimes | 0 \rangle_B - (\text{dito } BA) \Big],$$

$$\begin{aligned}
 D_7^{II} = 18 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{d\omega d\nu}{\pi^2} & \left[\langle 0 | \mu R_0(\omega) \mu R_0(\nu) \otimes | 0 \rangle_A \langle 0 | \mu R_0(\omega) R_0(\nu) \mu | 0 \rangle_B \right. \\
 & \left. - (\text{dito } BA) \right]. \quad (43)
 \end{aligned}$$

It is convenient to introduce symbols for the quantities involved in (42) and (43). Only one is well-known, namely the frequency-dependent polarizability

$$\alpha(i\omega) = -2 \langle 0 | \mu R_0(\omega) \mu | 0 \rangle. \quad (44)$$

Define

$$\gamma(\omega) = - \langle 0 | \mu R_0 \otimes R_0(\omega) \mu + \mu R_0 \mu R_0(\omega) \otimes | 0 \rangle, \quad (45)$$

$$\Gamma(u, v) = - \langle 0 | \mu R_0(u) \mu R_0(v) \otimes | 0 \rangle, \quad (46)$$

and

$$L(u, v) = 2 \langle 0 | \mu R_0(u) R_0(v) \mu | 0 \rangle, \quad (47)$$

where the signs have been chosen so that the quantities are always, or usually, positive for the ground state.

Then (42) and (43) become

$$D_7^I = 9 \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} [\alpha_A(i\omega) \gamma_B(\omega) - \alpha_B(i\omega) \gamma_A(\omega)], \quad (48)$$

$$D_7^{\text{II}} = 9 \int_{-\infty}^{+\infty} \int \frac{du dv}{\pi^2} [L_A(u,v) \Gamma_B(u,v) - L_B(u,v) \Gamma_A(u,v)]. \quad (49)$$

Equation (49) is essentially the same as Gersten's¹⁴ expression for D_7 . Clearly both parts of D_7 change sign if A and B are interchanged, and vanish if atoms A and B are the same, as they must. If D_7 is positive the polarity is A^-B^+ .

The formulae for D_7 appear too complex to be susceptible to helpful physical interpretation. Nor do the quantities γ , Γ and L appear to occur in exactly these forms in other properties. The closest relationships are as follows:

(1) Buckingham²⁰ has defined a third-order property as the energy coefficient of the electric field squared times the electric field gradient. It is a tensor of the fourth rank, whose irreducible component $m = 0$ for atoms can be written

$$B^{(0)} = 2 \langle 0 | \mu R_0 \odot R_0 \mu + 2 \mu R_0 \mu R_0 \odot | 0 \rangle. \quad (50)$$

This is related to γ and Γ by

$$B^{(0)} = -2 [\delta^{(0)} + \Gamma(0,0)] . \quad (51)$$

Only a preliminary measurement for methane has been reported²⁰.

(2) The quantity $L(0,0)$ is twice the norm of the first-order polarization wavefunction,

$$L(0,0) = 2 \langle R_0 \mu \psi_0 | R_0 \mu \psi_0 \rangle . \quad (52)$$

L is similar to the polarizability α , as may be seen by expressing them in the well-known sum-over-states forms,

$$\alpha(i\omega) = \sum_k' \frac{f_{k0}}{\omega_{k0}^2 + \omega^2} , \quad (53)$$

$$L(u,v) = \sum_k' \frac{f_{k0} \omega_{k0}}{(\omega_{k0}^2 + u^2)(\omega_{k0}^2 + v^2)} , \quad (54)$$

where f_{k0} are the oscillator strengths

$$f_{k0} = 2 \omega_{k0} |\langle 0 | \mu_0 | k \rangle|^2 , \quad (55)$$

and $\omega_{k0} = E_k - E_0$ are the excitation energies.

However, apart from these incomplete and not immediately helpful connections, the quantities $\gamma(\omega)$, $\Gamma(u,v)$ and $L(u,v)$ are mainly new, unknown and fairly sophisticated properties of atoms. Furthermore, since γ and Γ involve transition quadrupole moments in addition to oscillator strengths, they cannot be related to and estimated from optical properties, as can the polarizability²¹ $\alpha(i\omega)$ and presumably also $L(u,v)$. Unfortunately it is not yet possible to calculate properties as complicated as γ and Γ reliably for atoms larger than helium. Even if this were possible, one would still like to know what approximate property or properties of the separate atoms determine the sign of the interaction dipole. It is therefore natural to seek to approximate the formulae for D_7 . Buckingham¹ has already applied the familiar Unsöld approximation to his sum-over-states expression for D_7 . However, the formula which results contains unknown average excitation energies, and does not appear to be very accurate in the only case in which it can be tested (see below). Fortunately a simpler and apparently much more accurate approximation is made possible by starting from the expressions (48) and (49) involving the integrals over imaginary frequencies.

Approximate formula : part I

Since $\alpha(i\omega)$ is always positive, we can write (48) in the form

$$D_7^I = 9 \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \alpha_A(i\omega) \alpha_B(i\omega) \left[\frac{\gamma_B(\omega)}{\alpha_B(i\omega)} - \frac{\gamma_A(\omega)}{\alpha_A(i\omega)} \right]. \quad (56)$$

It is easy to see that both $\alpha(i\omega)$ and $\gamma(\omega)$ vary asymptotically like ω^{-2} , so that their ratio approaches a finite and non-zero limit. Suppose this ratio

$$g^I = \gamma(\omega) / \alpha(i\omega) \quad (57)$$

were independent of ω . Then since the dispersion energy coefficient C_6^{AB} of $-R^{-6}$ is given by²²

$$C_6^{AB} = \frac{3}{2} \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \alpha_A(i\omega) \alpha_B(i\omega), \quad (58)$$

(56) could be written

$$D_7^I = (g_B^I - g_A^I) 6 C_6^{AB}. \quad (59)$$

As $g^I(\omega)$ is unlikely to be constant, the question arises as to what value of g^I to use in (59). An obvious choice is $g^I(0)$, but this involves the third order property $\gamma(0)$,

which is unlikely to be easy to calculate or approximate.

Another possibility is $g^I(\infty)$, given by

$$g^I(\omega) = \lim_{\omega \rightarrow \infty} \gamma(\omega) / \alpha(i\omega). \quad (60)$$

Now from (36) it follows that asymptotically

$$R_0(\omega) \sim (E_0 - H) / \omega^2. \quad (61)$$

Hence

$$\gamma(\omega) \sim \frac{1}{2\omega^2} \langle 0 | \mu R_0 \otimes [H, \mu] + \mu R_0 \mu [H, \otimes] | 0 \rangle, \quad (62)$$

and, in agreement with the well-known sum rule,

$$\alpha(i\omega) \sim N / \omega^2, \quad (63)$$

where N is the number of electrons. Therefore

$$g^I(\infty) = \frac{1}{2N} \langle 0 | \mu R_0 \otimes [H, \mu] + \mu R_0 \mu [H, \otimes] | 0 \rangle. \quad (64)$$

Thus $g^I(\infty)$ involves only a second-order property (one resolvent factor). However, the weighting factor $\alpha_A(i\omega)\alpha_B(i\omega)$ in the integrand of (56) is a maximum at $\omega=0$ and falls off like ω^{-4} , so that the use of (64) is less appropriate than $g^I(0)$. A third alternative, which may be better than $g^I(0)$, is to replace $\gamma(\omega)$ and $\alpha(i\omega)$ by their average values over all frequencies, $\bar{\gamma}$ and $\bar{\alpha}$, and put $g^I = \bar{\gamma} / \bar{\alpha}$. It follows from (36) that

$$\bar{R}_0 \equiv \int_{-\infty}^{\infty} \frac{d\omega}{\pi} R_0(\omega) = -P_0 = |0\rangle\langle 0| - 1. \quad (65)$$

Hence, by substituting into (45) and (44),

$$\bar{\gamma} = 2 \langle 0 | \mu R_0 \mu | 0 \rangle, \quad (66)$$

$$\bar{\alpha} = 2 \langle 0 | \mu^2 | 0 \rangle, \quad (67)$$

and therefore

$$\frac{\bar{\gamma}}{\bar{\alpha}} = \frac{\langle 0 | \mu R_0 \mu | 0 \rangle}{\langle 0 | \mu^2 | 0 \rangle}. \quad (68)$$

This is an appealing compromise, since it involves only a fairly simple second-order property and an expectation

value. It is shown in appendix I that for the hydrogen atom in the ground state

$$\left. \begin{aligned} g^I(0) &= 103/12 = 8.58, \\ \bar{g}^I &= 33/4 = 8.25, \\ g^I(\infty) &= 15/2 = 7.5. \end{aligned} \right\} \quad (69)$$

Thus $g^I(\omega)$ does not vary drastically, and the average ratio is close to the zero frequency value.

Approximate formula : part II

Turning now to equation (49) for D_7^{II} , we can write it in a form analogous to (56),

$$D_7^{II} = 9 \iint_{-\infty}^{\infty} \frac{du dv}{u^2} L_A(u, v) L_B(u, v) \left[\frac{\bar{r}_B}{L_B} - \frac{\bar{r}_A}{L_A} \right], \quad (70)$$

and approximate it by

$$D_7^{II} = (\bar{g}_B^{II} - \bar{g}_A^{II}) 9 C_{AB}^{II} \quad (71)$$

where

$$\bar{g}^{II} = \bar{r}/L \quad (72)$$

and

$$C_{AB}^{\text{II}} = \iint_{-\infty}^{+\infty} \frac{du dv}{\pi^2} L_A(u, v) L_B(u, v). \quad (73)$$

The choice of the ratio of averages (72) in (71) is consistent with that for g^{I} . In addition, as will be shown, it is easy to calculate, less critical than the choice for g^{I} , and apparently a good approximation. It follows from (46) and (65) that

$$\bar{P} = - \langle 0 | \mu^2 \otimes | 0 \rangle, \quad (74)$$

so by combining this with (90) for $\bar{L}$ we get

$$\bar{g}^{\text{II}} = - \frac{\langle 0 | \mu^2 \otimes | 0 \rangle}{2 \langle 0 | \mu^2 | 0 \rangle}. \quad (75)$$

Since both numerator and denominator are first-order properties, $\bar{g}^{\text{II}}$ can be easily computed even for large atoms. To throw light on the behaviour of $g^{\text{II}}(u, v)$, it is shown in appendix I that for the hydrogen atom in the ground state it has the following limiting values and averages (-):

$g^{II}(u,v):$

$u \backslash v$	0	-	∞
0	1.36	1.83	2.5
-	1.11	1.5	2
∞	0.75	1	1.2

(76)

The extreme variations from the average are larger in this case, + 66% and -50%, than for $g^I(\omega)$.

Coefficient C^{II}

Unfortunately, the quantity C_{AB}^{II} , given by the integral (73), which occurs in formula (71) for D_7^{II} , is not a well-known property of the diatom AB like the Van der Waals coefficient C_6^{AB} occurring in D_7^I . However, (73) can be written in a sum-over-states form

$$C_{AB}^{II} = \sum_k' \sum_l' \frac{f_{k0}^a f_{l0}^b}{\omega_{k0}^a \omega_{l0}^b (\omega_{k0}^a + \omega_{l0}^b)^2} \quad (77)$$

which is similar to that for

$$C_6^{AB} = \frac{3}{2} \sum_k' \sum_l' \frac{f_{k0}^a f_{l0}^b}{\omega_{k0}^a \omega_{l0}^b (\omega_{k0}^a + \omega_{l0}^b)}, \quad (78)$$

and similar techniques could be used to obtain good estimates from optical data^{21,23}. Alternatively, it is not difficult to develop simple approximations for C_7^{II} , and as D_7^{II} is four or five times smaller than D_7^I , the additional approximation is not serious.

An upper bound for C_7^{II} can be obtained by replacing the arithmetic mean $\frac{1}{2}(\omega_{k0}^a + \omega_{l0}^b)$ by the geometric mean $\sqrt{\omega_{k0}^a \omega_{l0}^b}$ to get

$$C_{AB}^{II} \leq \frac{1}{4} \sum_k' \sum_l' \frac{f_{k0}^a f_{l0}^b}{(\omega_{k0}^a)^2 (\omega_{l0}^b)^2} = \frac{1}{4} \alpha_A(0) \alpha_B(0). \quad (79)$$

If A and B have spectra which are not too different,

(79) should be a reasonable approximation for C_{AB}^{II} . For two hydrogen atoms

$$\frac{1}{4} \alpha_H^2 = 81/16 = 5.0625, \quad (80)$$

whereas an accurate value calculated in the next section is

$$C^{II} = 4.9324, \quad (81)$$

which differs by less than 3%. The approximation (79) is equivalent to replacing (73) by

$$C_{AB}^{\Pi} \leq \int_{-\infty}^{+\infty} \frac{du}{\pi} L_A(u, u) \int_{-\infty}^{+\infty} \frac{dv}{\pi} L_B(v, v). \quad (82)$$

Now it follows from (36) that

$$\overline{R_0^2} = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} R_0^2(\omega) = -\frac{1}{2} R_0(0), \quad (83)$$

and hence

$$\begin{aligned} \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} L(\omega, \omega) &= -\langle 0 | \mu R_0 \mu | 0 \rangle, \\ &= \frac{1}{2} \alpha(0), \end{aligned} \quad (84)$$

which proves the equivalence.

An alternative approximation for C_{AB}^{II} , which probably always leads to a lower bound in practice, can be obtained by utilizing the projection operator

$$Q = \frac{\mu | 0 \rangle \langle 0 | \mu}{\langle 0 | \mu^2 | 0 \rangle} \leq 1.$$

Inserting Q between the resolvent operators in $L(u, v)$ given by (47) leads to the approximation (not necessarily a lower bound for all u, v)

$$L(u, v) \approx \frac{2 \langle 0 | \mu R_0(u) \mu | 0 \rangle \langle 0 | \mu R_0(v) \mu | 0 \rangle}{\langle 0 | \mu^2 | 0 \rangle},$$

$$= \alpha(iu) \alpha(iv) / \bar{\alpha} \quad (85)$$

where $\alpha(iu)$ is the dynamic polarizability defined by (44), and $\bar{\alpha}$ is the frequency average given by (67). The "product" approximation (85) has the virtue of satisfying the exact relations

$$\int_{-\infty}^{+\infty} \frac{d\nu}{\pi} L(u, \nu) = \alpha(iu), \quad (86)$$

and similarly for v , which follow from (47), (65) and (44). By substituting (85) into (73) and using (58) we get

$$C_{AB}^{\frac{11}{2}} \approx 4 (C_6^{AB})^2 / 9 \bar{\alpha}_A \bar{\alpha}_B. \quad (87)$$

For two hydrogen atoms, for which $C_6 = 6.50$ and $\bar{\alpha} = 2 \langle 0 | \mu^2 | 0 \rangle = 2$, the approximation yields

$$(2C_6/3\bar{\alpha})^2 = 4.69, \quad (88)$$

compared with the accurate value (81) of 4.93, and is therefore low by about 5%.

Yet another approximation, which is superior to (79) if A and B are different, can be obtained by supposing that

$$L(u, v) \approx \frac{K}{(\epsilon^2 + u^2)(\epsilon^2 + v^2)}, \quad (89)$$

and choosing K and ϵ to give (i) the correct integral (84), which leads to $K = \alpha_0 \epsilon^3$, and (ii) the correct frequency average

$$\bar{L} = \iint_{-\infty}^{+\infty} \frac{du dv}{\pi^2} L(u, v) = \bar{\alpha}, \quad (90)$$

so that $\epsilon = \bar{\alpha}/\alpha_0$. Then

$$C_{AB}^{\bar{L}} \approx \frac{\bar{\alpha}_A \bar{\alpha}_B}{(\epsilon_A + \epsilon_B)^2}; \quad (91)$$

for $A = B$ this reduces to the same expression as (79), $\alpha_0^2/4$. Note that if C_6^{AB} , given by (58), is treated in a similar way, by assuming

$$\alpha(i\omega) \approx \frac{J}{\epsilon^2 + \omega^2} \quad (92)$$

and choosing J and ϵ to give (i) $\alpha(0) = \alpha_0$ correctly, and (ii) the correct frequency average, so that $\epsilon = \bar{\alpha}/\alpha_0$, then

$$C_6^{AB} \approx \frac{3\bar{\alpha}_A\bar{\alpha}_B}{2(\epsilon_A + \epsilon_B)} \quad (93)$$

For two hydrogen atoms (93) gives 6.75 compared with the accurate 6.50, only 4% too high. By comparing (91) and (93) we see that yet another approximation for C^{II} is

$$C_{AB}^{II} \approx \frac{2C_6^{AB}}{3(\epsilon_A + \epsilon_B)} \quad (94)$$

This approximation lies midway between (87) and (91).

For two hydrogen atoms it yields

$$C_6 \alpha_0 / 3\bar{\alpha} = 4.875, \quad (95)$$

which is only 1% below the accurate value (81).

Model system : scaled hydrogen atoms

The simplest system which can be treated accurately and used to check approximate formulae for D_7 consists of a one-electron atom with a scaled hydrogenic wavefunction (scaled hydrogen atom, H_ζ) interacting with a hydrogen atom (unscaled, H). The more general case of two hydrogenic atoms differently scaled can be easily obtained from this special case. If the scale factor ζ is equal to unity or infinity $D_7(H_\zeta-H)$ must vanish, but between these limits it is non-zero and positive. An analytical expression for the function $D_7(\zeta)$ is probably quite difficult to derive, because even the exact one-electron dynamic polarizability $\alpha(i\omega)$ is a formidable function²⁴. However, it is not difficult to calculate accurate numerical values by using a technique introduced by Karplus and Kolker²⁵.

Let $\tilde{A}_k$ and $\tilde{B}_l$ ($k, l = 0, 1, \dots, n$) be orthonormal basis sets satisfying the conditions:

- (i) $\tilde{A}_0 = A_0, \tilde{B}_0 = B_0$.
- (ii) $\mu^a A_0$ and $\mu^b B_0$ are members of the sets.
- (iii) they diagonalize the unperturbed Hamiltonians H_A and H_B , so that

$$\tilde{H}_A \tilde{A}_k = \tilde{E}_k^A \tilde{A}_k$$

where

$$\tilde{H}_A = \tilde{O}_A H_A \tilde{O}_A, \quad \tilde{O}_A = \sum_{k=0}^n |\tilde{A}_k\rangle \langle \tilde{A}_k|, \quad (97)$$

and similarly for B. The approximation for D_7 consists in replacing the dynamic resolvent $R_0^A(\omega)$, given by (36), by

$$\tilde{R}_0^A(\omega) = - \sum_{k=1}^n \frac{\tilde{\omega}_k^a |\tilde{A}_k\rangle \langle \tilde{A}_k|}{(\tilde{\omega}_k^a)^2 + \omega^2}, \quad (98)$$

where the approximate excitation energies are

$$\tilde{\omega}_k^a = \tilde{E}_k^A - E_0^A, \quad (99)$$

and similarly for B. The approximation leads to a bound for second-order properties, but not for D_7 , which is a third-order property.

Let us write (48) in the form

$$D_7^I = \vec{D}_7^I - \overleftarrow{D}_7^I \quad (100)$$

where

$$\vec{D}_7^I = 9 \int_{-\infty}^{+\infty} \frac{d\omega}{\omega} \chi_A(i\omega) \gamma_B(\omega), \quad (101)$$

and $\vec{D}_7^I$ is the other term with A and B interchanged.

Similarly (49) can be written

$$\vec{D}_7^{\bar{II}} = \vec{D}_7^{\bar{I}} - \vec{D}_7^I \quad (102)$$

where

$$\vec{D}_7^{\bar{II}} = 9 \iint_{-\infty}^{+\infty} \frac{du dv}{\pi^2} L_A(u, v) \Gamma_B(u, v). \quad (103)$$

By substituting (98) into equations (44)-(47) for α, γ, Γ and L, then into (101) and (103) and carrying out the integrations, we obtain

$$\vec{D}_7^I = -18 \sum_{k=1}^n \sum_{l=1}^n \frac{|\tilde{\mu}_{k0}^a|^2 \tilde{\mu}_{al}^b}{\tilde{\omega}_l^b} \sum_{j=1}^n \left(\frac{\tilde{\mu}_{lj}^b \tilde{\omega}_{j0}^b + \tilde{\omega}_{lj}^b \tilde{\mu}_{j0}^b}{\tilde{\omega}_k^a + \tilde{\omega}_j^b} \right), \quad (104)$$

$$\vec{D}_7^{\bar{II}} = -18 \sum_{j=1}^n \sum_{k=1}^n \sum_{l=1}^n \frac{|\tilde{\mu}_{k0}^a|^2 \tilde{\mu}_{al}^b \tilde{\mu}_{lj}^b \tilde{\omega}_{j0}^b}{(\tilde{\omega}_k^a + \tilde{\omega}_l^b)(\tilde{\omega}_k^a + \tilde{\omega}_j^b)}, \quad (105)$$

where

$$\tilde{\mu}_{jk}^a = \langle \tilde{A}_j | \mu^a | \tilde{A}_k \rangle, \quad \tilde{\omega}_{jk}^a = \langle \tilde{A}_j | \hat{H} | \tilde{A}_k \rangle, \quad (106)$$

and similarly for B.

For the model system in which B is a hydrogen atom and A is a hydrogen atom scaled by ζ , the ground state wavefunctions are

$$A_0 = (\zeta^3/\pi)^{1/2} e^{-\zeta r}, \quad B_0 = \pi^{-1/2} e^{-r}. \quad (107)$$

The obvious choice of basis set for A is the ζ -scaled version of the set for the hydrogen atom B, say $\phi_k(r)$. The excitation energies and matrix elements for A and B are then simply related by scaling,

$$\tilde{\omega}_k^a = \zeta^2 \tilde{\omega}_k, \quad \tilde{\mu}_{jk}^a = \zeta^{-1} \tilde{\mu}_{jk}, \quad \tilde{Q}_{jk}^a = \zeta^{-2} \tilde{Q}_{jk}, \quad (108)$$

where the unsuperscripted quantities are for the hydrogen atom (B). A further simplification comes from the fact that only basis functions ϕ_k with p and d angular symmetries (and $m=0$) lead to non-vanishing matrix elements. The basis can therefore be divided into two groups of functions: $p_k(r)$ ($k=1, \dots, n_p$) with a factor $r \cos\theta$; $d_j(r)$ ($j=1, \dots, n_d$) with a factor $r^2 P_2(\cos\theta)$. The only matrix elements appearing in the formulae are as follows:

$$\tilde{\mu}_{k0} = \langle p_k | \mu | 0 \rangle, \quad \tilde{\mu}_{jk} = \langle p_j | \mu | d_k \rangle,$$

$$\tilde{\omega}_{k0} = \langle d_k | \omega | 0 \rangle, \quad \tilde{\omega}_{jk} = \langle p_j | \omega | p_k \rangle. \quad (109)$$

The basis functions used were of the forms employed by previous workers^{25,26},

$$p_k = \cos\theta e^{-r} \sum_{s=1}^{n_p} c_{ks}^p r^s, \quad d_k = r P_2(\cos\theta) e^{-r} \sum_{s=1}^{n_d} c_{ks}^d r^s. \quad (110)$$

In practice the Löwdin-Shull functions²⁸, which are orthonormal linear combinations like (110), were employed. We found that with $n_p = 10$ and $n_d = 20$ the convergence appeared to be satisfactory.

The results for $D_7(\zeta)$ are given in Table 1 and by the solid curve in Figure 1. Note that D_7 rises steeply to a maximum value of 107.0 (atomic units) at $\zeta = 1.223$ and then declines monotonically. It was discovered by approximate scaling arguments discussed in the next section that the calculated values are given to better than $\frac{1}{3}\%$ over the whole range of ζ considered by the function

$$D_7(\zeta) \approx \frac{2(\zeta^2-1)}{\zeta^6} \tilde{D}_7^I(1) + \frac{4(\zeta^2-1)}{\zeta^4(\zeta^2+1)^2} \tilde{D}_7^{II}(1), \quad (111)$$

where the constants are the accurate value of $\vec{D}_7^I$ and $\vec{D}_7^{II}$, calculated from (104) and (105) for $\zeta=1$; their values are given in equation (124). The values calculated from (111) are given in the last column of Table 1.

A most important check was obtained for the system of two hydrogen atoms ($\zeta=1$). Although D_7 vanishes in this case, the components

$$\vec{D}_7 = \vec{D}_7^I + \vec{D}_7^{II}$$

do not. Accurate values for $\vec{D}_7^I$ and $\vec{D}_7^{II}$ can be obtained by a completely different route thanks to the work of Hirschfelder and Eliason²⁷. The long-range dispersion force F between two neutral atoms A and B in S-states is given by the inverse-power series

$$F = \frac{F_7}{R^7} + \frac{F_9}{R^9} + \dots \quad (112)$$

By differentiating the well-known interaction energy series

$$\Delta E = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \dots, \quad (113)$$

it is obvious that

$$F_7 = 6C_6, \quad (114)$$

and similarly for the higher force coefficients. However, if instead the electrostatic Hellmann-Feynman theorem is used, say holding atom A fixed, then the coefficient F_7 in the force of attraction is

$$F_7 = F_7^I + F_7^{II}, \quad (115)$$

where

$$F_7^I = 18 \langle B_0 | f^b R_0^B \mu^b \langle A_0 | \mu^a R_0^{AB} \mu^a | A_0 \rangle \otimes^b + f^b R_0^B \otimes^b \langle A_0 | \mu^a R_0^{AB} \mu^a | A_0 \rangle \mu^b | B_0 \rangle, \quad (116)$$

and

$$F_7^{II} = 18 \langle A_0 | \mu^a \langle B_0 | \mu^b R_0^{AB} f^b R_0^{AB} \mu^b | B_0 \rangle \otimes^a | A_0 \rangle, \quad (117)$$

and f^b is the z-component of the electronic force operator for atom B, given in general by

$$f = \sum_{i=1}^N \frac{\partial}{\partial r_i^3}. \quad (118)$$

Since f is a one-electron operator, equations (116) and (117) can be written as integrals over perturbed charge densities,

$$F_7^I = \int \frac{z}{r^3} \rho_7^I d^3r, \quad (119)$$

$$F_7^{II} = \int \frac{z}{r^3} \rho_7^{II} d^3r. \quad (120)$$

Hirschfelder and Eliason²⁷ derived accurate approximations for $\rho_7^I(\underline{r})$ and $\rho_7^{II}(\underline{r})$ for two hydrogen atoms, which are quoted in appendix B. They calculated (atomic units)

$$F_7^I = 36.284 \quad \text{and} \quad F_7^{II} = 2.717, \quad (121)$$

so that $\frac{1}{6}F_7 = 6.500$, compared with the exact value^{28,29} $C_6 = 6.499$ (to four figures).

Clearly, the atomic contributions $\vec{D}_7^I$ and $\vec{D}_7^{II}$ to the interaction dipole coefficient can also be expressed in a form similar to (116) and (117), namely

$$\vec{D}_7^I = \int \vec{z} \rho_7^I d^3r, \quad (122)$$

$$\vec{D}_7^{II} = \int \vec{z} \rho_7^{II} d^3r. \quad (123)$$

It is therefore straightforward to use the Hirschfelder and Eliason²⁷ perturbed densities to calculate these quantities for two hydrogen atoms. Details are given in appendix B. The results are as follows (atomic units):

	$\bar{D}_7^I(1)$	$\bar{D}_7^{II}(1)$	$\bar{D}_7(HH)$
Ours, (104) & (105):	330.505	64.006	394.511
			(124)
H & E, (122) & (123):	330.512	64.007	394.519

The agreement is excellent. Our results are presumably more accurate since we used a larger basis set, and both basis sets were of the same kind. However, the difference is negligible. Note that the contribution of part I is over five times greater than part II.

Test of approximate formulae

The model system $H_\zeta - H$ treated in the last section provides a means of testing the basic approximation proposed for D_7 , given by (59) and (71). From the definitions (68) and (75) of the g factors it follows by scaling that

$$\bar{g}_A^I = \zeta^{-4} \bar{g}_H^I, \quad \bar{g}_A^{II} = \zeta^{-2} \bar{g}_H^{II}, \quad (125)$$

where $\bar{g}_B = \bar{g}_H$ are the values for a hydrogen atom, given numerically by (69) and (76). Hence, by substitution

$$D_7^I \approx (\zeta^4 - 1) \zeta^{-4} 6 \bar{g}_H^I C_6(\zeta), \quad (126)$$

$$D_7^{II} \approx (\zeta^2 - 1) \zeta^{-2} 9 \bar{g}_H^{II} C_6^{II}(\zeta). \quad (127)$$

Accurate values of $C_6(\zeta)$ and $C_6^{II}(\zeta)$ for the system $H_\zeta - H$ have been calculated for a range of values of ζ using the technique of the previous section, and are presented in Table 2. A check on the accuracy is given by comparing the calculated C_6 value for $H - H$ ($\zeta=1$) with the most accurate value²⁹,

Our method: $C_6(H-H) = 6.499027.$

(128)

Kolos: $C_6(H-H) = 6.499026.$

The agreement is excellent, better than 1 in 10^6 .

By substituting into equations (126) and (127) for various values of ζ we obtain the results in Tables 1 and 3. From Table 1 we see that the approximation for D_7 is good to about 1.5% over the range $\zeta = 1$ to 2. From Table 3 it can be seen that the approximation is good for both parts of D_7 , but especially part II.

The satisfactory agreement for this model system gives us confidence in applying the approximation to the rare-gas atoms. However, since the atomic property $\bar{\gamma}$ occurring in $\bar{g}^I$ is not available in the literature, it is necessary to make a further approximation. In view of this, it is not worth laboriously calculating very accurate values of C_{AB}^{II} from optical data if sufficiently accurate values can be calculated from one of the approximations derived for C^{II} in an earlier section. In Table 2 the simple approximations (91) and (94) for $C^{II}(H_\zeta-H)$ are compared with the accurate results for various values of ζ . Both approximations give results within a few per cent. Since

(94) involves C_6 , which appears naturally in part I of D_7 , we choose it. The approximate formula for D_7 , obtained by combining (59), (71) and (94) is then

$$D_7^{AB} \approx 6C_6^{AB} \left[g_B^I - g_A^I + \frac{g_B^{\bar{I}} - g_A^{\bar{I}}}{\epsilon_A + \epsilon_B} \right], \quad (129)$$

where we have dropped the bars on the g 's and

$$g^I = \langle 0 | \mu R_0 \mu | 0 \rangle / \langle 0 | \mu^2 | 0 \rangle, \quad (130)$$

$$g^{\bar{I}} = - \langle 0 | \mu^2 | 0 \rangle / 2 \langle 0 | \mu^2 | 0 \rangle, \quad (131)$$

$$\epsilon = 2 \langle 0 | \mu^2 | 0 \rangle / \alpha(0) = - \langle 0 | \mu^2 | 0 \rangle / \langle 0 | \mu R_0 \mu | 0 \rangle. \quad (132)$$

This formula gives

$$\vec{D}_7^{HH} \approx 321.8 + 65.81 = 387.6 \text{ (accurate 394.5)}, \quad (133)$$

which is still only in error by less than 2%.

The Unsöld Approximation

The bottleneck in estimating the dispersion contribution to the interaction dipole is now reduced to the calculation of g^I , which involves the unsymmetrical second-order property $\langle 0 | \mu R_0 \mu | 0 \rangle$. Its calculation is therefore a problem of the same order of difficulty as the static polarizability. The simplest approximation to use is that of Unsöld³⁰, which is equivalent to replacing the resolvent by

$$R_0 \approx - P_0 / \omega_*, \quad (134)$$

where ω_* is an average excitation energy. Thus

$$g^I \approx - \frac{\langle 0 | \mu^2 | 0 \rangle}{\omega_* \langle 0 | \mu^2 | 0 \rangle} = 2g^I / \omega_*. \quad (135)$$

The all-important question is: what value of ω_* should be chosen to give the best approximation? Three choices present themselves: (i) the ionization energy I of the atom; (ii) the static (dipole) polarizability average excitation energy ϵ , defined by (132); (iii) the quadrupole polarizability (α_0) average excitation energy

$$\epsilon_0 = 2 \langle 0 | \Theta^2 | 0 \rangle / \alpha_0, \quad (136)$$

where³¹

$$\alpha_0 = -2 \langle 0 | \odot R_0 \odot | 0 \rangle. \quad (137)$$

For hydrogen the three values are

$$I = \frac{1}{2} = 0.5, \quad \epsilon = \frac{4}{9} = 0.44, \quad \epsilon_0 = \frac{3}{5} = 0.6, \quad (138)$$

whereas the value of ω^* which would give g^I correctly is

$$\omega_* = 2g^{II}/g^I = \frac{4}{11} = 0.36. \quad (139)$$

Thus even the smallest of the three choices, ϵ , is over 20% too large, and will produce a corresponding error in the opposite direction in the terms of D_7 . However, in the absence of a better alternative it may be the only way of estimating g^I . The rough formula incorporating this approximation into (129) is

$$D_7^{AB} \approx 6C_6^{AB} \left[\left(\frac{2}{\epsilon_B} + \frac{1}{\epsilon_A + \epsilon_B} \right) g_B^{II} - \left(\frac{2}{\epsilon_A} + \frac{1}{\epsilon_A + \epsilon_B} \right) g_A^{II} \right]. \quad (140)$$

The systematic use of the Unsöld approximation in the original formula (40) for D_7 was proposed by Buckingham¹,

who chose the ionization energy I for both of the average excitation energies which appear in the formula. This leads to

$$D_2 \approx \frac{18}{(I_A + I_B)} \left[\left(\frac{2}{I_A} + \frac{1}{I_A + I_B} \right) \langle 0 | \mu^2 | 0 \rangle_A \langle 0 | \mu^2 | 0 \rangle_B - \left(\frac{2}{I_B} + \frac{1}{I_A + I_B} \right) \langle 0 | \mu^2 | 0 \rangle_B \langle 0 | \mu^2 | 0 \rangle_A \right], \quad (141)$$

or re-arranging in accordance with (140),

$$D_2 \approx 6 \left[\frac{6 \langle 0 | \mu^2 | 0 \rangle_A \langle 0 | \mu^2 | 0 \rangle_B}{I_A + I_B} \right] \left[\left(\frac{2}{I_B} + \frac{1}{I_A + I_B} \right) \delta_B^H - \left(\frac{2}{I_A} + \frac{1}{I_A + I_B} \right) \delta_A^H \right]. \quad (142)$$

Hence, by comparison with (140), Buckingham's approximation replaces the Van der Waals coefficient C_6 by the first factor in parentheses in (142). For two hydrogen atoms the forward component of the dipole coefficient given by (142) is

$$\begin{aligned} D_2^{HH} &= 216 + 54 = 270 \\ (\text{accurate: } 330.5 + 64.0 &= 394.5) \end{aligned} \quad (143)$$

which is over 30% too small.

A further approximation made by Buckingham and useful in rough work concerns the expectation values occurring in g^{II} . The operator μ^2 is

$$\mu^2 = \left(\sum_{i=1}^N z_i \right)^2 = \sum_i z_i^2 + 2 \sum_{i < j} z_i z_j, \quad (144)$$

and has therefore one- and two-electron parts. The expectation value for an S-state is

$$\langle 0 | \mu^2 | 0 \rangle = \frac{N}{3} \langle 0 | r^2 | 0 \rangle + 2N(N-1) \langle 0 | z_1 z_2 | 0 \rangle. \quad (145)$$

The two-electron term would vanish in the absence of electron exchange, and is often neglected. Similarly

$$\begin{aligned} -\mu^2 \textcircled{4} &= \left(\sum_i z_i \right)^2 \left(\sum_i r_i^4 p_{2i} \right), \\ &= \sum_i r_i^4 p_{2i} p_{1i}^2 + \sum_{i \neq j} (2r_i^3 p_{2i} p_{1i} z_j + r_i^2 p_{2i} z_j^2) \\ &\quad + \sum_{i \neq j \neq k} r_i^4 p_{2i} z_j z_k, \end{aligned} \quad (146)$$

has one-, two- and three-electron parts. Neglecting all but the one-electron contribution we have for an S-state

$$-\langle 0 | \mu^2 \textcircled{4} | 0 \rangle \approx \frac{2}{15} N \langle 0 | r^4 | 0 \rangle. \quad (147)$$

Using these simplifications, (131) becomes

$$g^{\text{II}} \approx \langle r^4 \rangle / 5 \langle r^2 \rangle, \quad (148)$$

and (132) becomes

$$\epsilon \approx 2N \langle r^2 \rangle / 3\alpha_0; \quad (149)$$

Note that both (148) and (149) are exact for one and two-electron atoms.

Estimates of the dispersion dipole for rare-gas diatoms

In view of the interest in the interaction dipoles of the rare-gas diatoms, discussed in the introduction, it seems worth-while attempting to estimate the magnitude of the dispersion contribution represented by the leading term D_7/R^7 of (21). For this purpose we shall select formula (140) with g^{II} given by (148) and ϵ given by (149), as the most accurate compromise for which data are available. The relevant data for the hydrogen and rare-gas atoms in their ground states are collected in Tables 4 and 5. The expectation values $\langle r^2 \rangle$ and $\langle r^4 \rangle$ in Table 4 are Hartree-Fock values calculated by Fraga and Malli³², except for H(exact) and He(accurate³³). The static polarizabilities α_0 are taken from a review by Dalgarno³¹, where the original references are given; most of the values were deduced from optical measurement. The collision diameters, σ , are taken from Hirschfelder, Curtiss

and Bird³⁴, except for H, which is estimated from the $^3\Sigma_u^+$ state of H_2 . The C_6 coefficients in Table 2 are taken from a table of recommended values by Dalgarno²³, where the original references are given.

Before calculating the actual values of D_7^{AB} from the data in Tables 4 and 5, let us consider its sign. The dominant terms are those of D_7^I , given by (59), which is positive corresponding to A^-B^+ if $g_B^I > g_A^I$. In (140) g^I is approximated by $2g^{II}/\epsilon$, so that the atom with the larger value of this quantity will be positive. From Table 4 it can be seen that the order of decreasing values of $2g^{II}/\epsilon$ is H, Xe, Kr, Ar, He, Ne. The order of decreasing values of g^{II} is H, Kr, Xe, Ar, He, Ne, so that except for Xe and Kr, D_7^{II} contributes in the same sense as D_7^I . Even apart from hydrogen, the order is irregular because Ne is below He.

We note in passing the difference between the ordering and magnitudes estimated here and those of Levine's semi-classical Drude model formula^{11,35},

$$D_7^{AB} \approx 10 \alpha_A \alpha_B (\alpha_B^{2/3} - \alpha_A^{2/3}), \quad (150)$$

which predicts that the atom with the larger polarizability is positive; from Table 4 the Drude order would therefore

be Xe, Kr, Ar, H, Ne, He. Also (150) predicts much larger values than (140); for HeAr Levine calculates $D_7=827$ a.u. (compare the Table 6 value of 26 a.u.). The failure of the Drude formula is presumably connected with the assumption of harmonic motion by the electrons, which is incapable of allowing for the difference in the spread of the radial electron distribution represented by the ratio g^{II} .

The values of D_7 calculated from (140) are given in Table 6; it should be borne in mind that, on the basis of the error in g^I for hydrogen, the magnitudes may be 20% low. The interaction dipole due to the leading dispersion term at the conventional collision diameter $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$, that is

$$\mu(\sigma_{AB}) = D_7^{AB} / \sigma_{AB}^7,$$

is given in Table 7 in atomic units. The values are all extremely small, less than 0.001 Debye, when compared with the dipole moments of bonded heteropolar diatomic molecules near equilibrium.

OVERLAP DIPOLE

In this section we shall outline a simple perturbation approach to the overlap or exchange contribution to the interaction dipole $\mu(R)$ for distances R such that the overlap between the electron clouds of atoms A and B is small. This should include distances around the conventional collision diameters σ_{AB} for the rare-gas atoms.

We shall consider the overlap contribution to be essentially the interaction dipole as calculated by the Hartree-Fock approximation for the diatom AB. Two effects can be distinguished. First, the pure exchange effect due to the electrons exchanging between the undistorted atoms A and B, in accordance with the Pauli principle. Second, the distortion of the atomic orbitals of A and B due to the interaction. The Hartree-Fock calculations of Matcha and Nesbet⁷ included both effects. At small distances ($R=2$ Bohr) they state that the only orbitals which make a significant contribution to the interaction dipole, which is of the order of one Debye, are those added to the atomic basis to describe distortion. Nevertheless, near the collision diameter (5-6 Bohr), where the energy of interaction is very small, it is

unlikely that appreciable distortion occurs; the overlap dipole is now only of the order of 0.001 of a Debye.

Exchange dipole

Let us assume that for $R \gtrsim \sigma_{AB}$ the wavefunction Ψ for the diatom AB can be approximated satisfactorily by antisymmetrizing the product of the ground state wavefunctions A_0 and B_0 of the separate atoms, as in a conventional Heitler-London treatment,

$$\Psi = \mathcal{A} A_0 B_0. \quad (151)$$

Let the Hartree-Fock spatial atomic orbitals for A and B be $a_1, a_2, \dots, a_m$ and $b_1, b_2, \dots, b_n$ where $N_a = 2m$ and $N_b = 2n$.

Then since

$$A_0 = \mathcal{A} a_1(1)\alpha(1)a_1(1)\beta(1)a_2(2)\alpha(2) \dots a_m(2m)\beta(2m), \quad (152)$$

and similarly for B, we have, ignoring normalization,

$$\Psi = \mathcal{A} a_1\alpha a_1\beta \dots a_m\alpha a_m\beta \cdot b_1\alpha b_1\beta \dots b_n\alpha b_n\beta. \quad (153)$$

Note that this wavefunction is not quite as restrictive as it seems. It is essentially the same as the Hartree-Fock wavefunction

$$\Psi_{\text{HF}} = \mathcal{A} \psi_1(1) \psi_2(2) \dots \psi_N(N) \quad (154)$$

where the molecular spin-orbitals ψ_i consist of linear combinations of the atomic spin-orbitals $a_i\alpha, a_i\beta, b_j\alpha, b_j\beta$.

The exchange dipole moment, as we shall call the overlap dipole when distortion is neglected or does not contribute, is given in the Hartree-Fock approximation by

$$\mu_{\text{ex}}(R) = \langle \Psi | \mu_0 | \Psi \rangle / \langle \Psi | \Psi \rangle, \quad (155)$$

where the z-component of the dipole moment operator μ_0 is given by (17) and (18) and Ψ by (153). Since μ_0 is a one-electron operator, and the dipole moment is independent of origin for a neutral system, (155) can be reduced to

$$\mu_{\text{ex}}(R) = - \int z \rho(\underline{r}) d^3r + (n-m)R, \quad (156)$$

where $\rho(\underline{r})$ is the electron density defined by

$$\rho(\underline{r}) = \sum_{i=1}^N \langle \Psi | \delta^3(\underline{r} - \underline{r}_i) | \Psi \rangle / \langle \Psi | \Psi \rangle, \quad (157)$$

and $z = z^a - R/2 = z^b + R/2$ is an electronic coordinate with respect to the mid-point of AB as origin. Since the orbitals on A and B are separately orthonormal, if A and B did not overlap the density would be

$$\rho^{(0)}(z) = 2 \sum_{i=1}^m |a_i(z)|^2 + 2 \sum_{j=1}^n |b_j(z)|^2, \quad (158)$$

and the dipole moment (156) would vanish. When A and B overlap the density involves the orbital overlap functions

$$S_{ji}(R) = \langle b_j | a_i \rangle. \quad (159)$$

An expression for the single-particle density matrix $\gamma(\underline{x}; \underline{x}')$ ($\underline{x} = \underline{r}, \sigma$) of two non-orthogonal groups of electrons, such as two overlapping atoms, has been given by Sutcliffe and McWeeny³⁶. However, their formula is completely general, and so advantage cannot be taken of the simplifying features of orbital wavefunctions. The formula for the density matrix $\gamma(\underline{x}; \underline{x}')$ in the present case will therefore be derived, and leads immediately to the density $\rho(\underline{r})$.

Exchange density

Consider a system of N electrons described by a Slater determinant of non-orthogonal spin orbitals $\psi_1(\underline{x}), \psi_2(\underline{x}), \dots, \psi_N(\underline{x})$, as in (154). It follows from the definition

$$\gamma(\underline{x}; \underline{x}') = N(N-1) \int \dots \int \Psi^*(\underline{x}', \underline{x}_2, \dots, \underline{x}_N) \Psi(\underline{x}, \underline{x}_2, \dots, \underline{x}_N) d\underline{x}_2 \dots d\underline{x}_N \quad (160)$$

that

$$\gamma(\underline{x}; \underline{x}') = \psi(\underline{x}) \cdot \Delta^{-1} \psi^{\dagger}(\underline{x}'), \quad (161)$$

where ψ is the row vector $(\psi_1, \psi_2, \dots, \psi_N)$ and Δ is the overlap matrix

$$\Delta = \langle \psi^{\dagger} | \psi \rangle \quad (162)$$

with elements $\Delta_{ij} = \langle \psi_i | \psi_j \rangle$. If

$$\psi = (\psi_1^a, \psi_2^a, \dots, \psi_{2m}^a, \psi_1^b, \psi_2^b, \dots, \psi_{2n}^b) \quad (163)$$

where the ψ_i^a and ψ_j^b form separately orthonormal sets, then

$$\Delta = \begin{bmatrix} A & D^\dagger \\ D & 1 \end{bmatrix} \quad (164)$$

where D is a $2n \times 2m$ matrix

$$D = \langle \psi_b^\dagger | \psi_a \rangle. \quad (165)$$

It is easy to see by partitioning Δ^{-1} that

$$\Delta^{-1} = \begin{bmatrix} (A - D^\dagger D)^{-1} & -(A - D^\dagger D)^{-1} D^\dagger \\ -(A - D D^\dagger)^{-1} D & (A - D D^\dagger)^{-1} \end{bmatrix} \quad (166)$$

Hence, by substituting (166) and (163) into (161) we get

$$\begin{aligned} \gamma(x; x') &= \psi_a(x) \cdot (A - D^\dagger D)^{-1} \cdot \psi_a^\dagger(x') - \psi_a(x) \cdot (A - D^\dagger D)^{-1} D^\dagger \cdot \psi_b^\dagger(x') \\ &\quad - \psi_b(x) \cdot (A - D D^\dagger)^{-1} D \cdot \psi_a^\dagger(x') + \psi_b(x) \cdot (A - D D^\dagger)^{-1} \cdot \psi_b^\dagger(x'). \end{aligned} \quad (167)$$

Now if ψ_a consists of two sets of m spin-orbitals

$a_1\alpha, a_2\alpha, \dots, a_m\alpha$ and $a_1\beta, a_2\beta, \dots, a_m\beta$, and ψ_b consists

of two sets of n spin-orbitals $b_1\alpha, b_2\alpha, \dots, b_n\alpha$ and

$b_1\beta, b_2\beta, \dots, b_n\beta$, then since the spin eigenfunctions α and

β are orthogonal, the matrix $\mathbb{D}$ has the form

$$\mathbb{D} = \left[\begin{array}{c|c} \mathbb{S} & \mathbb{O} \\ \hline \mathbb{O} & \mathbb{S} \end{array} \right] \quad (168)$$

where

$$\mathbb{S} = \langle \mathbf{b}^T | \mathbf{a} \rangle \quad (169)$$

is the $n \times m$ overlap matrix for spatial orbitals, with elements given by (159). By putting $\underline{x}' = \underline{x}$ in (167) and integrating over spin it follows that the spinless density is

$$\begin{aligned} \rho(\underline{r}) = & 2 \mathbf{a}(\underline{r}) \cdot (\mathbb{I} - \mathbb{S}^T \mathbb{S})^{-1} \mathbf{a}^T(\underline{r}) - 2 \mathbf{a}(\underline{r}) \cdot (\mathbb{I} - \mathbb{S}^T \mathbb{S})^{-1} \mathbb{S}^T \mathbf{b}^T(\underline{r}) \\ & - 2 \mathbf{b}(\underline{r}) \cdot (\mathbb{I} - \mathbb{S} \mathbb{S}^T)^{-1} \mathbb{S} \mathbf{a}^T(\underline{r}) + 2 \mathbf{b}(\underline{r}) \cdot (\mathbb{I} - \mathbb{S} \mathbb{S}^T)^{-1} \mathbf{b}^T(\underline{r}). \end{aligned} \quad (170)$$

A simple check is given by integrating, which leads after reduction of the right-hand side to the correct result $2m + 2n = N$.

The exchange density, $\rho - \rho^{(0)}$, can be expanded in powers of the orbital overlap functions, which decrease exponentially with R . The leading terms in the exchange

density, of order S^2 , which should be adequate at the conventional collision diameter, are

$$\begin{aligned} \rho - \rho^{(0)} = & -2 \sum_{i=1}^m \sum_{j=1}^n (b_j S_{ji} a_i^* + a_i S_{ij}^* b_j^*) \\ & + 2 \sum_{i=1}^m \sum_{j=1}^m a_i (S^\dagger S)_{ij} a_j^* + 2 \sum_{i=1}^n \sum_{j=1}^n b_i (S S^\dagger)_{ij} b_j^* + \dots \quad (171) \end{aligned}$$

Note that these terms integrate to zero. For the closed shells assumed here, they correspond roughly to a loss of density between the atoms, and an increase on the atoms. By substituting (171) into equation (156) for the exchange dipole, and cancelling out diagonal atomic contributions, we get

$$\begin{aligned} \mu_{ex}(R) \approx & 4 \sum_{i=1}^m \sum_{j=1}^n \langle a_i | z | b_j \rangle S_{ji} \\ & - 4 \sum_{i=1}^m \sum_{j=1}^m \langle a_i | z | a_j \rangle (S^\dagger S)_{ji} - 4 \sum_{i=1}^n \sum_{j=1}^n \langle b_i | z | b_j \rangle (S S^\dagger)_{ji}; \quad (172) \end{aligned}$$

as before, if $\mu_{ex}(R)$ is positive the polarity is $A^- B^+$.

The first term gives the contribution due to the orbital overlap dipoles $\langle a_i | z | b_j \rangle$, which vanish only if the orbitals a_i and b_j are identical. The last two terms in (172) involve orbital transition dipoles of the separate atoms, which vanish

unless the orbitals i and j have different parity.

It does not appear to be possible to write the exchange dipole as the sum of two atomic contributions, μ_A and μ_B , as suggested by Matcha and Nesbet⁷. The last two terms in (172) have this character, but in general one would expect the first terms to dominate. The concept of atomic contributions, if it is valid at all, probably belongs to the realm of shorter distances, where the effects of atomic orbital distortions dominate. Nor does it appear possible to make any general statement about the sign of the exchange dipole. However, in the absence of actual calculations, some insight can be gained by looking at a few special cases.

Hydrogen-Helium

Let us consider first the case of two one-electron atoms with single orbitals a and b on each centre in a non-bonding triplet state. Equation (172) cannot be applied directly to this simple case, but it is easy to see that

$$\mu_{ex}(R) \approx 2 \langle a | z | b \rangle \langle b | a \rangle. \quad (173)$$

If a and b are s-type orbitals with orbital a larger than orbital b , so that their cross-sections through the z -axis

are as drawn in figure 2, it is easy to see that $\langle a|z|b \rangle$ is positive. Hence the long range exchange dipole μ_{ex} is positive corresponding to A^-B^+ .

This argument can be applied to hydrogen interacting with helium. Orbital $a = \pi^{-\frac{1}{2}} \exp(-r_a)$ and there are two Hartree-Fock 1s orbitals b , which can be approximated by $\pi^{-\frac{1}{2}} \zeta^{\frac{3}{2}} \exp(-\zeta r_b)$ with $\zeta > 1$. Hence we conclude that the exchange dipole has the polarity H^-He^+ . Buckingham¹ quotes the integrals, which for large R reduce to the asymptotic form ($\zeta > 1$)

$$\mu_{ex}(R) \sim \frac{64\zeta^5}{(\zeta^2-1)^4} R e^{-2R}, \quad (174)$$

which is approximately of form (2). For the collision diameter, $\sigma(HHe) = 5.48$, and taking $\zeta = \sqrt{2I(He)} = 1.3444$, formula (173), gives $\mu = 0.00214$.

Helium-Neon

Let atom A be He with two 1s orbitals denoted simply by a , and atom B be Ne with orbitals $1s^2 2s^2 2p_0^2 2p_+^2 2p_-^2$. By symmetry only $2p_0$ will occur in equation (172), which becomes

$$\mu_{ex}(R) \approx 8 \left[\langle a|z|1s \rangle \langle 1s|a \rangle + \langle a|z|2s \rangle \langle 2s|a \rangle + \right. \\ \left. \langle a|z|2p \rangle \langle 2p|a \rangle - \langle 1s|z^b|2p \rangle \langle 2p|a \rangle \langle a|1s \rangle \right. \\ \left. - \langle 2s|z^b|2p \rangle \langle 2p|a \rangle \langle a|2s \rangle \right]. \quad (175)$$

At large distances the term $\langle a|z|2p \rangle \langle 2p|a \rangle$ will dominate, and it is clear from figure 3 that both factors will be negative, and the product positive. Actually all terms in (175) appear to be positive, so the long-range exchange dipole will be positive, corresponding to He^-Ne^+ . This is the polarity calculated by Matcha and Nesbet⁷.

Helium-Xenon

We consider this case as an example of He interacting with a large atom. There are many terms coming from the Xe orbitals $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$. Let them be denoted by b_j as before. Then from (172)

$$\mu_{ex}(R) \approx 8 \left[\sum_{j=1}^n \langle a|z|b_j \rangle \langle b_j|a \rangle - \sum_{i>j=1}^n \sum_{i>j=1}^n \langle a|z^b|b_j \rangle (\mathcal{S}\mathcal{S}^\dagger)_{ij} \right]. \quad (176)$$

Let us assume, as seems likely, that the first sum will dominate. Now if the orbitals of Xe formed a complete set then

$$\sum_{j=1}^n |b_j\rangle\langle b_j| = 1, \quad (177)$$

and hence

$$\sum_{j=1}^n \langle a | g | b_j \rangle \langle b_j | a \rangle = \langle a | g | a \rangle = -R/2. \quad (178)$$

It is therefore possible that in interaction with a large atom like Xe the polarity is He^+Xe^- . This argument enables one to understand the existing Hartree-Fock calculations⁷ according to which the polarity of the overlap dipole for HeAr is He^+Ar^- . Clearly, in order to proceed further it is necessary to calculate $\mu_{\text{ex}}(R)$ given by (172) using the known³⁷ Hartree-Fock orbitals of the atoms of interest.

The approach to the exchange dipole suggested in this section makes two assumptions. The first, mentioned above, is that the orbital distortion described by the Hartree-Fock approximation can be neglected about and beyond the conventional collision diameter σ . The second is that, notwithstanding the failure of the Heitler-London wavefunction to describe exchange correlation correctly at very long range³⁸, it will nevertheless lead to reasonable results

for distances around σ .

DISCUSSION

The work on the interaction dipole presented in this report is preliminary and incomplete. Nevertheless, certain interesting conclusions can be drawn.

Firstly, the estimates of the coefficient D_7 given in Table 6 suggest that the dispersion contribution to the interaction dipole can be of the same order of magnitude as the overlap dipole. A comparison of the two contributions to the interaction dipole for three rare-gas diatoms and HeH at their conventional collision diameters, obtained from references 7, 1 and table 7, is as follows; all values are in atomic units.

	σ	overlap	dispersion
HeNe	5.03	+ 0.000171	- 0.000149
HeAr	5.65	- 0.00323	+ 0.000141
NeAr	5.82	- 0.00566	+ 0.000570
HeH	5.48	- 0.00214	+ 0.000701

We see that the estimated dispersion contribution is smaller than the overlap contribution in all cases, but that for HeNe and HeH they are comparable.

Secondly, the sign of the dispersion contribution as given by the leading term D_7 is opposite to that of the overlap contribution for the diatoms HeH, NeHe, HeAr, NeAr (dispersion $-$, overlap $+$). This suggests it may be a general rule, at least for the interaction of closed shell atoms. A pictorial plausibility argument supporting this suggestion is illustrated in figures 4(a) and 4(b). The argument assumes that the attractive response of the electron density to correlation is matched by the repulsive displacement of density by the Pauli principle. There is no clear and obvious basis for this assumption.

If the above conclusions are correct, the dipole moment function $\mu(R)$ for two closed shell atoms will have the behaviour sketched in figure 5. The long range behaviour, R^{-7} is followed by a zero dipole and an exponential rise as the atoms overlap and distort. This must reach a maximum value, because the dipole moment vanishes for the united atom at $R=0$, and behaves^{39,40} like R^3 for small R . It may even have another zero and extremum, as shown by the dashed curve, since the polarity at short range depends on the relative atomic numbers, Z_a and Z_b . For the united atom

in an S state, the atom with the smaller atomic number is probably always positive⁴⁰. Thus the dipole moment functions of HeH and HeNe seem likely to have the extraordinary behaviour indicated by the dashed curve.

The existence of a maximum dipole moment for the rare-gas diatoms in particular, means that the extrapolation procedure used by Matcha and Nesbet⁷ to calculate the overlap dipole at long range from that at short range may not be reliable. For this reason it will be interesting to calculate the long range exchange dipole given by the simpler approach suggested in this paper.

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APPENDICES

A. g ratios for hydrogen atom

In this appendix we calculate analytically the exact limiting and average values of $g^I(\omega) = \gamma(\omega)/\alpha(i\omega)$ and $g^{II}(u,v) = \Gamma(u,v)/L(u,v)$ for the ground state of the hydrogen atom. The quantities α, γ, Γ and L are defined by equations (44) - (47).

(1) $g^I(0)$.

From (45)

$$\begin{aligned} \gamma(0) &= -\langle 0 | \mu R_0 \mu R_0 \oplus | 0 \rangle - \langle 0 | \mu R_0 \oplus R_0 \mu | 0 \rangle, \\ &= -\langle \psi_\mu^{(1)} | \mu | \psi_0^{(1)} \rangle - \langle \psi_\mu^{(1)} | \oplus | \psi_\mu^{(1)} \rangle, \end{aligned} \quad (A.1)$$

where $\psi_\mu^{(1)}$ and $\psi_0^{(1)}$ are the first-order perturbed wavefunctions for dipole and quadrupole perturbations, defined by the differential equations

$$(H_0 - E_0) \psi_\mu^{(1)} + \mu \psi_0 = 0, \quad (A.2)$$

$$(H_0 - E_0) \psi_0^{(1)} + \oplus \psi_0 = 0. \quad (A.3)$$

For one electron, in polar coordinates,

$$\mu = -r \cos \theta, \quad \oplus = -r^2 P_2(\cos \theta), \quad (\text{A.4})$$

and for the ground state of hydrogen

$$|0\rangle \equiv \psi_0 = \pi^{-1/2} e^{-r}. \quad (\text{A.5})$$

The solutions of (A.2) and (A.3) are well known³¹:

$$\psi_{\mu}^{(1)} = r \cos \theta \left(1 + \frac{r}{2}\right) \psi_0, \quad (\text{A.6})$$

$$\psi_0^{(1)} = \frac{1}{2} r^2 P_2(\cos \theta) \left(1 + \frac{2r}{3}\right) \psi_0. \quad (\text{A.7})$$

By substituting and integrating we get

$$-\langle \psi_{\mu}^{(1)} | \mu | \psi_0^{(1)} \rangle = 117/8 = 14.625, \quad (\text{A.8})$$

$$-\langle \psi_{\mu}^{(1)} | \oplus | \psi_{\mu}^{(1)} \rangle = 24. \quad (\text{A.9})$$

Hence by (A.1)

$$\gamma(0) = 309/8 = 38.625, \quad (\text{A.10})$$

and since²⁸ $\alpha(0) = 9/2 = 4.5$ we have

$$g^I(0) = \gamma(0)/\alpha(0) = 103/12 = 8.583 \quad (A.11)$$

(ii) $g^I(\infty)$.

The asymptotic limit $g^I(\infty)$ is given by (64). The straightforward way of evaluating such quantities would appear to be to reduce them to commutators, and then use the fundamental quantal commutator identities. However, the presence of the resolvent R_0 makes this difficult. A better technique is to avoid commutators involving R_0 , by stopping at the half-way stage and evaluating integrals involving differential operators.

Put

$$g^I(\infty) = g_1 + g_2 \quad (A.12)$$

where

$$g_1 = \frac{1}{2N} \langle 0 | [\mu R_0 \mu, [H, \Theta]] | 0 \rangle, \quad (A.13)$$

$$= \frac{1}{N} \langle \psi_\mu^{(u)} | \mu | [H, \Theta] \psi_0 \rangle, \quad (A.14)$$

since $[H, \Theta]$ is a real anti-hermitian operator. Now

$$\begin{aligned}
 [H, \Theta] &= -i \frac{d\Theta}{dt}, \\
 &= i \sum_j \frac{d}{dt} \left(g_j^2 - \frac{1}{2}(x_j^2 + y_j^2) \right), \\
 &= i \sum_j (2g_j \dot{g}_j - x_j \dot{x}_j - y_j \dot{y}_j), \\
 &= \sum_j \left(2g_j \frac{\partial}{\partial g_j} - x_j \frac{\partial}{\partial x_j} - y_j \frac{\partial}{\partial y_j} \right). \quad (A.15)
 \end{aligned}$$

Hence, for the hydrogen atom, with $\psi_0(r)$ given by (A.5),

$$[H, \Theta] \psi_0 = 2P_2 r \frac{\partial}{\partial r} \psi_0 = -2P_2 r \psi_0. \quad (A.16)$$

By substituting from (A.4), (A.6) and (A.16) into (A.14) we get

$$g_1 = 8 \langle P_1^2 P_2 \rangle_{Av} \int_0^\infty e^{-2r} (1 + \frac{1}{2}r) r^5 dr = 5. \quad (A.17)$$

Similarly

$$g_2 = \frac{1}{2N} \langle 0 | \mu R_0 \Theta [H, \mu] - [H, \mu] \Theta R_0 \mu | 0 \rangle, \quad (A.18)$$

$$= \frac{1}{N} \langle \psi_\mu^{(0)} | \Theta | [H, \mu] \psi_0 \rangle. \quad (A.19)$$

In this case

$$\begin{aligned} [H, \mu] &= i \sum_j p_{3j} , \\ &= \sum_j \frac{\partial}{\partial z_j} . \end{aligned} \quad (\text{A.20})$$

Hence for hydrogen

$$[H, \mu] \psi_0 = \cos \theta \frac{\partial}{\partial r} \psi_0 = -P_1 \psi_0 . \quad (\text{A.21})$$

By substituting from (A.4), (A.5), (A.6) and (A.21) into (A.19) we get

$$g_2 = 4 \langle P_1^2 P_2 \rangle_{\text{av}} \int_0^\infty e^{-2r} (1 + \frac{1}{2}r) r^5 dr = \frac{5}{2} . \quad (\text{A.22})$$

Hence by (A.12)

$$g^I(\infty) = 15/2 = 7.5 . \quad (\text{A.23})$$

(iii) $\bar{g}^I$

The ratio of averages is defined by (68). From (66)

$$\bar{f} = 2 \langle \psi_\mu^{(u)} | \mu \odot | \psi_0 \rangle . \quad (\text{A.24})$$

By substituting from (A.4), (A.5) and (A.6) and integrating we get for hydrogen

$$\bar{J} = 8 \langle p_1^2 p_2 \rangle_{\Delta V} \int_0^\infty e^{-2r} (1 + \frac{1}{2}r) r^6 dr = 33/2, \quad (\text{A.25})$$

and from (67) $\bar{\alpha} = 2$, so

$$\bar{g}^I = 33/4 = 8.25 \quad (\text{A.26})$$

(iv) $\underline{g^{II}(0,0)}$

From (46)

$$\Gamma(0,0) = - \langle 0 | \mu R_0 \mu R_0 \otimes | 0 \rangle, \quad (\text{A.27})$$

$$= - \langle \psi_\mu^{(u)} | \mu | \psi_0^{(u)} \rangle = 117/8 \quad (\text{A.28})$$

according to (A.8). From (47)

$$L(0,0) = 2 \langle 0 | \mu R_0^2 \mu | 0 \rangle,$$

$$= 2 \langle \psi_\mu^{(u)} | \psi_\mu^{(u)} \rangle. \quad (\text{A.29})$$

By substituting from (A.6) and integrating

$$L(0,0) = 43/4 = 10.75, \quad (A.30)$$

Hence

$$g^{\text{II}}(0,0) = \Gamma(0,0)/L(0,0) = 117/86 = 1.360, \quad (A.31)$$

$$(v) \quad \underline{g^{\text{II}}(\infty, \infty)}$$

The asymptotic form of $\Gamma(u,v)$ can be obtained by substituting (61) into (46), and is

$$\begin{aligned} \Gamma(u,v) &\sim -u^{-2}v^{-2} \langle 0 | [H, \mu] \mu [H, \Theta] | 0 \rangle, \\ &= u^{-2}v^{-2} \langle [H, \mu] \psi_0 | \mu | [H, \Theta] \psi_0 \rangle. \end{aligned} \quad (A.32)$$

By substituting from (A.21) and (A.16) into (A.32) and integrating we get

$$\Gamma(u,v) \sim u^{-2}v^{-2} \frac{4}{5}. \quad (A.33)$$

From (47) likewise we have

$$\begin{aligned} L(u,v) &\sim 2u^{-2}v^{-2} \langle 0 | [H, \mu]^2 | 0 \rangle, \\ &= 2u^{-2}v^{-2} \langle 0 | (\sum_j p_{ji})^2 | 0 \rangle. \end{aligned} \quad (A.34)$$

For the hydrogen atom in the ground 1s state

$$\begin{aligned} L(u, v) &\sim 2u^{-2}v^{-2} \frac{2}{3} \langle 0 | \frac{1}{2} p^2 | 0 \rangle, \\ &= -2u^{-2}v^{-2} \frac{2}{3} E_0 = u^{-2}v^{-2} \frac{2}{3}, \end{aligned} \quad (\text{A.35})$$

Hence

$$g^{\text{II}}(\infty, \infty) = \lim_{\substack{u \rightarrow \infty \\ v \rightarrow \infty}} \frac{\Gamma(u, v)}{L(u, v)} = \frac{6}{5} = 1.2. \quad (\text{A.36})$$

(vi) The remaining values of g^{II} given in (76) can be calculated by similar means. $\bar{g}^{\text{II}}$ is trivial. The formulae and values required for the others are as follows:

$$\Gamma(0, v) \sim v^{-2} N g_1 = 5v^{-2}. \quad (\text{A.37})$$

$$L(0, v) \sim 2v^{-2} \langle 0 | \mu^2 | 0 \rangle = 2v^{-2}. \quad (\text{A.38})$$

$$\Gamma(u, 0) \sim u^{-2} \langle [H, \mu] \psi_0 | \mu | \psi_0^{(u)} \rangle = \frac{3}{2} u^{-2}. \quad (\text{A.39})$$

$$\Gamma(0, -) = \int_{-\infty}^{+\infty} \frac{dv}{\pi} \Gamma(0, v) = \langle 0 | \mu R_0 \mu | 0 \rangle = \frac{33}{4}. \quad (\text{A.40})$$

$$L(0, -) = \kappa(0) = \frac{9}{2}. \quad (\text{A.41})$$

$$\Gamma(-, 0) = \langle 0 | \mu^2 R_0 | 0 \rangle = 5. \quad (\text{A.42})$$

$$\Gamma(-, v) \sim -v^{-2} \langle 0 | \mu^2 [H, \Theta] | 0 \rangle = 2v^{-2}, \quad (\text{A.43})$$

$$L(-, v) \equiv \alpha(v) \sim N v^{-2} = v^{-2}. \quad (\text{A.44})$$

$$\Gamma(u, -) \sim u^{-2} \langle 0 | [H, \mu] \mu \Theta | 0 \rangle = u^{-2}. \quad (\text{A.45})$$

B. $\vec{D}_7$ for hydrogen - hydrogen

The perturbed densities ρ_7^I and ρ_7^{II} for atom B occurring in equations (119), (120), (122) and (123), can be defined by replacing the operator f^b in (116) and (117) by the operator

$$\sum_{i=1}^{N_b} \delta^3(\underline{r} - \underline{r}_i^b).$$

Hirschfelder and Eliason²⁷ obtained accurate approximations for these densities for two hydrogen atoms based on a Löwdin-Shull set used in earlier work²⁸. The approximations may be expressed in the form

$$\rho_7 = \frac{3}{4\pi} \cos\theta e^{2r} \sum_{m=1}^8 \frac{c_m (2r)^m}{m!} + P_3(\cos\theta) \text{ component,} \quad (\text{B.1})$$

where the coefficients c_m^I and c_m^{II} are given in table 8.

It is then easy to compute

$$\vec{D}_7^I(H-H) = \frac{1}{4} \sum_{m=1}^8 (m+1) c_m^I = 330.512, \quad (\text{B.2})$$

$$\vec{D}_7^{II}(H-H) = \frac{1}{4} \sum_{m=1}^8 (m+1) c_m^{II} = 64.007. \quad (\text{B.3})$$

TABLE 1

Comparison of accurate and approximate values of D_7
for $H(\zeta$ scaled) - H system (atomic units)

ζ	Accurate	Approx. (126-7)	Approx. (111)
1	0	0	0
1.05			55.44
1.1	85.65	84.32	85.87
1.2	106.29	104.65	106.53
1.223			107.03
1.3	102.87	101.29	103.04
1.4	91.48	90.11	91.58
1.5	78.49	77.33	78.52
1.6	66.29	65.33	66.27
1.6875	56.88	56.08	56.83
1.7	55.64	54.86	55.59
1.8	46.65	46.01	46.57
1.9	39.17	38.65	39.08
2	33.00	32.57	32.90
2.5			14.87

TABLE 2

Accurate and approximate values of C_s and C_{II} for $H-H$ (atomic units)

ζ	C_s	C_{II}	
		Accurate	(91) (94)
1	6.499027	4.932417	5.0625 4.8743
1.1	4.862103	3.340541	3.4265 3.3001
1.2	3.703157	2.306445	2.3620 2.2765
1.3	2.865143	1.620665	1.6559 1.5977
1.4	2.247960	1.157293	1.1792 1.1392
1.5	1.785978	0.8387895	0.85207 0.82430
1.6	1.435108	0.61637577	0.62414 0.60468
1.7	1.165113	0.4587684	0.46305 0.44927
1.8	0.9548598	0.3455498	0.34765 0.33780
1.9	0.7893366	0.2631760	0.26395 0.25684
2.0	0.6577167	0.2025257	0.20250 0.19732

TABLE 3

Comparison of accurate and approximate values of
parts I and II of D_7 for $H_\zeta-H$ (atomic units)

ζ	D_7^I		D_7^{II}	
	Accurate	Eq. (126)	Accurate	Eq. (127)
1	0	0	0	0
1.1	77.74	76.29	7.91	8.03
1.2	96.68	94.91	9.61	9.74
1.3	93.84	92.17	9.02	9.13
1.4	83.76	82.31	7.73	7.80
1.5	72.14	70.94	6.35	6.39
1.6	61.18	60.20	5.12	5.13
1.7	51.56	50.77	4.09	4.09
1.8	43.46	42.76	3.25	3.24
1.9	36.58	36.07	2.59	2.58
2.0	30.93	30.52	2.07	2.05
∞	0	0	0	0

TABLE 4

Properties of hydrogen and rare-gas atoms (atomic units)

Property	H	He	Ne	Ar	Kr	Xe
$N\langle r^2 \rangle$	3	2.385	9.372	26.03	39.52	56.60
$N\langle r^4 \rangle$	22.5	7.889	27.29	144.9	245.1	312.9
α_0	4.5	1.384	2.67	11.1	16.8	27.3
g_{II}	1.5	0.6616	0.5824	1.113	1.240	1.127
ϵ	0.4444	1.150	2.34	1.56	1.57	1.38
$2g_{II}/\epsilon$	6.75	1.15	0.498	1.43	1.58	1.63
σ	(6.10)	4.86	5.20	6.43	6.80	8.14

TABLE 5

Dispersion energy coefficients C_6^{AB} for diatoms (atomic units)

	H	He	Ne	Ar	Kr	Xe
H	6.50	2.83	5.6	20	29	42
He		1.47	3.0	9.6	13	19
Ne			6.3	20	27	38
Ar				65	91	130
Kr					130	190
Xe						270

TABLE 6

Dispersion dipole coefficients D_{AB}^{AB} for diatoms ($A B^+$) (atomic units)

A \ B	H	He	Ne	Ar	Kr	Xe
H	0	-104	-221	-662	-922	-1340
He		0	-12.1	25.7	50.1	75.7
Ne			0	128	203	292
Ar				0	104	160
Kr					0	13.3
Xe						0

TABLE 7

Dispersion dipole D_7^{AB}/σ^7 at conventional collision diameter (atomic units)

(Multiply by 2.54 to convert to Debyes)

A \ B						
	H	He	Ne	Ar	Kr	Xe
H	0	-0.000701	-0.00120	-0.00174	-0.00199	-0.00145
He		0	-0.000149	+0.000141	+0.000219	+0.000154
Ne			0	+0.000570	+0.000723	+0.000496
Ar				0	+0.000188	+0.000147
Kr					0	+0.0000103
Xe						0

TABLE 8

Coefficients²⁷ in perturbed densities ρ , equation (E.3)

m	C_m^I	C_m^{II}
1	35.232764	0
2	17.616382	0
3	10.569833	1.567252
4	7.046555	3.098280
5	2.592724	1.375320
6	-0.551494	-0.762546
7	0.061489	0.170829
8	0	-0.0155350

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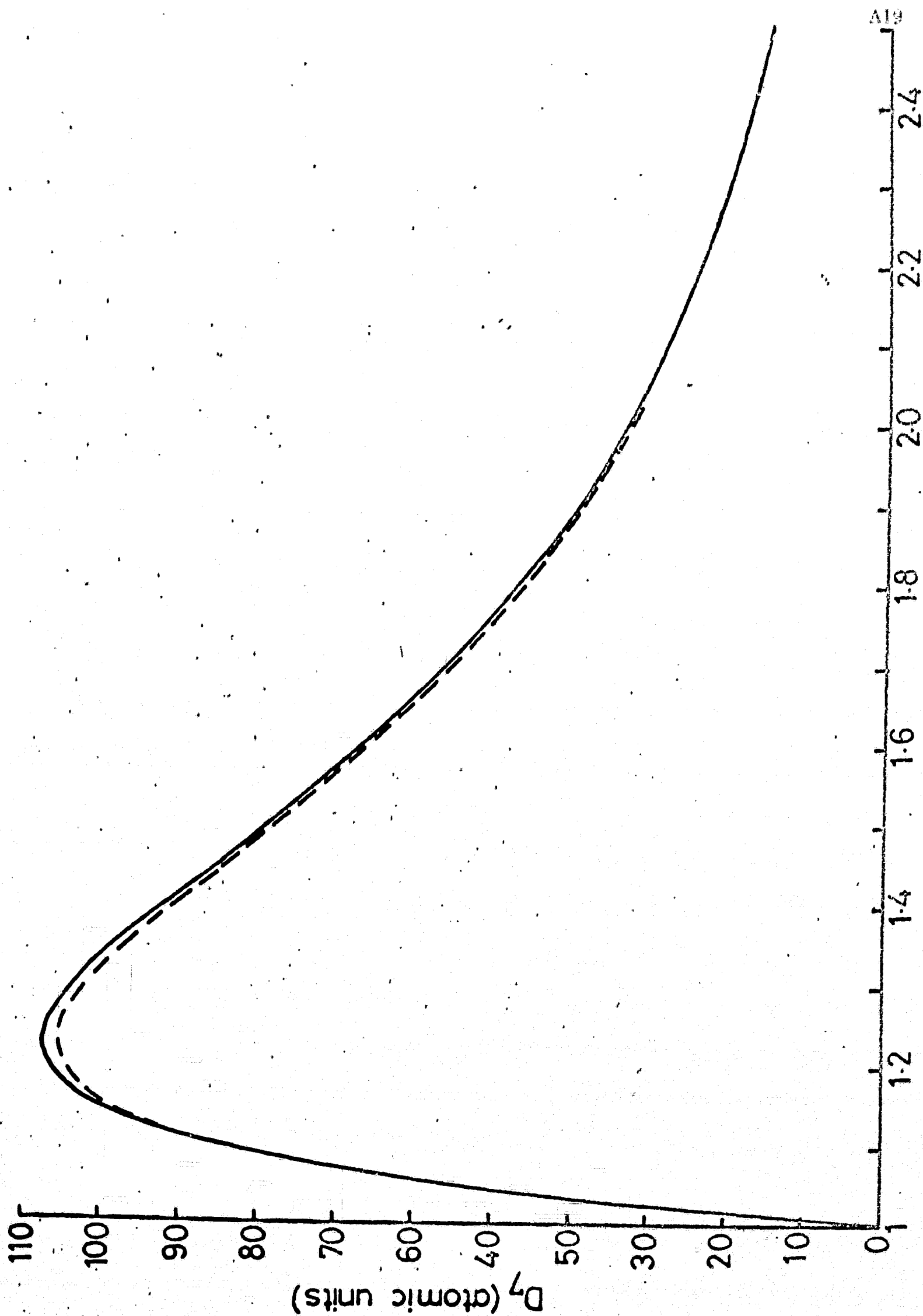


Figure 1 Dispersion dipole coefficient D_7 for ζ -scaled hydrogen-hydrogen diatom as a function of ζ . Accurate —, approximation (125+127) ----.

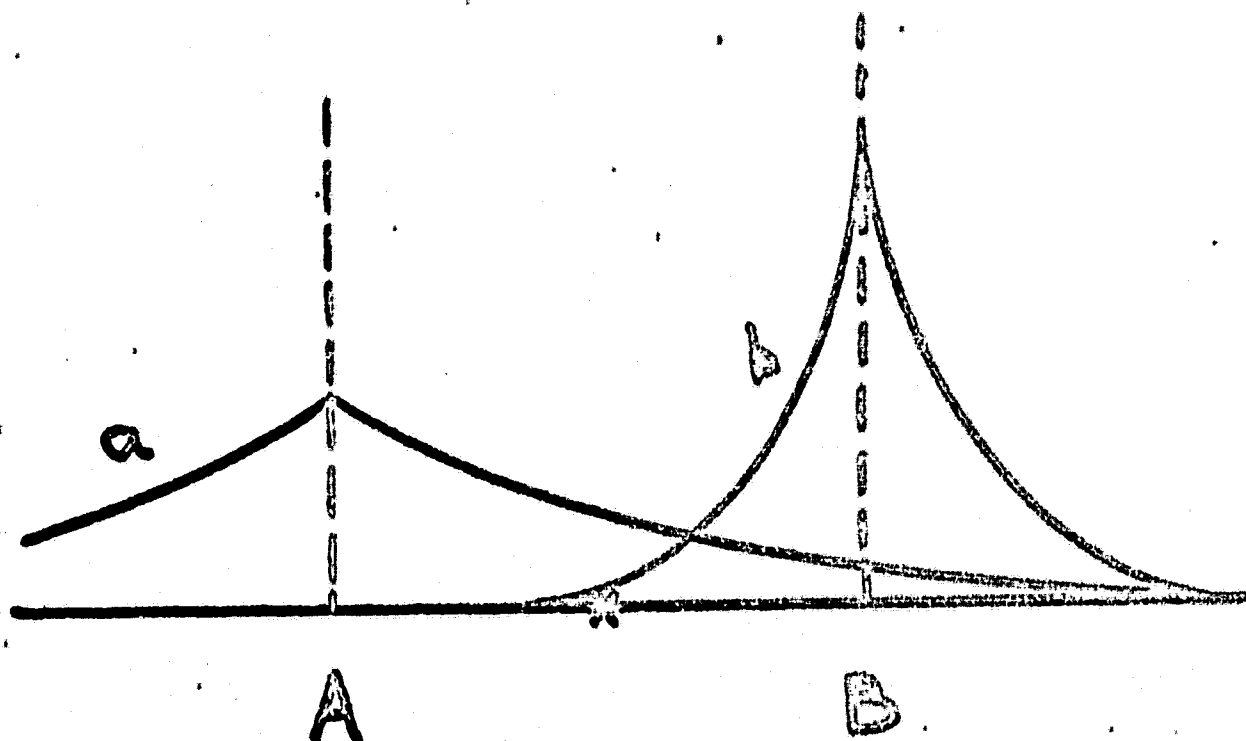


Figure 2 Cross-section through z-axis of s orbitals a and b

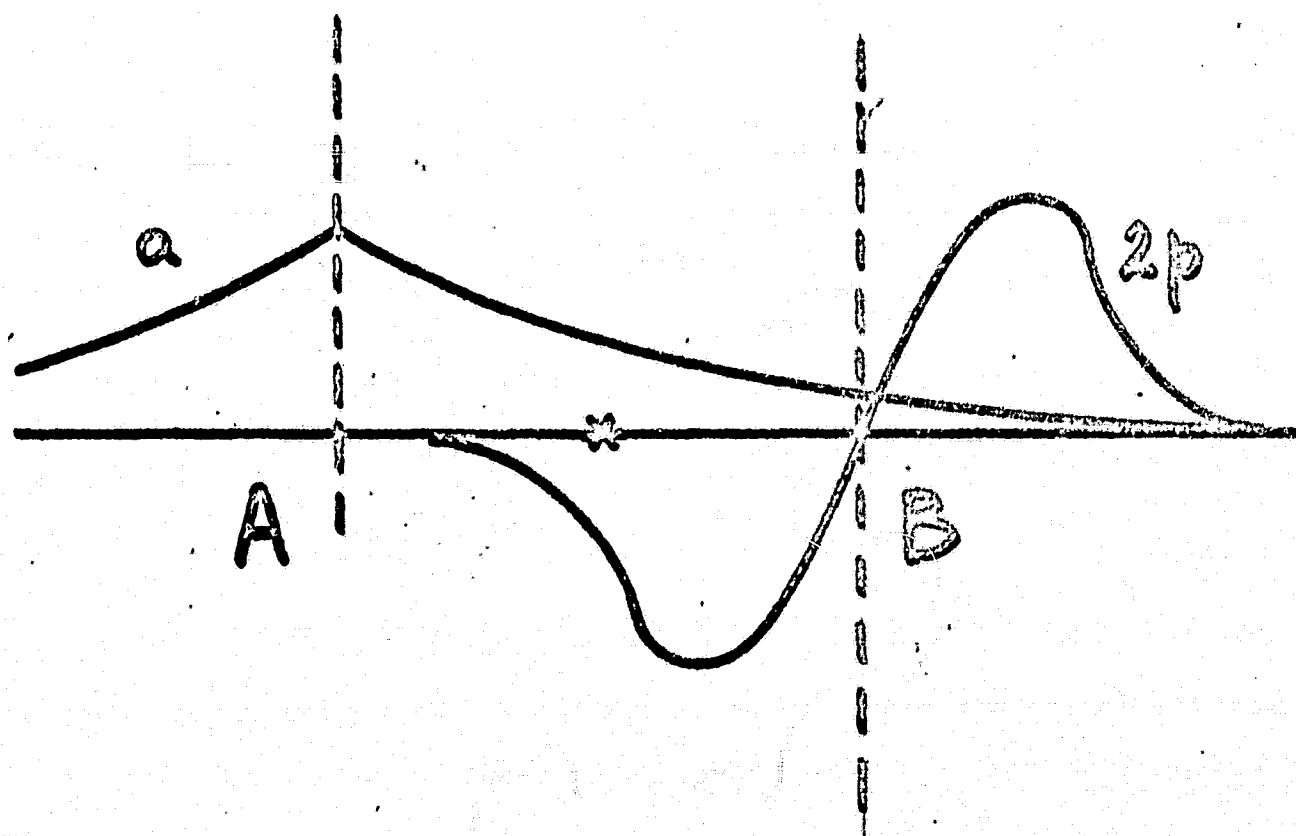


Figure 3 Cross-section through z-axis for HeNe orbitals

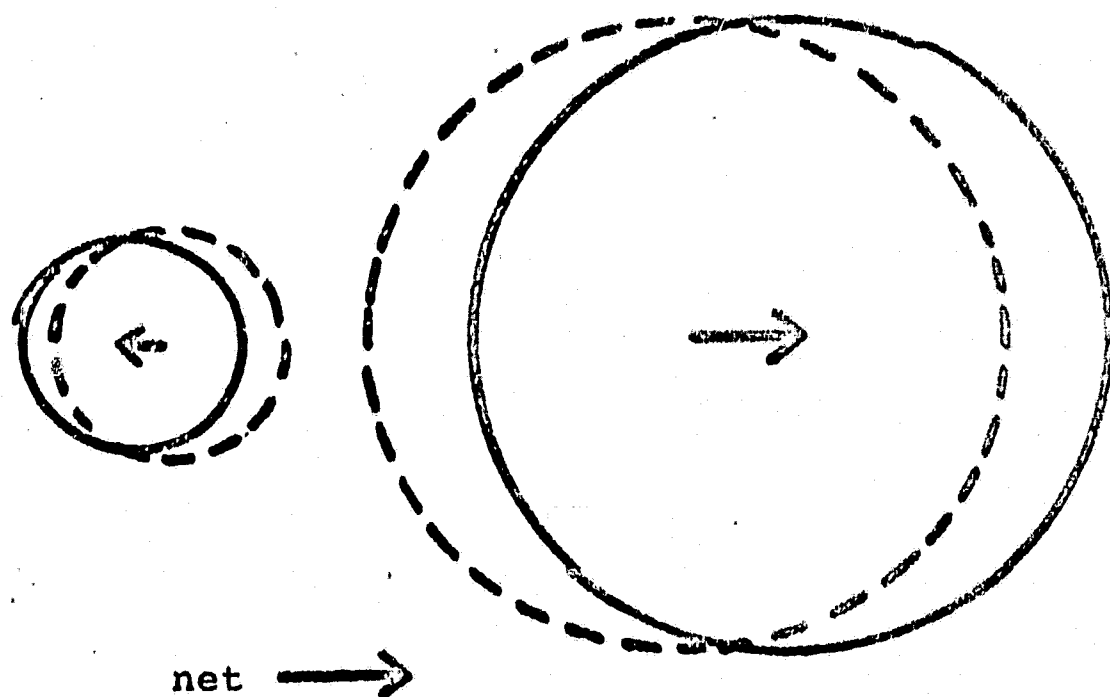


Figure 4(a) Long range dispersion density and dipole due to electron correlation. Unperturbed—, perturbed----

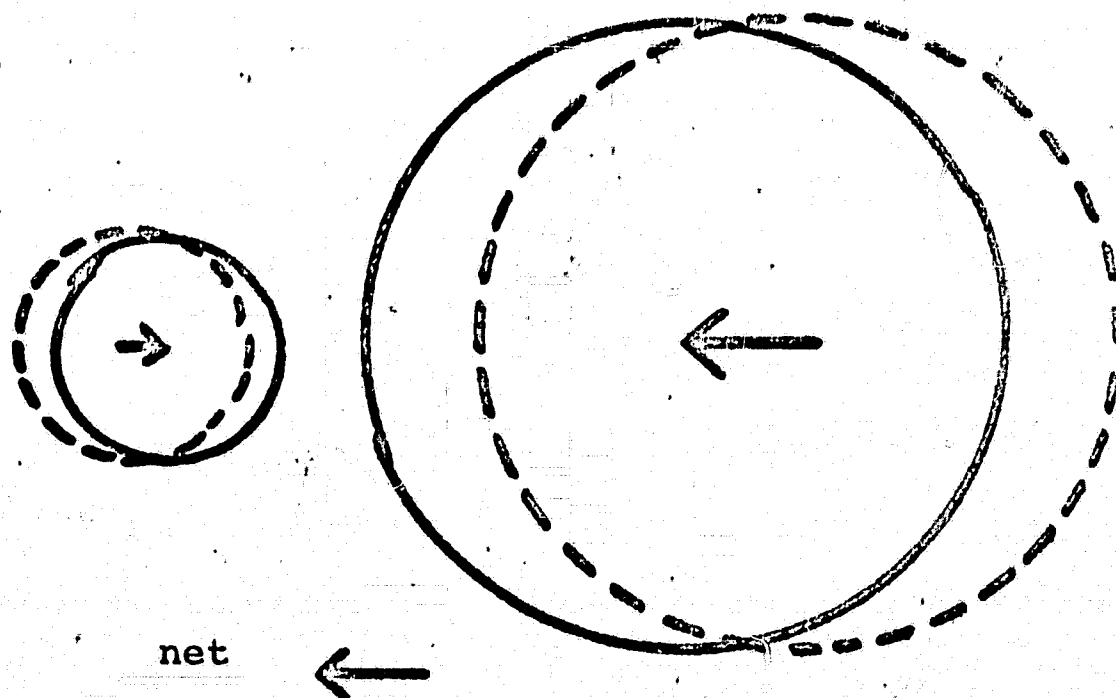


Figure 4(b) Long range exchange density and dipole due to Pauli exclusion principle

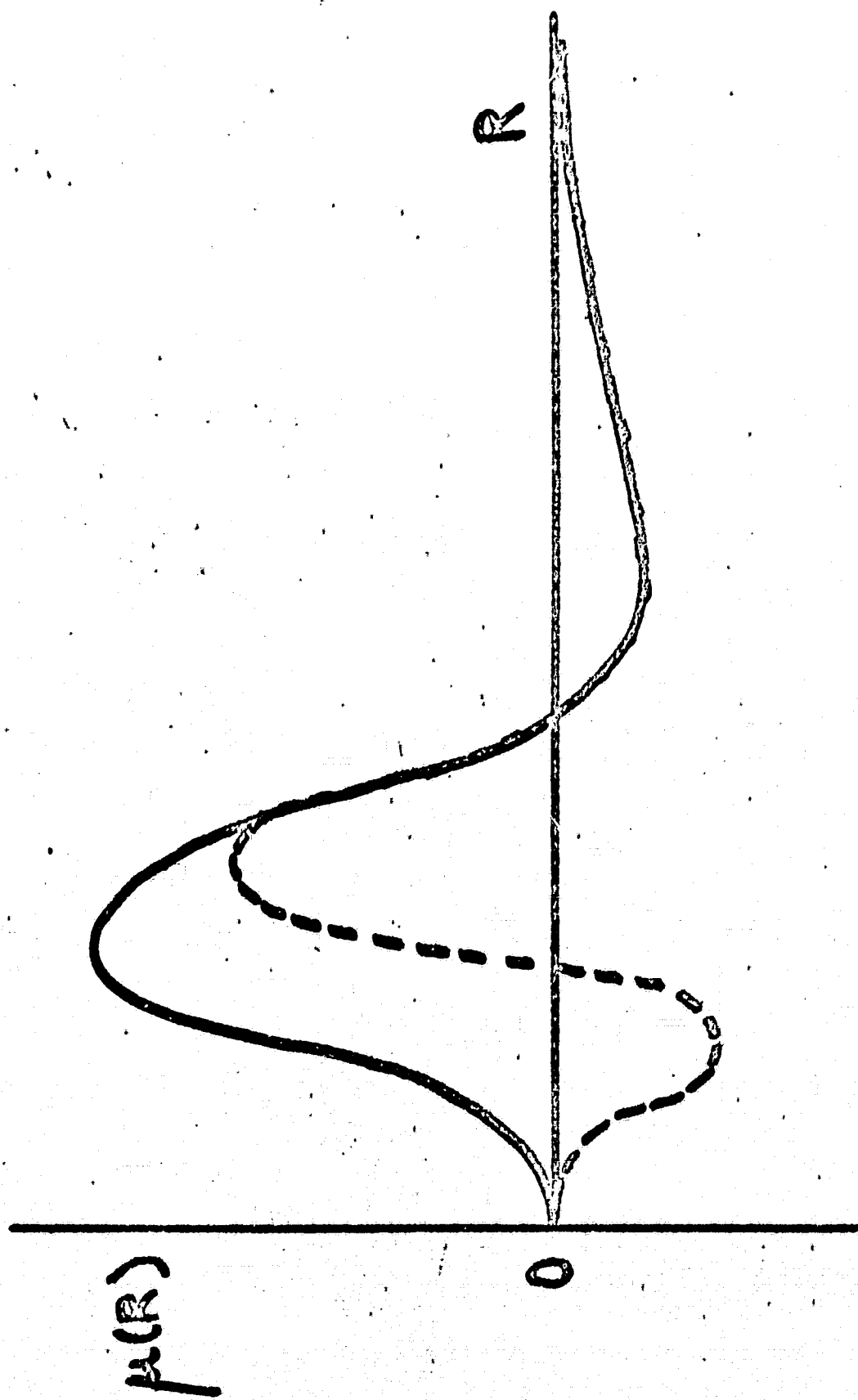


Figure 5 Sketch of possible dipole moment functions $\mu(R)$