

The Interaction of Differently Excited Like Atoms at Large Distances*

ROBERT S. MULLIKEN

Laboratory of Molecular Structure and Spectra, Physics Department, University of Chicago, Chicago, Illinois

(Received August 1, 1960)

The theory of long-range first-order interaction energies is discussed for two like odd-electron atoms in different doublet states, for the case that spin-orbit coupling is smaller than the other splittings. The treatment involves some revision and some extension of previous work. At interatomic distances sufficiently large that overlap of the wave functions of the two atoms is negligible, only the first-order dispersion (dipole-dipole and higher multipole) forces remain, but it is shown that even at rather large distances there often is sufficient overlap that valence forces predominate over first-order dispersion forces.

For the case of two H atoms one in a 2S and the other in a 2P state it is shown that the first-order dispersion energy corresponds explicitly to a particular e^2/r_{12} integral which represents precisely

the mutual electrostatic energy, falling off approximately as $1/R^3$, of two dipolar charge distributions one on each atom. (All the other, valence-force e^2/r_{12} integrals fall off exponentially with R .) Tables are given for the first-order dispersion splitting patterns (out to terms in $1/R^3$) for the interaction of a 2P with a 2S or with a 2D atom.

Finally, the first-order splittings for pairs of like even-electron atoms is discussed. The results are simpler than for odd-electron atoms, and are applicable also to any pair of such atoms either in singlet states or in *any* states in which spin-orbit coupling is *strong*. For atoms both in, for example, triplet, states with *weak* spin-orbit coupling, different formulas will be needed.

I. INTRODUCTION

THE London dispersion forces (second-order dispersion forces, with approximately $1/R^6$ potentials) which account for much of the ground-state van der Waals attraction between atoms or molecules are well known. The existence of stronger longer-range forces (first-order dispersion forces, or excitation-exchange forces, with approximately $1/R^3$ potential) between an atom in its ground state and another atom of the same kind in an excited state to which spectroscopic transitions from the ground state are allowed, was first discussed for the case of two hydrogen atoms with one in its $2p\pi$ excited state by Eisenschitz and London.¹ King and Van Vleck² developed the discussion further for atoms with one and two valence electrons, and showed that experimental data on the low $^1\Pi_u$ states of Na_2 , Cd_2 , and Hg_2 (including the existence of a small maximum in the potential curve at large R values) are in agreement with the theory. Unfortunately their results, while correct for *singlet* states ($^1\Sigma^+$ and $^1\Pi$ states), appear to be in error for triplet states. (Eisenschitz and London's results for both $^1\Pi$ and $^3\Pi$ states of H_2 appear to be correct.) The present paper contains a new and in part rather different and more general discussion. From this it is seen that errors of sign are very likely to arise unless great care is taken.

The initial discussion, in Sec. II, deals with the general case of two like atoms in any two different doublet states. In Secs. III–V the simpler case of two H atoms is examined in more detail, and it is shown that the discussion of first-order dispersion forces for the Σ states (though not the Π states) of $\text{H}(1s) + \text{H}(2p)$

is somewhat academic, because valence-type interactions (including those with $\text{H}^+ + \text{H}^-$) predominate out to large R values. However, it is shown in Secs. IV and VI that there are other cases (e.g., one normal Na atom and one Na atom in its first excited state), where valence forces do not yet dominate at large R .

II. THE FIRST-ORDER INTERACTION OF LIKE ATOMS IN DIFFERENT DOUBLET STATES

It has seemed desirable to treat first, in Sec. II, the general case of two like atoms in doublet electronic states. However, the reader may find it illuminating at various points in the argument to specialize the discussion (as is easily done) to the relatively simple case of two H atoms.

For the interaction of two like atoms in any two different doublet electronic states, the normalized first order wave functions may be expressed in the general form

$$\Psi = (\Psi_I + \eta \Psi_{II}) / (2 + 2\eta S_{II}), \quad (1)$$

where $\eta = \pm 1$ and S_{II} is the nonorthogonality integral $\int \Psi_I^* \Psi_{II} d\tau$. (In the applications below, S_{II} is usually small or negligible.)

In (1), if the atoms are in doublet states,

$$\Psi_I = \alpha(i; j) \Phi_I; \Psi_{II} = \alpha(i; j) \Phi_{II}, \quad (2)$$

where for $M_S = 0$ for the total system,

$$\begin{aligned} \Phi_I &= 2^{-1/2} [\Phi_{ma}(i) \Phi_{nb}'(j) + \sigma \Phi_{ma}'(i) \Phi_{nb}(j)], \\ \Phi_{II} &= \text{Ref}^M \Phi_I = 2^{-1/2} [\Phi_{mb}(i) \Phi_{na}'(j) + \sigma \Phi_{mb}'(i) \Phi_{na}(j)], \end{aligned} \quad (3)$$

while for $M_S = +1$ or -1 , respectively,

$$\begin{aligned} \Phi_I &= \Phi_{ma}(i) \Phi_{nb}(j), \quad \text{or} \quad \Phi_I = \Phi_{ma}'(i) \Phi_{nb}'(j); \\ \Phi_{II} &= \text{Ref}^M \Phi_I. \end{aligned} \quad (3a)$$

In Eqs. (3), (3a), Ref^M refers to the operation of reflection of any electronic wave function (e.g., Φ_I) in

* This work was assisted in part by the Air Force Ballistics Division under a contract with the General Electric Space Science Laboratory, Philadelphia, Pennsylvania, and in part by the Office of Naval Research under a contract with the University of Chicago. Presented at the March, 1959 Cambridge meeting of the American Physical Society [Bull. Am. Phys. Soc. 4, 173 (1959)].

¹ R. Eisenschitz and F. London, Z. Physik 60, 491 (1930).

² G. W. King and J. H. Van Vleck, Phys. Rev. 55, 1165 (1939).

the median plane perpendicular to the line joining the two atoms a and b . Here and throughout the following discussion, the nuclei of atoms a and b are considered as centers of force which always remain in fixed locations in space. $\Phi_{ma}(i)$ represents the exact electronic eigenfunction of any one Zeeman or Stark component of any doublet state (m) of atom a with $M_S = +\frac{1}{2}$, written as a function of N electrons $1 \cdots N$ (collectively designated as i); while Φ_{nb}' represents the exact electronic eigenfunction of any *different* doublet state (n) of another atom b of the same kind with $M_S = -\frac{1}{2}$, written as a function of N electrons $N+1, \cdots 2N$ (collectively designated as j). For example, Φ_{ma} may correspond to a set of closed shells plus one electron in an atomic spin-orbital (ASO) $m_a\alpha$ and Φ_{nb}' to a like set of closed shells plus one electron in an ASO $n_b\beta$; but Eqs. (3), (3a) are not restricted to this special case. Eqs. (3) and (3a) are directly applicable only insofar as spin-orbit coupling can be neglected (see below).

In Eqs. (2), the "supplementary antisymmetrizer" $\mathcal{A}(i; j)$ is an operator which converts a product such as $\Phi_{ma}(i)\Phi_{nb}'(j)$, in which Φ_{ma} and Φ_{nb} are normalized and Φ_{ma} is antisymmetric in electrons $1 \cdots N$, Φ_{nb}' in electrons $N+1 \cdots 2N$, into a function which is normalized and is antisymmetric in *all* the electrons $1 \cdots 2N$. It follows that

$$\mathcal{A}(i; j) = [(N!)^2 / (2N)!]^{1/2} \sum_k (-1)^{\sigma_P} P_k(i; j), \quad (4)$$

where the $P_k(i; j)$ effect such permutations $[2N! / (N!)^2$ in number] between electrons of the groups i and j as are necessary to make Ψ antisymmetric in all the electrons.³

For the case of two H atoms, $\Phi_{ma}(i)$ and $\Phi_{nb}'(j)$ reduce to $m_a\alpha_1$ and $n_b\beta_2$, where m and n now refer to any two atomic orbitals (AO's), α and β are the usual one-electron spin functions, and 1 and 2 index the two electrons. $\mathcal{A}(i; j)$ now becomes the ordinary antisymmetrizer.

In the present paper, the positive directions of the z_a and z_b axes will both be taken *toward the center* of the molecule; but x_b will be taken parallel to x_a and y_b to y_a . (If the axis-system is right-handed on a , it is then left-handed on b .) If polar coordinates are used, θ_a will be measured from z_a and θ_b from z_b ; with the axes chosen as stated, $\phi_a = \phi_b$. It is then seen that for *any* AO, say m , $Ref^M m_a = m_b$, hence for any doublet-state atomic wave function, $Ref^M \Phi_{ma}(i) = \Phi_{mb}(i)$; and so on.

In some cases, Eqs. (3) and (3a) must be replaced by more general expressions. $\Phi_{ma}(i)$ and $\Phi_{nb}'(j)$ are

characterized not only by $S = \frac{1}{2}$ and $M_S = +\frac{1}{2}$ or $-\frac{1}{2}$, but also by L and M_L values (in the case of two H atoms, by l and m_l values). Equations (3) and (3a) are valid except in the case of the Σ^+ and Σ^- states which arise when both $M_L(a)$ and $M_L(b)$ are nonzero and $M_L(a) = -M_L(b)$. Equations (3) are then replaced usually^{3a} by the following expressions, in which ρ can be $+1$ or -1 :

$$\begin{aligned} \Phi_I = & \frac{1}{2} [\Phi_{m^+a}(i)\Phi_{n^-b}'(j) + \sigma\Phi_{m^+a}'(i)\Phi_{n^-b}(j) \\ & + \rho\Phi_{m^-a}(i)\Phi_{n^+b}'(j) + \rho\sigma\Phi_{m^-a}'(i)\Phi_{n^+b}(j)]; \\ \Phi_{II} = & Ref^M \Phi_I. \end{aligned} \quad (3b)$$

Equations (3a) for $M_S = \pm 1$ are replaced by

$$\begin{aligned} \Phi_I = & 2^{-1/2} [\Phi_{m^+a}(i)\Phi_{n^-b}(j) + \rho\Phi_{m^-a}(i)\Phi_{n^+b}(j)] \\ & \text{or } 2^{-1/2} [\Phi_{n^+a}'(i)\Phi_{n^-b}'(j) + \rho\Phi_{m^-a}'(i)\Phi_{n^+b}'(j)]; \quad (3c) \\ \Phi_{II} = & Ref^M \Phi_I. \end{aligned}$$

In the H+H case ($i=1$ only, $j=2$ only), Φ_{m^+} may, for example, correspond to a $2p\pi^+$ AO and Φ_{n^-} to a $3d\pi^-$ AO, in which case the interaction of the two atoms gives rise to singlet and triplet, g and u , Σ^+ and Σ^- states; it can readily be verified that the $+1$ value of the index ρ corresponds *in all cases* (i.e., for singlet or triplet, g or u) to Σ^+ , the value -1 to Σ^- states. Completely analogous examples occur for doublet atoms in general (e.g., if m^\pm is $M_L = \pm 1$ of any 2P state and n^\mp is $M_L = \mp 1$ of any 2D state, Σ^+ and Σ^- states again result).

The wave functions given by Eqs. (1), (2), and (3b) contain three indices η , σ , and ρ , of which $\sigma = \pm 1$ correspond always to triplet and singlet states, respectively. The *parity* p ($+1$ for g , -1 for u) of any diatomic electronic wave function corresponds to the behavior of the latter for the operation of inversion at the center of the system. This operation is equivalent to the product of the two operations of reflection in the mid-plane Ref^M and rotation by 180° around the symmetry axis (Ro^π). Ref^M yields $+1$ or -1 according as η is $+1$ or -1 . It is readily seen that the effect of Ro^π is given by $(-1)^\Lambda$, hence that $p = \eta(-1)^\Lambda$, the same whether Eqs. (3) and (3a) or (3b) and (3c) hold, and independent of the values of σ and ρ . For Σ states a further symmetry property exists, namely their behavior (1 for Σ^+ , -1 for Σ^- states) toward the operation Ref^A of reflection in *any* plane through the symmetry axis. Σ states described by Eqs. (1), (2), and (3) or (3a) are always Σ^+ states, while those described by Eqs. (1), (2), and (3b) or (3c) are Σ^+ or Σ^- according as ρ is $+1$ or -1 .

For convenient reference, Table I lists the values of the various indices just mentioned, also of the composite index $-\eta\sigma\rho$ or $-\eta\sigma$ (which will be seen below to be important), for the various types of states which can

³ Note that each of $\Phi_{ma}(i)$ and $\Phi_{nb}'(j)$ already consists of a linear combination of $N!$ functions obtained by permutations of the electrons within the group i or the group j . This is true whether or not Φ_{ma} and Φ_{nb}' correspond to a single ASO configuration, and still holds if Φ_{ma} and Φ_{nb}' are *exact* wave functions of particular atomic states, since these may in principle always be expanded as infinite sums of single-determinant forms (configuration-interaction description).

^{3a} But not if the states differ only in M_L (see paragraph following Table I).

TABLE I. Summary of indices for various diatomic state-types.

State	σ	Λ	η	ρ	$-\eta\sigma\rho$ or $-\eta\sigma^a$
$^1\Sigma_g^+, ^3\Sigma_g^+$	∓ 1	0	1	1	± 1
$^1\Sigma_u^-, ^3\Sigma_u^-$	∓ 1	0	-1	-1	± 1
$^1\Sigma_u^+, ^3\Sigma_u^+$	∓ 1	0	-1	1	∓ 1
$^1\Sigma_g^-, ^3\Sigma_g^-$	∓ 1	0	1	-1	∓ 1
$^1\Pi_u, ^3\Pi_u$	∓ 1	1	1		± 1
$^1\Pi_g, ^3\Pi_g$	∓ 1	1	-1		∓ 1
$^1\Delta_g, ^3\Delta_g$	∓ 1	2	1		± 1
$^1\Delta_u, ^3\Delta_u$	∓ 1	2	-1		∓ 1
$^1\Phi_u, ^3\Phi_u$	∓ 1	3	1		± 1

^a The index ρ exists only for Σ^+ and Σ^- states derived from the interaction of atoms in states of equal $\Lambda > 0$. In other cases (Σ^+ states derived from atoms with $\Lambda = 0$, and Π , Δ , Φ , \dots states), the index $-\eta\sigma$ takes the place of $-\eta\sigma\rho$. Or, formally, one may set $\rho = +1$ in these cases.

arise from the interaction of two like atoms in different doublet states.

The foregoing discussion, and Table I, do not apply in the case of two like atoms in *identical* states (e.g., 2S , 2S or $^2P\Sigma$, $^2P\Sigma$, or $^2\Pi\Pi$, $^2\Pi\Pi$). *Even for pairs such as $^2\Pi\Pi^+$, $^2\Pi\Pi^-$ which differ in the sign of M_L but which are otherwise identical* (e.g., $2p\pi^+$, $2p\pi^-$ for two H atoms), they do not apply. In all these cases, Eq. (1) must be replaced by $\Psi = \Psi_I$; that is, η , Ψ_{II} , and Φ_{II} in Eqs. (1)–(3c) must be dropped. For cases such as $^2\Pi\Pi^+$, $^2\Pi\Pi^-$, the Φ_I equations of Eqs. (3b), (3c) are valid. To determine the parity of any molecular state, the result of the operation Ref^M can now be determined only by applying it to the complete antisymmetrized Ψ . The resulting Pauli-allowed states in some typical cases are as follows: for 2S , 2S or $^2P\Sigma$, $^2P\Sigma$ (e.g., $1s$, $1s$ or $2s$, $2s$ or $2p\sigma$, $2p\sigma$ for two H atoms) they are $^1\Sigma_g^+$ and $^3\Sigma_u^+$; for $^2\Pi\Pi^+$, $^2\Pi\Pi^+$, $^1\Delta_g$ and $^3\Delta_u$; for $^2\Pi\Pi^+$, $^2\Pi\Pi^+$ they are $^1\Sigma_g^+$, $^1\Sigma_u^-$, $^3\Sigma_u^+$, and $^3\Sigma_g^-$.

The first-order energy E of any state given by Eq. (1), taking into account that $\mathcal{H}_{II\ II} = \mathcal{H}_{I\ I}$ for a homopolar molecule and that $\mathcal{H}_{II\ I} = \mathcal{H}_{I\ II}^*$, is easily seen to be

$$E = \int \Psi^* \mathcal{H} \Psi d\tau = (\mathcal{H}_{I\ I} + \eta \text{Re} \mathcal{H}_{II\ I}) / (1 + \eta \mathcal{S}_{II\ I}), \quad (5)$$

where $\text{Re} \mathcal{H}_{II\ I}$ denotes the real part of $\mathcal{H}_{II\ I}$.

To compute $\mathcal{H}_{I\ I}$ and $\mathcal{H}_{II\ I}$, it will be sufficient to use Eqs. (2), (3) or (2), (3b), since for triplet states with $M_S = \pm 1$ [Eqs. (3a), (3c)], E is the same as for those with $M_S = 0$ [Eqs. (3), (3b)], if we neglect spin-orbit coupling terms and suppose that no external fields are present.

Using Eqs. (2), $\mathcal{H}_{I\ I}$ and $\mathcal{H}_{II\ I}$ have the forms

$$\mathcal{H}_{I\ I} = \int \alpha(i; j) \Phi_I^* \mathcal{H} \alpha(i; j) \Phi_I d\tau,$$

$$\mathcal{H}_{II\ I} = \int \alpha(i; j) \Phi_{II}^* \mathcal{H} \alpha(i; j) \Phi_I d\tau.$$

Taking into account the properties of $\alpha(i; j)$,—see Eq. (4),— $\mathcal{H}_{I\ I}$ and $\mathcal{H}_{II\ I}$ can be simplified to:

$$\mathcal{H}_{I\ I} = \sum_k (-1)^{\sigma_P} \int \left[P_k(i; j) \Phi_I^* \right] \mathcal{H} \Phi_I d\tau, \quad (5a)$$

$$\mathcal{H}_{II\ I} = \sum_k (-1)^{\sigma_P} \int \left[P_k(i; j) \Phi_{II}^* \right] \mathcal{H} \Phi_I d\tau.$$

The procedure and results are similar to those obtained by a familiar theorem due to Slater.

For the computation of long-range interactions between differently-excited like atoms, it is convenient to express the total Hamiltonian \mathcal{H} as a sum of free-atom Hamiltonians \mathcal{H}_{ia}^0 and \mathcal{H}_{jb}^0 plus an interaction Hamiltonian \mathcal{H}^{int} :

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}^{\text{int}}; \quad \mathcal{H}^0 = \mathcal{H}_{ia}^0 + \mathcal{H}_{jb}^0,$$

with

$$\mathcal{H}^{\text{int}} = \sum_i (-e^2/r_{ib}) + \sum_j (-e^2/r_{ja}) + \sum_i \sum_j (e^2/r_{ij}) + e^2/R. \quad (6)$$

Equations (6) are applicable directly only if, in the wave function operated on by \mathcal{H} , all electrons of group i remain on atom a and those of group j on atom b . This condition is fulfilled when we use Eqs. (5a) in computing $\mathcal{H}_{I\ I}$ and $\mathcal{H}_{II\ I}$. \mathcal{H} then has to operate only on products such as $\Phi_{ma}(i) \Phi_{nb}'(j)$ of Eq. (3), in which there are no exchanges between the i and j groups of electrons.

If R is large, it becomes a rather good approximation to expand \mathcal{H}^{int} in powers of R^{-1} and to retain only the first term, with the familiar result,^{1,2} used extensively by London in discussing van der Waals forces,

$$\mathcal{H}^{\text{int}} = (e^2/R^3) [\sum_i \sum_j (x_{ia} x_{jb} + y_{ia} y_{jb} + 2z_{ia} z_{jb})] + (\text{terms in higher powers of } R^{-1}), \quad (7)$$

or if c^+ and c^- , where $c^+ \equiv 2^{-\frac{1}{2}}(x + iy)$ and $c^- \equiv 2^{-\frac{1}{2}}(x - iy)$, are used as coordinates instead of x and y ,

$$\mathcal{H}^{\text{int}} = (e^2/R^3) [\sum_i \sum_j (c_{ia}^+ c_{jb}^- + c_{ia}^- c_{jb}^+ + 2z_{ia} z_{jb})] + \dots \quad (7a)$$

The coordinate origin for electrons of group i is at nucleus a , that for group j at nucleus b . In Eqs. (7), (7a), the usual^{1,2} minus sign before $2z_{ia} z_{jb}$ has been changed to a plus sign because in the present discussion the positive z direction for each atom is taken toward the other atom. Equations (7) and (7a) can be written in a manner which will shortly prove convenient, as follows

$$\mathcal{H}^{\text{int}} = (e^2/R^3) (\sum_q \gamma_q \sum_i \sum_j q_{ia} q_{jb}) + \dots, \quad (7b)$$

with $\gamma_q = 1$ for x , y or c^+ , c^- , and $\gamma_q = 2$ for z .

Using Eqs. (5a) and (6) one now has

$$\begin{aligned} \mathcal{H}_{\text{I I}} = E^0 & \left\{ 1 + \sum'_k (-1)^{\sigma_P} \int [P_k(i; j) \Phi_{\text{I}}^*] \mathcal{H}^0 \Phi_{\text{I}} d\tau \right\} \\ & + \sum_k (-1)^{\sigma_P} \int [P_k(i; j) \Phi_{\text{I}}^*] \mathcal{H}^{\text{int}} \Phi_{\text{I}} d\tau, \\ \mathcal{H}_{\text{II I}} = E^0 & \left\{ S_{\text{II I}} + \sum'_k (-1)^{\sigma_P} \int [P_k(i; j) \Phi_{\text{II}}^*] \mathcal{H}^0 \Phi_{\text{I}} d\tau \right\} \\ & + \sum_k (-1)^{\sigma_P} \int [P_k(i; j) \Phi_{\text{II}}^*] \mathcal{H}^{\text{int}} \Phi_{\text{I}} d\tau, \end{aligned} \quad (5b)$$

where \sum'_k omits the identity permutation, and $E^0 = E_{ma}^0 + E_{nb}^0$. At this point, it is desirable to distinguish two possible situations: (1) R is so large that overlap between the wave functions of atoms a and b is negligible; (2) R is large, but overlap of the two wave functions is not negligible.

In situation (1),

$$\begin{aligned} \mathcal{H}_{\text{I I}} = E^0, \quad \text{and} \quad E = E^0 + \eta \mathcal{H}_{\text{II I}}, \\ \mathcal{H}_{\text{II I}} = \sum_k (-1)^{\sigma_P} \int [P_k(i; j) \Phi_{\text{II}}^*] \mathcal{H}^{\text{int}} \Phi_{\text{I}} d\tau, \end{aligned} \quad (5c)$$

and, as we shall see, only dispersion-type interactions remain. In situation (2), valence-type interactions are also present. A special case of situation (2) will be thoroughly considered in Secs. V and VI for the case of two H or two Na atoms, but the general discussion will now be continued for situation (1) only.

To proceed further, the expressions for Φ_{I} and Φ_{II} from Eqs. (3) or (3b), and for \mathcal{H}^{int} from Eq. (7b), must first be substituted into the $\mathcal{H}_{\text{II I}}$ expression of Eq. (5c). Using Eqs. (3b), one obtains

$$\begin{aligned} \mathcal{H}_{\text{II I}} = (e^2/4R^3) \sum_k (-1)^{\sigma_P} \int & \{ P_k(i; j) [\Phi_{m+b}^*(i) \Phi_{n-a}^{*\prime}(j) \\ & + \rho \Phi_{m-b}^*(i) \Phi_{n+a}^{*\prime}(j) + \sigma \Phi_{m+b}^{*\prime}(i) \Phi_{n-a}^*(j) \\ & + \rho \sigma \Phi_{m-b}^{*\prime}(i) \Phi_{n+a}^*(j)] \} [\sum_q \gamma_q \sum_i \sum_j q_{ia} q_{jb}] \\ & \times [\Phi_{m+a}(i) \Phi_{n-b}^{\prime}(j) + \rho \Phi_{m-a}(i) \Phi_{n+b}^{\prime}(j) \\ & + \sigma \Phi_{m+a}^{\prime}(i) \Phi_{n-b}(j) + \rho \sigma \Phi_{m-a}^{\prime}(i) \Phi_{n+b}(j)] d\tau + \dots \end{aligned}$$

This expression contains $2N!(N!)^2$ permutations on sixteen integrals of the type $\int \chi_{1b}(i) \chi_{2a}^*(j) \mathcal{H}^{\text{int}} \chi_{3a}(i) \chi_{4b}(j) \times d\tau$ times a factor, in which each χ also includes $N!$ permutations on the N electrons of group i or group j . However, a survey shows that only *four* of the sixteen yield a nonzero result, these four being those which include a $\rho\sigma$ factor. Let us consider *one* of these, with

its permutations, for example,

$$\begin{aligned} (\rho\sigma)(e^2/4R^3) \sum_k (-1)^{\sigma_P} \int & [P_k(i; j) \Phi_{m+b}^*(i) \Phi_{n-a}^{*\prime}(j)] \\ & \times \mathcal{H}^{\text{int}} \Phi_{m-a}^{\prime}(i) \Phi_{n+b}(j) d\tau. \\ \text{A canvass shows that there is one, and only one, of} \\ \text{the } P_k\text{'s in this expression which gives a nonzero result,} \\ \text{namely that permutation,}^4 \text{ an odd one since } N \text{ is odd,} \\ \text{which exchanges all the } N \text{ electrons of the } i \text{ group with} \\ \text{those of the } j \text{ group. The expression thus reduces to} \\ (-\rho\sigma)(e^2/4R^3) \sum_q \gamma_q \int & [\Phi_{n-a}^{*\prime}(i)] [\sum_i q_{ia}] [\Phi_{m-a}^{\prime}(i)] d\tau_i \\ & \times \int [\Phi_{m+b}^*(j)] [\sum_j q_{jb}] [\Phi_{n+b}(j)] d\tau_j + \dots \end{aligned}$$

Now, for example, $e^2 \int \Phi_{n-a}^{*\prime}(i) \sum_q q_{ia} \Phi_{m-a}^{\prime}(i) d\tau_i$ is $\mu_{m^-n^-}$, the dipole moment of the $m^- \leftrightarrow n^-$ spectroscopic transition in atom a or b .⁵ Noting also that out of $\sum_q \gamma_q$, only one particular q is involved in any one spectroscopic transition between two Φ 's of an atom, the above expressions becomes $(-\rho\sigma\gamma_q) \mu_{m^-n^-} \mu_{m^+n^+} / 4R^3$. This contribution to $\mathcal{H}_{\text{II I}}$ is one of four which are readily seen to be equal, so that

$$\mathcal{H}_{\text{II I}} = (-\rho\sigma\gamma_q) \mu_{m^-n^-} \mu_{m^+n^+} / R^3 + \dots$$

Hence [see Eq. (5c), and noting that always $\mu_{m^-n^-} = \mu_{m^+n^+}$],

$$\begin{aligned} E - E^0 = (-\eta\rho\sigma\gamma_q) \mu_{m^+n^+}^2 / R^3 + \dots = -2\eta\rho\sigma\mu_{m^+n^+}^2 / R^3 \\ + (\text{terms in higher powers of } R^{-1}), \end{aligned} \quad (8b)$$

since here states m^+ and n^+ (or m^- and n^-) are alike in M_L , q is z , and $\gamma_q = 2$. $E - E^0$ is the *first-order dispersion energy* corresponding to Σ^+ and Σ^- interactions for which Eq. (3b) holds.

A discussion closely similar to the preceding, but using Eq. (3) instead of Eq. (3b), yields

$$\begin{aligned} E - E^0 = (-\eta\sigma\gamma_q) \mu_{mn}^2 / R^3 \\ + (\text{terms in higher powers of } R^{-1}), \end{aligned} \quad (8)$$

where now q is one of c^+ , c^- (or x or y), or z depending on the particular m and n considered, and $\gamma_q = 1$ for $q = c^+$, c^- , x , or y , 2 for $q = z$. If μ_{mn} and R in Eqs. (8) and (8b) are measured in *atomic units*, $E - E^0$ is also in atomic units (1 a.u. = $e^2/a_0 = 27.1$ ev). This can be seen by rewriting, for example, Eqs. (8) in the form

$$E - E^0 = (-\eta\sigma\gamma_q)(e^2/a_0)(\mu_{mn}^2/e^2a_0^2)/(R/a_0)^3 + \dots$$

⁴ Every expression of the type $\sum_k (-1)^{\sigma_P} P_k(i; j) \Phi_{m+b}^*(i) \Phi_{n-a}^{*\prime}(j)$ is antisymmetric in all the $2N$ electrons of groups i and j , and (see reference 3) can in general be written as a linear combination of determinants each with $2N$ rows and $2N$ columns. An odd number (N) of exchanges of rows converts for example each $\Phi_{m+b}(i) \Phi_{n-a}^*(j)$ determinant into the corresponding $\Phi_{n-a}^{\prime}(i) \Phi_{m+b}(j)$ determinant.

⁵ It will be recalled that each Φ or Φ' corresponds to one particular Zeeman component, i.e., M_L and M_S value, of the doublet state which it represents, neglecting spin-orbit coupling as we are here doing. Further, in the dipole moment integral, the value of M_S ($+\frac{1}{2}$ for Φ , $-\frac{1}{2}$ for Φ') does not matter, except that M_S must match for the Φ^* and Φ , or Φ'^* and Φ' , which appear in the integral.

Equation (8) or (8b) can conveniently be rewritten in terms of the oscillator strengths of spectroscopic transitions. In general, the oscillator strength f_{mn} for the single nonvanishing polarized component of a spectroscopic transition $m \rightarrow n$ of frequency ν_{mn} is

$$f_{mn} = (\nu_{mn}/\text{ry})\mu_{mn}^2$$

if μ_{mn} is in a.u.; ry is the rydberg constant; ν_{mn} and ry may conveniently be expressed in cm^{-1} . Combining this equation with Eq. (8) or (8b),

$$E - E^0 = -\eta\sigma\gamma_q(\text{ry}/\nu_{mn})f_{mn}/R^3 + \dots, \quad (9)$$

or

$$E - E^0 = -2\eta\sigma\rho(\text{ry}/\nu_{mn})f_{m^+n^+}/R^3 + \dots \quad (9b)$$

It is important to note that f_{mn} in these equations corresponds to a *single* Stark or Zeeman component of a spectroscopic transition, and is *not* in general equal to the mean oscillator strength \bar{f}_{mn} commonly used.

The *mean* oscillator strength \bar{f} , averaged over all polarizations and over all AO's of a degenerate initial state (e.g., in the (1+1)-electron H + H case over the AO's $2p\pi_{+1}$, $2p\sigma$, and $2p\pi_{-1}$ in a transition to $3d$) and summed over all AO's of a degenerate final state (e.g., $3d\delta_{+2}$, $3d\pi_{+1}$, $3d\sigma$, $3d\pi_{-1}$, $3d\delta_{-2}$) is given (see Bethe and Salpeter⁶ and second paragraph of Sec. IV below) by

$$\bar{f}_{if} = \frac{1}{3}(\nu_{if}/\text{ry}) \frac{\max(l_i, l_f)}{2l_i + 1} (R_i f)^2,$$

where i and f refer to the initial and final states, respectively. In the important special case that i and f are, respectively, ms and np , $\bar{f}_{ms,np} = \frac{1}{3}(\nu_{ms,np}/\text{ry}) \times (R_{ms,np})^2 = f_{ms,np}$, where np refers to any one of np_x , np_y , or np_z , for all of which μ_{mn} in Eq. (9) is the same.⁷ For the interaction of an ms with an np atom, f_{mn} in Eq. (9) is $f_{ms,np}$ and is equal to $\bar{f}_{ms,np}$.

A point of considerable interest is the fact that first-order dispersion interactions between atoms in states m and n can be large even where f_{mn} is very small or even zero. This is because the first-order dispersion splittings are approximately proportional to μ_{mn}^2 , but f_{mn} to $\nu_{mn}\mu_{mn}^2$. Thus, for example, large effects are predicted for the interaction of a $2s$ and a $2p$ H atom because $\mu_{2s,2p}^2$ is large, even though $f_{2s,2p} \approx 0$.

⁶ See H. A. Bethe and E. E. Salpeter, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35, Part I, Eqs. (60.7) and (60.11) for general expressions for the matrix elements $\int \psi_n^* q m dV = \mu_{mn}^{(q)}$ of q for the transition from any initial AO m to any final AO n . See also especially (59.14), (60.8), (61.2), (61.3). The correctness of the transformation from the first to the second form of $D_{e^{\pm}}$ in Eqs. (12a) can be seen from Eqs. (60.11). The fact that *only* one, if any, of $\mu_{mn}^{(c^+)}$, $\mu_{mn}^{(c^-)}$, $\mu_{mn}^{(z)}$ is nonvanishing when complex AO's are used is also demonstrated in connection with the derivation of Eqs. (60.7) and (60.11); in view of this fact, it is seen that *either* the c^+ or the c^- term in the second form of $D_{e^{\pm}}$ in Eqs. (12a) always vanishes.

⁷ If i and f are mp and ns , respectively, $\bar{f}_{mp,ns} = (\frac{1}{3})f_{ns,mp} = (\frac{1}{3})f_{ns,mp}$. In other cases than (ms,np) and (mp,ns) , μ_{mn} of Eq. (9) or (9b) is no longer the same for all m, n belonging to a given pair of degenerate states, and so \bar{f}_{if} is not equal to any individual f_{mn} .

The discussion leading to Eqs. (8) and (9) is similar to that of reference 2 (Φ_m and Φ_n here correspond to S and P there), but more detailed, resulting in the uncovering of the factor $-\sigma$ in $\mathcal{H}_{\text{II I}}$, omitted in reference 2. The present discussion is also more general, and shows the need of Eq. (8b) in certain situations.

In view of the assumptions made in their derivation, Eqs. (8), (8b), (9), (9b) should be good approximations only at R values sufficiently large that overlap of atoms a and b with resulting valence-type interaction, is negligible. For still larger R values, a new complication enters. Namely, when the magnitudes of the dispersion-force splittings become small enough to be comparable with spin-orbit splittings, as for example in the $3s3p$, 2P state of Na with its $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ sub-states, one must consider the joint effects of the dispersion and spin-orbit forces in splitting each of $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ into several components. However, the $^2P_{\frac{3}{2}} - ^2P_{\frac{1}{2}}$ separation for the Na atom is only 0.0021 eV (17.20 cm^{-1}), which (see Sec. VI) is smaller than the dispersion-force splittings until R exceeds 40 a.u. For the heavier alkali metals, the spin-orbit coupling becomes more important. For cesium, $^2P_{\frac{3}{2}} - ^2P_{\frac{1}{2}}$ is 0.069 eV, about equal to the dispersion-force splitting constant at 12 a.u. Calculation of the rather complicated dispersion-force splittings of the individual components of a 2P or other doublet state can be carried out in a straightforward way, but will not be attempted here. In such a treatment, it would be necessary to classify the atomic states and the states of any interacting atom-pair not by the usual strong-field quantum numbers Λ or M_L , and M_S , but by the weak-field ("far-nuclei case c' ") quantum numbers Ω ($0_g^+, 0_u^+$, $0_g^-, 1_u$, etc., atom pair states, from 0^+ , 0^- , 1 , \dots , atomic states).⁸

Some examples of atom-pair states to which Eqs. (8) or (8b), (9) or (9b) are directly applicable are: Li $1s^2 2s(^2S)$, $1s^2 mp(^2P^o)$; B $1s^2 2s^2 2p(^2P^o)$, $1s^2 2s^2 3s(^2S)$ or $1s^2 2s^2 2p^2(^2P$ or 2D or $^2S)$; N $1s^2 2s^2 2p^3(^2D^o$ or $^2P^o)$, $1s^2 2s^2 2p^4(^2P$ or 2D or $^2S)$. Some examples where the treatment based on strong spin-orbit coupling would have to be used are: Tl $s^2 p(^2P_{\frac{1}{2}}$ or $^2P_{\frac{3}{2}})$, $s^2 s(^2S)$ or $s p^2(^2P_{\frac{1}{2}}, ^2P_{\frac{3}{2}}, ^2D, ^2S)$; Br $s^2 p^5(^2P_{\frac{1}{2}}$ or $^2P_{\frac{3}{2}})$, $s p^6, ^2S$.

III. FIRST-ORDER DISPERSION AND VALENCE INTERACTIONS BETWEEN H ATOMS IN DIFFERENT STATES

All of Eqs. (1)–(7b) of Sec. II are applicable to the computation of complete first-order interaction energies, including both dispersion-type and valence-type interactions.^{8a} All these equations are directly applicable to the case of two H atoms, with the following simplifications: i, j become merely 1 and 2, $\alpha(i; j)$ becomes α [equal to $2^{-\frac{1}{2}}(1 - P_{12})$] and $\sum_i \sum_j$ can be omitted in Eqs. (7)–

⁸ See R. S. Mulliken, *Revs. Modern Phys.* **3**, 113–115 (1930); **4**, 28–9 (1932).

^{8a} But further interactions of both types may occur if degeneracies remain (see Sec. V).

(7b). If m and n are two suitable H atom AO's, Eqs. (3) become

$$\begin{aligned}\Phi_I &= 2^{-1/2} [m_a(1)\alpha(1)n_b(2)\beta(2) \\ &\quad + \sigma m_a(1)\beta(1)n_b(2)\alpha(2)], \\ \Phi_{II} &= 2^{-1/2} [m_b(1)\alpha(1)n_a(2)\beta(2) \\ &\quad + \sigma m_b(1)\beta(1)n_a(2)\alpha(2)].\end{aligned}\quad (3')$$

Equations for Φ_I and Φ_{II} for H+H corresponding to Eqs. (3b) can easily be written when needed.

Let us now, however, consider *only cases where Eqs. (3') are applicable* and proceed with the detailed development of Eqs. (5b), *without assuming negligible overlap* of the wave functions of atoms a and b . Equations (5b) now become

$$\begin{aligned}\mathcal{H}_{I\ I} &= E^0 \left(1 - \int P_{12} \Phi_I^* \mathcal{H}^0 \Phi_I d\tau \right) \\ &\quad + \int (\Phi_I^* - P_{12} \Phi_I^*) \mathcal{H}^{\text{int}} \Phi_I d\tau,\end{aligned}\quad (5b')$$

$$\begin{aligned}\mathcal{H}_{II\ II} &= E^0 \left(S_{II\ II} - \int P_{12} \Phi_{II}^* \mathcal{H}^0 \Phi_{II} d\tau \right) \\ &\quad + \int (\Phi_{II}^* - P_{12} \Phi_{II}^*) \mathcal{H}^{\text{int}} \Phi_{II} d\tau.\end{aligned}$$

If, for example, m is $1s$ and n is $2s$ or $2p\sigma$ or $2p\pi^\pm$, $E_0 = E_{1s} + E_{2s,p} = -0.625$ a.u. = 17.0 eV.

It is instructive to evaluate E first using the exact form of \mathcal{H}^{int} [see Eq. (6)], then the approximate form [Eqs. (7-7b)]. The results from the former evaluation will give the exact first order energy for all values of R , those from the latter should give a good approximation at sufficiently large R .

Using the *exact* form of \mathcal{H}^{int} , the following results are obtained.⁹

$$E(1 + \eta S_{mm} S_{nn}) = E_0 (1 + \eta S_{mm} S_{nn} - \sigma S_{mn}^2) + (e^2/R) [M - \sigma P + \eta Q - \eta \sigma D], \quad (10)$$

where

$$\begin{aligned}M &= 1 + (m_a^2 | n_b^2) - (m_a^2 | \rho_b) - (n_a^2 | \rho_b); \\ P &= S_{mn}^2 - (m_a n_b^* | m_a^* n_b) - S_{mn} (m_a^* n_b | \rho_a) \\ &\quad - S_{mn} (m_a n_b^* | \rho_b); \\ Q &= S_{mm} S_{nn} + (m_a m_b^* | n_a^* n_b) - S_{mm} (n_a^* n_b | \rho_a) \\ &\quad - S_{nn} (m_a m_b^* | \rho_a); \\ D &= (n_a^* m_a | m_b^* n_b).\end{aligned}\quad (11)$$

In Eqs. (10) and (11), S_{mm} means $\int m_a^* m_b dV$, S_{mn} means $\int m_a^* n_b dV (= \int m_b^* n_a dV)$. Symbols such as $(m_a^2 | \rho_b)$, $(m_a m_b^* | n_a^* n_b)$ have the following meanings:

$$\begin{aligned}(m_a^2 | \rho_b) &\equiv \int m_a^* m_a (R/r_b) dV; \quad (m_a m_b^* | n_a^* n_b) \\ &\equiv \int \int m_a(1) m_b^*(1) (R/r_{12}) n_a^*(2) n_b(2) dV_1 dV_2.\end{aligned}$$

⁹ The M and P terms in Eq. (10) come from $\mathcal{H}_{I\ I}$, the Q and D terms from $\mathcal{H}_{II\ II}$.

The former of these last two integrals is a one-electron, the latter a two-electron integral. In Eqs. (11), note that, for example (of course only in a homopolar case, as here), $(m_a m_b^* | \rho_a) = (m_a m_b^* | \rho_b)$, but $(m_a^* n_b | \rho_a) \neq (m_a n_b^* | \rho_b)$. All the integrals in Eqs. (11) are real, even when complex orbitals are involved.

To a high order of approximation, if R is fairly large, the terms $\eta S_{mm} S_{nn}$ in Eq. (10) can be dropped, since $(1 + \eta S_{mm} S_{nn})$ on the left and right sides of Eq. (10) very nearly balance each other out.

Now using the expansion Eq. (7) or (7a) for \mathcal{H}^{int} , one obtains again⁹ Eq. (10), but Eqs. (11) are replaced by the following Eqs. (12) if m and n are real, or by Eqs. (12a) if m and/or n are complex.

$$\begin{aligned}M &= 0 + \dots, \\ P &= \gamma_q \int m_a n_b (q_a/R) dV \int m_a n_b (q_b/R) dV + \dots, \\ Q &= 2 \int m_a m_b (z_a/R) dV \int n_a n_b (z_b/R) dV + \dots, \\ D &= \gamma_q \int n_a m_a (q_a/R) dV \int m_b n_b (q_b/R) dV + \dots.\end{aligned}\quad (12)$$

In Eqs. (12), q is an appropriate *one* of x, y, z , and γ_q is $+1$ for $q=x$ or y , $+2$ for $q=z$. In, for example, $\int m_a n_b (q_a/R) dV$ or $\int m_b n_b (q_b/R) dV$, if m is $1s$, q is x if n is $2p\pi x$, y if n is $2p\pi y$, z if n is $2s$ or $2p\sigma$. When n is $2s$, D vanishes, but P and Q do not. If m and/or n are complex,⁶

$$\begin{aligned}M &= 0 + \dots, \\ P_z &= 2 \int n_b^* m_a (z_a/R) dV \int m_a^* n_b (z_b/R) dV + \dots, \\ R^2 P_{c^\pm} &= \int n_b^* m_a c_a^+ dV \int m_a^* n_b c_b^- dV \\ &\quad + \int n_b^* m_a c_a^- dV \int m_a^* n_b c_b^+ dV + \dots, \\ Q &= 2 \int m_b^* m_a (z_a/R) dV \int n_a^* n_b (z_b/R) dV + \dots, \\ D_z &= 2 \int n_a^* m_a (z_a/R) dV \int m_b^* n_b (z_b/R) dV + \dots, \\ R^2 D_{c^\pm} &= \int n_a^* m_a c_a^+ dV \int m_b^* n_b c_b^- dV \\ &\quad + \int n_a^* m_a c_a^- dV \int m_b^* n_b c_b^+ dV + \dots, \\ &= \int n_a^* m_a c_a^+ dV \int n_b^* m_b c_b^+ dV \\ &\quad + \int n_a^* m_a c_a^- dV \int n_b^* m_b c_b^- dV + \dots.\end{aligned}\quad (12a)$$

It is easily seen by inspection of the forms of P and Q in Eqs. (11) or (12) that these quantities, times e^2/R from Eq. (10), vanish as S^2/R^3 , hence somewhat faster than exponentially with R , since each S (when not identically zero) vanishes exponentially with R ; here S^2 refers to either S_{mn}^2 or $S_{mm}S_{nn}$.¹⁰ It should, however, be noted that the magnitudes of these integrals vary considerably with the particular orbitals involved. Further, in spite of their vanishing as S^2/R , Pe^2/R and Qe^2/R for $H(1s)+H(2p)$ do not become negligible compared with the long-range term De^2/R until R attains quite large values (see Sec. V). However, if R is sufficiently large so that overlaps are negligible, Pe^2/R and Qe^2/R vanish leaving only the term in De^2/R .

IV. FIRST-ORDER DISPERSION INTERACTIONS BETWEEN DIFFERENTLY EXCITED H ATOMS

Of major interest at R values large enough so that all overlaps between a and b AO's are negligible is the first-order dispersion term $(-\eta\sigma)(De^2/R)$. This term is then all that remains of the interaction energy $E-E_0$ of Eq. (10). From Eqs. (12) or (12a), based on the

TABLE II. First-order dipole-dipole dispersion energy coefficients^a of molecular states of two H atoms one in an ms , the other in an ns or np AO.

	ns	$np\sigma$	$np\pi$
ms	0	$2 \times 1 = 2$ (+) $^1\Sigma_g^+, ^3\Sigma_u^+$ (-) $^1\Sigma_u^+, ^3\Sigma_g^+$	$1 \times 1 = 1$ (+) $^1\Pi_u, ^3\Pi_g$ (-) $^1\Pi_g, ^3\Pi_u$

^a The top line in each box give $\gamma_q \times \mu_{mn}^2$ with μ_{mn}^2 in units of $(R_{ms}^{np})^2/3$, as obtained using references 6 and 11. For z polarization, $\gamma_q=2$; for x or y or c^\pm polarization, $\gamma_q=1$. The following lines marked (+) and (-) give the corresponding states of $ms \cdot np$ for which $-\eta\sigma$ in Eq. (8') is, respectively, positive or negative. The $np\pi$ AO's here may be taken equally well as real or complex.

expanded interaction Hamiltonian of Eqs. (7)-(7b), it is then easily seen⁴ (noting that $\int n_a^* m_a q_a dV = \int n_b^* m_b q_b dV$) that the same result is obtained for $E-E_0$ as is given [see Eq. (8)] in Sec. II in the general case of any two like odd-electron atoms:

$$E-E_0 = \eta\sigma De^2/R + \dots = -\eta\sigma\gamma_q \mu_{mn}^2/R^3 + \dots \quad (8')$$

Results of the application of Eq. (8'), omitting the terms in higher powers of R^{-1} than $1/R^3$, thus keeping

¹⁰ Each of the two individual integrals in P_z or Q of Eqs. (12) computes the mean value of z_a/R or z_b/R for a charge distribution whose magnitude is given by the corresponding overlap integral S_{mn} or S_{mm} or S_{nn} . In each case the charge distribution in question (overlap distribution) is very weak and very diffuse, and is centered about the mid-point of the molecule, or (where $\int m_a n_b dV$ is involved) at least far from both nuclei. A little reflection shows that the mean value of z_a/R or of z_b/R for the overlap distribution is about $\frac{1}{2}$ for Q and somewhat less (perhaps about $\frac{1}{3}$) for P_z . Hence each of the integrals P_z and Q is of the order of magnitude of S^2 , more or less independent of R . The integrals P_x and P_y can also be seen to vanish exponentially in a similar way; although in this case S_{mn} is identically zero, the same is not true of P_x or P_y . The exponential vanishing of P and Q can also be seen from Eqs. (11).

TABLE III. First-order dipole-dipole dispersion coefficients^a of molecular states of two H atoms one in an mp the other in an nd AO.

	$nd\sigma$	$nd\pi^\pm$	$nd\delta^\pm$
$mp\sigma$	$2 \times 4 = 8$ (+) $^1\Sigma_g^+, ^3\Sigma_u^+$ (-) $^1\Sigma_u^+, ^3\Sigma_g^+$	$1 \times 3 = 3$ (+) $^1\Pi_u, ^3\Pi_g$ (-) $^1\Pi_g, ^3\Pi_u$	0 $1, ^3\Delta_g, 1, ^3\Delta_u$
$mp\pi^\pm$	$1 \times 1 = 1$ (+) $^1\Pi_u, ^3\Pi_g$ (-) $^1\Pi_g, ^3\Pi_u$	$2 \times 3 = 6$ (+) $^1\Delta_g, ^3\Delta_u$ (-) $^1\Delta_u, ^3\Delta_g$	$1 \times 6 = 6$ (+) $^1\Phi_u, ^3\Phi_g$ (-) $^1\Phi_g, ^3\Phi_u$
$mp\pi^\mp$		$2 \times 3 = 6$ (+) $^1\Sigma_g^+, ^1\Sigma_u^-,$ $^3\Sigma_u^+, ^3\Sigma_g^-$ (-) $^1\Sigma_u^+, ^1\Sigma_g^-$ $^3\Sigma_g^+, ^3\Sigma_u^-$	0 $1, ^3\Pi_u, 1, ^3\Pi_g$

^a The top line in each box gives $\gamma_q \times \mu_{mn}^2$, with the latter in units of $(R_{mp}^{nd})^2/15$, as obtained using references 6 and 11. For z polarization, $\gamma_q=2$, for c^\pm polarization, $\gamma_q=1$. The following lines marked (+) or (-) give the corresponding states of $mp \cdot nd$ for which $-\eta\sigma$ in Eq. (8) or, for the Σ states of $mp\pi^\pm nd\pi^\pm$, $-\eta\sigma\rho$ in Eq. (8b), is respectively positive or negative. It will be noted that it is best to use complex AO's here. In the table, combinations such as $mp\pi^\pm nd\pi^\pm$ mean $mp\pi^\pm nd\pi^\pm$ or $mp\pi^\mp nd\pi^\mp$ only, not $mp\pi^\pm nd\pi^\mp$ or $mp\pi^\mp nd\pi^\pm$; the latter are listed separately as $mp\pi^\mp nd\pi^\pm$.

only the "dipole-dipole" terms, are given below in Tables II and III for two specific examples.

For a given pair of suitably chosen AO's, $\mu_{mn}^{(q)}$ is nonvanishing for at most one particular q . For example, $\mu_{ms,ns}=0$ for all q ; in a.u., $\mu_{ms,np}x^2(x)=\mu_{ms,np}z^2(z)=\mu_{ms,np}y^2(y)=(\frac{1}{3})(R_{ms}^{np})^2$, where in general $R_{ml}^{nl'} \equiv \int R_{nl'}(r)R_{ml}(r)r^3dr$,¹¹ $R_{ml}(r)$ being the radial factor in the ml AO, in a.u.

Tables II and III give the values of γ_q and μ_{mn}^2 for the respective cases that m is an ms and n an np AO, and that m is an mp and n an nd AO. In the case of Σ^\pm and Σ^\mp states resulting from $mp\pi^\pm$, $nd\pi^\mp$ or other π^\pm , π^\mp or δ^\pm , δ^\mp combinations, Eqs. (3b), (8b), as specialized to the H+H cases mentioned, have been used in obtaining the results listed. Making use of Table I, the states corresponding to any combination of orbitals belonging to $ms \cdot np$ or to $mp \cdot nd$ and associated with a positive or negative sign of $-\eta\sigma$ in Eq. (8') or of $-\eta\sigma\rho$ in Eq. (8b) are readily determined, and are listed in the tables. It will be noted that μ_{mn}^2 takes the form $\alpha(R_{ms}^{np})^2/3$ for $ms \cdot np$ and $\alpha(R_{mp}^{nd})^2/15$ for $mp \cdot nd$, where α is 1 for all $ms \cdot np$ states but takes various integral values 0, 1, 3, 4, 6 for various $mp \cdot nd$ states

TABLE IV. Overlap integrals for H atom orbitals.^a

R (a.u.)	S_{mm} $S_{1s, 1s}$	S_{nn} $S_{2s, 2s}$	S_{nn} $S_{2p\sigma, 2p\sigma}$	S_{nn} $S_{2p\pi, 2p\pi}$	S_{mn} $S_{1s, 2s}$	S_{mn} $S_{1s, 2p\sigma}$	S_{mn} $S_{1s, 2p\pi}$
5	0.0966	0.729	0.005	0.578	0.286	0.413	0.000
6	0.0471	0.637	0.159	0.468	0.222	0.336	0.000
8	0.0102	0.456	0.319	0.287	0.121	0.194	0.000
10	0.0020	0.302	0.319	0.164	0.061	0.100	0.000
12	0.0004	0.188	0.250	0.089	0.029	0.048	0.000
16	0.0000	0.062	0.107	0.023	0.006	0.010	0.000

^a R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. 17, 1248 (1949).

¹¹ Values of $(R_{mn}^{nl})^2$ are tabulated in atomic units on p. 350 of reference 6. Equations for f_{mn} and \bar{f}_{mn} are also given.

TABLE V. Approximate values of terms in Eq. (10) for $R=10$ a.u. (all in ev), for the interaction of normal and 2-quantum excited H atoms.^a

State	σ	η	$-\sigma S_{mn}^2 E_0^b$	$-\sigma P e^2/R$	$+\eta Q e^2/R$	$-\eta \sigma D e^2/R$	Total ($E-E_0$)
$1s2s\ ^1\Sigma_g^+$	-1	+1	-0.0622	+0.0050	+0.0082	0.000	-0.049
$1s2s\ ^1\Sigma_u^+$	-1	-1	-0.0622	+0.0050	-0.0082	0.000	-0.067
$1s2s\ ^3\Sigma_g^+$	+1	+1	+0.0622	-0.0050	+0.0082	0.000	+0.067
$1s2s\ ^3\Sigma_u^+$	+1	-1	+0.0622	-0.0050	-0.0082	0.000	+0.049
$1s2p\sigma\ ^1\Sigma_g^+$	-1	+1	-0.170	+0.0136	+0.0087	+0.0302	-0.118
$1s2p\sigma\ ^1\Sigma_u^+$	-1	-1	-0.170	+0.0136	-0.0087	-0.0302	-0.195
$1s2p\sigma\ ^3\Sigma_g^+$	+1	+1	+0.170	-0.0136	+0.0087	-0.0302	+0.135
$1s2p\sigma\ ^3\Sigma_u^+$	+1	-1	+0.170	-0.0136	-0.0087	+0.0302	+0.178
$1s2p\pi\ ^1\Pi_u$	-1	+1	0.000	+(0.0001)	+0.0045	+0.0151	+0.0197
$1s2p\pi\ ^1\Pi_g$	-1	-1	0.000	+(0.0001)	-0.0045	-0.0151	-0.0195
$1s2p\pi\ ^3\Pi_u$	+1	+1	0.000	-(0.0001)	+0.0045	-0.0151	-0.0107
$1s2p\pi\ ^3\Pi_g$	+1	-1	0.000	-(0.0001)	-0.0045	+0.0151	+0.0105

^a For the Σ states, where q_a and q_b are z_a and z_b in Eqs. (12) for P and Q , each integral has been approximated as illustrated by $\int m_a n_b (q_a/R) dV \approx \frac{1}{2} \int m_a n_b dV = \frac{1}{2} S_{mn}$ (see reference 10). Q for the Π states, where also q is z , has similarly been approximated as $\frac{1}{2} S_{mn} S_{nn}$. For P for the Π states, only very rough guesstimates were made.

^b $E_0 = -17.0$ ev.

(μ_{mn} and R_m^n in a.u.). Table III illustrates the fact that the splitting caused by first-order dispersion forces can in general be rather complex, although for the $ms \cdot np$ case discussed by King and Van Vleck it is relatively simple.

With regard to the magnitudes of the splittings, the needed values of $(R_{ms}^{np})^2$ or $(R_{mp}^{nd})^2$ and from these of $\mu_{ms, np}^2$ and $\mu_{mp, nd}^2$, can be obtained¹¹ from reference 6. For the case of $1s \cdot 2p$, the values of $E-E_0$ in Eq. (8), times 27.21 to convert from a.u. to ev, are obtained by setting $\mu_{1s, 2p}^2 = 15.10$. Thus, for example, for the $^1\Sigma_g^+$ and $^1\Pi_u$ states of $1s \cdot 2p$ (see Table II), $E-E_0 = 30.20/R^3$ ev and $15.10/R^3$ ev if R is in a.u. Larger μ_{mn}^2 values and splittings are predicted in various cases where both atoms are excited. For example for the $^1\Sigma_g^+$ states of the pairs $2s \cdot 2p\sigma$, $2p\sigma \cdot 3d\sigma$, $3s \cdot 3p\sigma$, $3p\sigma \cdot 3d\sigma$, $4p\sigma \cdot 4d\sigma$, and $4s \cdot 4p\sigma$, the predicted values of $E-E_0$ times R^3 (R in a.u.) are, respectively, 490, 327, 2940, 1470, 6275, and 9800 in ev. In connection with the foregoing, it should be noted that terms involving higher powers of R^{-1} than $1/R^3$ are important for a more accurate treatment, as has been shown especially in a study by Fontana.¹²

The interaction energies in Table II agree with those of King and Van Vleck² in the case of the singlet states, but are reversed in sign for the triplet states. The discrepancy may be attributed to the failure of King and Van Vleck to consider effects which give rise to the factor $-\sigma$ which multiplies $\eta D e^2/R$ in Eq. (10). This factor, which they omitted, is $+1$ for singlet states so that their results are correct for these, but it is -1 for triplet states. Referring to Eqs. (3'), (5b'), and (10)–(11), the dipole-dipole interaction terms are seen to arise from those parts of the terms $\mathcal{F} - n_a^*(1) \times \beta(1) m_b^*(2) \alpha(2) \mathcal{J}^{int} \sigma m_a(1) \beta(1) n_b(2) \alpha(2) d\tau + \mathcal{F} - \sigma n_a^*(1) \times (1) \alpha(1) m_b^*(2) \beta(2) \mathcal{J}^{int} m_a(1) \alpha(1) n_b(2) \beta(2) d\tau$ in $\mathcal{J}C_{II}$ of Eqs. (5b') which come from the term $e^2/r_{1a\ 2b}$ in $\mathcal{J}C^{int}$.

¹² P. R. Fontana (to be published).

The minus signs occur because the terms $-n_a^*(1) \times \beta(1) m_b^*(2) \alpha(2)$ and $-\sigma n_a^*(1) m_b^*(2) \beta(2)$ are those which have arisen from *electron exchange* (P_{12} in Eq. (5b') for $\mathcal{J}C_{II}$), and the factor σ occurs for reasons that can be seen in the combination of Eq. (3') with Eq. (5b') for $\mathcal{J}C_{II}$.

In Eqs. (10)–(11), based on the *exact* form [see Eq. (6)] of the interaction Hamiltonian, $D e^2/R$ appears as an e^2/r_{12} integral of unusual long-range character. Inspection shows in a particularly illuminating way that if m is $1s$ and n is one of the real forms of $2p$, this integral represents the mutual electrostatic energy of two dipolar charge distributions $em_a n_a$ and $em_b n_b$ located on atoms a and b , respectively. The integral can be evaluated after expanding $(1/r_{12})$ in powers of $1/R$, with exactly the same result as in Eq. (8').¹³ However, if m and n are $1s$ and $2s$, one no longer has dipolar charge distributions, and, in agreement with Eq. (8'), the integral vanishes unless one goes to higher terms ($1/R^5$ and higher) in the expansion of $1/r_{1a\ 2b}$ in Eqs. (10)–(11) and/or of $\mathcal{J}C^{int}$ in Eqs. (7), (10), (12).

It seems worth emphasizing here that the first-order dispersion energy can in all cases be computed *exactly* if $D e^2/R$ can be accurately computed as an e^2/r_{12} integral, instead of as a series in $1/R$ which is broken off at the term in $1/R^3$. This can now be done readily with the aid of existing tables of "Coulomb" integrals or corresponding digital computer programs.^{13a}

¹³ Expansion of $(1/r_{1a\ 2b})$ yields precisely $\mathcal{J}C^{int}$ of Eqs. (7), plus the following: $e^2/R + e^2(z_{1a} + z_{2b})/R^2 + e^2(z_{1a}^2 + z_{2b}^2 - \frac{1}{2}y_1^2 - \frac{1}{2}y_2^2 - \frac{1}{2}x_1^2 - \frac{1}{2}x_2^2)/R^3$ plus terms in R^{-4} , R^{-5} , etc. On integration after substitution in $(m_a n_a | m_b n_b)$, the *extra* terms in $1/R$, $1/R^2$, and $1/R^3$ all yield precisely zero contributions to the integral.

^{13a} In this connection see H. C. Longuet-Higgins, Proc. Roy. Soc. 235A, 537 (1956). Further, on "the representation of long-range forces by series expansions," see A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) A69, 57 (1956). For tables ($1s$, $2s$, $2p$ AO's only) see for example C. C. J. Roothaan, Special ONR Technical Report 1955, available from this Laboratory.

V. VALENCE FORCES BETWEEN NORMAL AND 2-QUANTUM EXCITED H ATOMS AT LARGE DISTANCES

A consideration of the magnitudes of the terms in S_{mn}^2 , P , and Q in Eqs. (10) shows that they often predominate in importance over the term in D unless R is so large that the latter is scarcely worth talking about. Thus for the interaction of $1s$ with $2s$ or $2p$ atoms, the terms in S_{mn}^2 , P , and Q are important out to quite large R values, as will be seen from Tables IV and V. Table IV shows the magnitudes of the various overlap integrals involved in Eqs. (10)–(11) for several R values. Table V shows the contributions of the terms $-\sigma E_0 S^2$, $-\sigma P e^2/R$, $+\eta Q e^2/R$, and $-\eta \sigma D e^2/R$ to $E-E_0$ when $R=10$ a.u. (5.28 Å), using the R^{-3} terms of Eqs. (12), (8') to estimate P , Q , and D , and neglecting $\eta S_{mm} S_{nn}$ in Eq. (10).¹⁴

It is seen from Table V that even at $R=10$ a.u. the term $-\sigma S_{mn}^2 E_0$ predominates in the case of the Σ states, and that the terms in P and Q are by no means negligible compared with that in D (for $1s\ 2s$, the latter out to terms in R^{-3} is of course zero). For the Π states, on the other hand, the term in D definitely predominates, but the term in Q is still almost a third as large. One is forced to conclude that, on the whole, first-order dispersion forces do not represent at all well the interaction between normal H atoms and 2-quantum or higher excited H atoms until R values so large are reached that all interactions have become rather unimportant. However, things are not quite so bad for the $1s\ 2p\ \pi$ Π states: the dispersion forces are definitely dominant at $R=10$ a.u. (though they lose their dominance somewhat below 9 a.u.).

In the case of the Σ states, the situation is really considerably worse than that portrayed by Table V. Namely, because of the degeneracy between $2s$ and $2p$, there are valence-type interactions between pairs of Σ^+ functions of like symmetry arising from $1s\ 2s$ and $1s\ 2p\sigma$; for example, between $1s\ 2s$, $^3\Sigma_g^+$ and $1s\ 2p\sigma$, $^3\Sigma_g^+$, or $1s\ 2s$, $^1\Sigma_g^+$ and $1s\ 2p\sigma$, $^1\Sigma_g^+$, causing each such pair of wave functions to mix and their energy curves to repel each other. These interactions are probably of the same order of magnitude as those listed in Table V. For the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ pairs of functions things are even worse, since each of these pairs must mix with a further wave function, namely the $^1\Sigma_g^+$ or $^1\Sigma_u^+$, respectively, coming from $H^+ + H^-$. These interactions are very strong for R values near 10 a.u., but become weak beyond 12 a.u.¹⁵

None of the complications which exist for the Σ states occur for the $1s\ 2p\ \pi$ Π states. However, when one goes to $1s\ 3p\ \pi$, there are pairwise degeneracies with the

$1s\ 3d\ \pi$ Π wave functions; also, overlaps are larger and D values smaller at any given R .

On the other hand, when one considers *certain pairs where both atoms are excited*, much larger D values are again encountered (see Sec. IV), and first-order dispersion forces should be large and important at R values where valence forces have become small. Additional first-order dispersion effects due to configurational degeneracies (e.g., $2s\ 2s$ with $2p\sigma\ 2p\sigma$) also occur for the case of two H atoms.¹²

An interesting feature of the discussion in Sec. IV was the demonstration that the first-order dispersion forces for $H+H^*$ are attributable to one particular e^2/r_{12} integral [D in Eqs. (11)] which vanishes only about as $1/R^3$, whereas all the other e^2/r_{12} integrals vanish about as S^2/R^3 . In a *complete* first-order calculation valid at all R values, both types of e^2/r_{12} integrals would of course be included.

For a still more adequate treatment, second-order terms must be included. Most of these become appreciably large only as R becomes smaller, though for increasingly excited states they become important at larger and larger R values. But in addition, paralleling the situation for the first-order terms, there are some long-range second-order terms, namely the familiar $1/R^6$ and further second-order dispersion terms.¹²

VI. LONG-RANGE INTERACTIONS BETWEEN ALKALI-METAL ATOMS

Although it has been shown that the resonance interactions between normal and excited H atoms are complicated and confused by valence-force effects out to R values so large that they are becoming rather unimportant, the same is not true for atom-pairs such as $Li+Li^*$ and $Na+Na^*$. To a rather good approximation, these may be treated as 1-electron atoms, like $H+H^*$. Tables (not included here) similar to Tables IV and V for $H+H^*$, for the cases $3s\ 3p\sigma$ (four Σ states) and $3s\ 3p\ \pi$ (four Π states) of $Na+Na^*$, constructed using rough estimates of relevant overlap integrals, then indicate that the overlaps and corresponding valence-force terms are roughly similar in magnitude at 10 a.u. to those for $1s\ 2p\sigma$ and $1s\ 2p\ \pi$ of $H+H^*$. (The term $-\sigma S_{mn}^2 a_0$ for $3s\ 3p\sigma$, however, is perhaps somewhat larger than the corresponding H atom $1s\ 2p\sigma$ term.) However, De^2/R is now very much larger ($172\gamma_q/R^3$ in eV instead of $15.1\ \gamma_q/R^3$, for R in a.u.) and for Π states it appears that the first-order dispersion forces should be important and completely dominant at 10 a.u. (except perhaps for second-order effects—see below). Further, the present $3s\ 3p$ case is simpler than that of $H+H^*$ in that there is of course no degeneracy like that between $1s\ 2p\sigma$ and $1s\ 2s$.

For the Σ states of Na_2 , the term $-\sigma S_{mn}^2 E_0$ may be of the same order of magnitude as De^2/R at 10 a.u., but at perhaps 12 a.u. De^2/R should definitely be dominant, and still large (± 0.2 eV). In the case of the

¹⁴ The neglect of $\eta S_{mm} S_{nn}$ on both sides of Eq. (10) is obviously justified. The use of the R^{-3} terms of Eqs. (12), (8') for M , P , Q , and D should be a good approximation at $R=10$ a.u. for the cases $1s\ 2s$, $1s\ 2p\sigma$, or $1s\ 2p\ \pi$.

¹⁵ J. T. Lewis, Proc. Phys. Soc. (London) 68, 632 (1955).

$^1\Sigma^+$ states an added complication occurs, analogous so that for $H+H^*$, namely that their potential curves are crossed near 10 a.u. by the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ curves of Na^++Na^- , with which strong interaction may be expected. However, beyond 12 a.u. this interaction is probably negligible, so that the potential curves of all the $3s\ 3p\sigma\ \Sigma$ states should then probably be well described by the De^2/R term alone.

Returning to the Π states, consideration should be given to the likelihood (which, in accordance with molecular orbital theory, because a certainty at stable molecular distances, near 6 a.u.) that second-order interactions, with Π states of Na^++Na^- , become important near 10 a.u. in addition to the first-order valence interactions already considered. (By Na^-* is meant an excited virtual state of Na^- which becomes stabilized on approaching an Na^+ .) Inspection of the experimental potential curve² of the observed lowest $^1\Pi_u$ state of Na_2 , a stable state with a pronounced minimum at 6.45 a.u. but with evidence of a dispersion-force maximum near 12 a.u., suggests that this is the case.¹⁶ In any event, however, there would seem to be very little doubt that the dispersion forces are dominant and important beyond 12 a.u. for both the Π and the Σ states.

VII. RESONANCE FORCES BETWEEN LIKE ATOMS WITH EVEN NUMBERS OF ELECTRONS

For the interaction of two like atoms in different states of excitation, relations are simpler when the number of electrons (N) in each atom is even than when it is odd. The following cases will be considered here: (1) both atoms are in singlet states; (2) one atom is in a singlet, the other in a triplet state in which the spin-orbit coupling is strong compared with the first-order dispersion interaction energies; (3) both atoms are in states in which the spin-orbit coupling is strong compared with the first-order dispersion energies (this case includes the possibility of states of higher than triplet multiplicity, also that of j, j or similar coupling in one or both states).

The treatment is completely identical in these three cases; no distinction between them is needed. In all, Eqs. (1) and (2) of Sec. II hold, but instead of Eqs. (3), (3a) and (3b), (3c) we have³:

$$\Phi_I = \Phi_{ma}(i)\Phi_{nb}(j); \quad \Phi_{II} = \text{Ref}^M \Phi_I, \quad (13)$$

$$\Phi_I = 2^{-\frac{1}{2}} [\Phi_{m^+a}(i)\Phi_{n^-b}(j) + \rho \Phi_{m^-a}(i)\Phi_{n^+b}(j)];$$

$$\Phi_{II} = \text{Ref}^M \Phi_I. \quad (13b)$$

In Eqs. (13b), ρ can be $+1$ (Σ^+ states in case 1, 0^+ states in case 2 or 3) or -1 (Σ^- states in case 1, 0^- states in case 2 or 3), the designations 0^+ and 0^- being those usual for "far-nuclei case c " for diatomic molecules.⁸ Φ_{m^+a} and Φ_{m^-a} , etc., refer to wave functions of

¹⁶ As mentioned earlier, the present results for the theoretical first-order dispersion energies agree entirely with those of reference 2 for *singlet* states.

TABLE VI. Electronic state types for the interaction of like atoms in singlet or triplet atoms with strong spin-orbit coupling.^a

States	η	ρ	$\eta\rho$
$^1\Sigma_g^+, ^1\Pi_u, ^1\Delta_g, \dots; 0_g^+, 1_u, 2_g, \dots$	1	1	1
$^1\Sigma_g^-, ^1\Pi_u, ^1\Delta_g, \dots; 0_g^-, 1_u, 2_g, \dots$	1	-1	-1
$^1\Sigma_u^+, ^1\Pi_g, ^1\Delta_u, \dots; 0_u^+, 1_g, 2_u, \dots$	-1	1	-1
$^1\Sigma_u^-, ^1\Pi_g, ^1\Delta_u, \dots; 0_u^-, 1_g, 2_u, \dots$	-1	-1	1

^a The symbols $^1\Sigma_g^+$, etc., are applicable in case 1 (both states singlets), 0_g^+ , etc. in cases 2 and 3 (one or both states nonsinglets with strong spin-orbit coupling, defined by their J values); the symbols 0, 1, 2, etc., refer to the Ω (i.e., over-all $|M|$) value of case c coupling.⁸ In those cases where Eqs. (14) apply, ρ (though really not defined) may be taken as $+1$.

atom a with M (the component of J along the line joining the atoms) values $\neq 0$ of equal magnitude but opposite sign.

Equations (4)–(7b) are the same as in Sec. II. For R values large enough so that atoms a and b do not overlap we now find, by reasoning parallel to that in Sec. II though now simpler, that

$$E - E_0 = \eta\gamma_q \mu_{mn}^2 / R^3 = \eta\gamma_q (\text{ry} / \nu_{mn}) f_{mn} / R^3, \quad (14)$$

$$E - E_0 = 2\eta\rho \mu_{m^+n^+}^2 / R^3 = 2\eta\rho (\text{ry} / \nu_{mn}) f_{mn} / R^3 \quad (14b)$$

corresponding to Eqs. (8), (9) and (8b), (9b). Table VI shows the relation of state-species to η and ρ values, replacing Table I of Sec. II.

In the case that both atoms are in singlet states, Eq. (14) and Table VI are in agreement with reference 2, while Eq. (14b) corresponds to less common situations not considered there. A simple example of case (2a) where Eq. (14) is applicable is that of the interaction of a normal Hg atom with a Hg atom in the lowest sp , 3P_1 state (upper state of the $\lambda 2537$ resonance line). Here, due to admixture of 1P into 3P_1 , f_{mn} is of appreciable magnitude. Other similar examples occur in the interaction of p^6 , 1S ground state with p^5s , 3P_1 resonance-excited rare gas atoms. Another case, (2b), may be defined in which one atom is in a singlet state and the other is in a triplet state in which spin-orbit coupling is weak; in such cases singlet-triplet mixing, hence f_{mn} , is small, and the first-order dispersion energy is negligible. In both of cases (2a) and (2b), the atom-pair states are triplet or nearly triplet states. As examples of case (3), one may cite the interaction of a ground-state configuration (p^4) S atom in one of the states 3P_0 , 3P_1 , 3P_2 with an excited S atom in one of the p^3p' states 3P_0 , 3P_1 , 3P_2 . Various state-pairs, each of them with various modes of interaction, will involve various f_{mn} values, with $E - E^0$ values given by Eq. (14) or, when $M_a = -M_b$, by Eq. (14b).

In the case of two atoms in different triplet states having spin-orbit coupling which is comparable to or weaker than the first-order dispersion effects, a more complicated treatment is required. With relatively weak spin-orbit coupling in both atoms (for example, one s^2p^2 and one s^2pp' C atom), the atom-pair states are characterized (as they are not in case 3) by definite

values (0, 1, and 2) of the total spin S . A preliminary examination indicates that the first-order dispersion energies then depend on a parameter related to S , somewhat as they depended on σ for doublet atoms in Section II. However, this matter will not be pursued further here.

A point of some interest (especially if approximate theoretically computed values of μ_{mn} are to be used in the absence of experimental values) is the relation of μ_{mn} to the value of μ_{mn} for a one-electron transition. The cases of the bivalent alkaline-earth and Hg-type atoms and of the rare gas atoms when one atom is in its ground state and the other in its sp or p^5s resonance state are especially simple. In both cases, a 2-electron approximation should be fairly accurate (see the 1-electron approximation for alkali metal atoms in Sec. VI). In this approximation it is easily shown for the bivalent metal atoms that μ_{mn} is $2^{1/2}$ times as large, hence μ_{mn}^2 and f_{mn} are twice as large, as for a similar transition $p \leftarrow s$ of a single electron. In the case of the rare gas atoms, μ_{mn}^2 and f_{mn} are again just twice as

large as for a similar $s \leftarrow p$ transition of a single electron (*not*, as one might perhaps casually surmise, six times as large because of the six electrons in the p^6 shell). If one uses real AO's and Φ 's, as is convenient here, μ_{mn} in Eq. (14) corresponds in the bivalent metal case to any *one* of the transitions $sp_q, {}^1P_q \leftarrow s^2, {}^1S$, where q may be x, y , or z . All of these give the same value of $(\mu_{mn}^{(q)})^2$, each time twice that for the corresponding transition $p_q, {}^2P_q \leftarrow s, {}^2S$, because *either* of the two electrons in s^2 can jump. In the rare gas case, one has again three equal μ_{mn}^2 's, of which, for example, $(\mu_{mn}^{(x)})^2$ corresponds to $p_x^2 p_y^2 p_z s, {}^1P_x \leftarrow p_x^2 p_y^2 p_z^2, {}^1S$, with a value twice that for $p_x^2 p_y^2 s, {}^2S \leftarrow p_x^2 p_y^2 p_z^2, {}^2P_x$. It will be noted that for any one q , only two electrons of p^6 can be active.

In all the foregoing cases, of course, account must be taken of the fact that a fraction of μ_{mn}^2 is lost from 1P to 3P_1 , depending on the energy difference between 3P and 1P and on how strong the spin-orbit coupling in 3P is. This loss can readily be computed by standard methods if one knows the positions of the ${}^3P_0, {}^3P_1, {}^3P_2$, and 1P energy levels.

Theory of the Hyperfine Anomalies of Deuterium, Tritium, and Helium-3⁺⁺

DANIEL A. GREENBERG[†] AND HENRY M. FOLEY
Columbia University, New York, New York

(Received July 18, 1960)

The covariant equation for the three-body deuterium system is discussed, and reduced to a three-dimensional equation for the case of instantaneous two-body interactions. A noncovariant perturbation scheme, based on this three-dimensional equation, was employed to calculate the hyperfine structure (hfs) to order $\alpha m/M$ (hfs) for ${}_1\text{H}^2, {}_1\text{H}^3, {}_2\text{He}^{3+}$. The results are compared with the experimental values, and shown to be compatible. Final determination of the theoretical values and the adequacy of the theory is shown to depend critically on the determination of a number of experimental quantities, in particular on a more precise measurement of α , of the nucleon electric and magnetic form factors and associated nucleon polarization, of the presence and magnitude of a two-nucleon spin-orbit potential, and of the singlet n - p effective range.

I. INTRODUCTION

THE hyperfine splitting of hydrogen has been calculated to order α^2 (hfs) in the relativistic and radiative corrections,¹ $\alpha m/M$ in the mass corrections,² and $(r\text{-nucleus})/a_0$ in the structure corrections.³ These orders are of comparable magnitude, and the following formula for the H^1 hfs is good to a few ppm:

$$\Delta\nu_{\text{H}} = (16/3)\alpha^2 c R_{\infty} (\mu_p/\mu_e) \{1 + m/M\}^{-3} \\ \times \{1 + \alpha/2\pi + 0.386\alpha^2/\pi^2\}^2 \{1 + 3\alpha^2/2\} \\ \times \{1 - \alpha^2(5/2 - \ln 2)\} \{1 - 35(\pm 3.5) \times 10^{-6}\} \\ \times \{1 - \Delta\}, \quad (1)$$

where R_{∞} is the rydberg constant for a nucleus of infinite mass; μ_p is the magnetic moment of the proton; μ_e the magnetic moment of the electron; the first bracket is the reduced mass correction⁴; the second bracket is the ratio of the magnetic moment of the electron to the Bohr magneton; the third bracket is the relativistic Breit correction; the fourth bracket is the radiative correction of Kroll and Pollock¹; the fifth bracket is the mass correction and the nucleon structure correction; the sixth bracket includes all other possible

* This work was supported in part by the U. S. Atomic Energy Commission and the National Science Foundation.

[†] Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Faculty of Pure Science, Columbia University.

¹ G. Breit, Phys. Rev. **46**, 1447 (1930); C. M. Sommerfield, Phys. Rev. **107**, 328 (1957); N. Kroll and F. Pollock, Phys. Rev. **86**, 876 (1952).

² W. A. Newcomb and E. E. Salpeter, Phys. Rev. **97**, 1146 (1955); R. A. Arnowitt, Phys. Rev. **92**, 1002 (1953).

³ A. C. Zemach, Phys. Rev. **104**, 1771 (1956); C. K. Iddings and P. M. Platzman, Phys. Rev. **113**, 192 (1959).

⁴ G. Breit and R. E. Meyerott, Phys. Rev. **72**, 1023 (1947).