from the back of the last slit seems to be definitely outlawed. The effect could at best be only of the second order of small quantities.

Just what mechanisms are involved in the space charge detector containing gas and used for fast ions is still difficult to conclude. Scattering from the walls and from gas atoms has already been advanced. I am indebted however to Professor L. B. Loeb[8] for an additional and important suggestion concerning the operation of the detector. If the filament of the detector is run at a very high temperature and the applied voltage is small, the space charge may be so heavy that an actual positive ion trap or potential trough of appreciable size exists between the filament and cylinder. If as the result of collisions or any other process, a positive ion finds itself in this trough with insufficient energy to escape, it may be extremely effective in neutralizing electron space charges. That this does occur is indicated by the frequent observations of the writer of an apparent increase in sensitivity of considerable magnitude with increase of filament temperature. Neither the space charge limited current nor the applied voltage was allowed to vary as the temperature was raised. The filament was already far into the space charge controlled region of emission at the start. The slight increase in potential drop down the filament was readily shown to be inadequate explanation of the sensitivity increase, for the plain variation of the applied potential gave no such effect.

Rostagni[1] has challenged the writer's negative results in some cases on the grounds that such results are surprising after all the positive ones with other noble gases. Without attempting to discuss what should or should not be expected, the writer feels obliged to point out that his statement that ionization efficiency in helium must be less than 5 percent of that in argon is hardly a denial of all ionization of helium by helium atoms. Rostagni's challenge could possibly be directed at the smallness of the result but not at its absence.

It has been pointed out previously, furthermore, that Beeck's data on the onset of ionization by positive ions fail to be even self-consistent in the cases (and only in those) where the writer has found no ionization by the balanced space charge method. Rostagni's[6] brilliant work on ionization by neutral atoms is clouded by a similar difficulty; the onset potential has been observed in every case to rise as the atomic weight decreases and as the ionization efficiency decreases. His result on He – He is the only one incompatible with this law.

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[8] Private correspondence.

MAY 1, 1938 PHYSICAL REVIEW VOLUME 53

Quadrupole-Quadrupole Interatomic Forces

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(Received March 15, 1938)

Atoms the normal states of which are not S states experience quadrupole-quadrupole repulsive and attractive forces which vary as the inverse fifth power of the separation distance. At large distances, exchange being negligible, the expression for the interaction energy contains as factors two atomic coefficients and a root of a secular equation determined by the molecular state of the system. For a given atom the coefficient is determined by the nature of its lowest level. If one uses the Hartree-Fock approximation, it is proportional to the average of the square of the radial atomic distance for those electrons with orbital angular momentum not in complete shells. Atomic coefficients have been calculated for most of the atoms of the periodic table having incomplete p and d shells and the secular equations have been solved for a number of cases. At distances of twice the sum of the atomic radii, diatomic molecules resulting from the combination of such atoms of the first row of the periodic table have quadrupole-quadrupole energies of a few tenths of a volt, such energies becoming rapidly larger for smaller distances because of the inverse fifth power dependence.

1

When two atoms are far enough apart that overlapping and consequent exchange effects are negligible, the interaction can be considered as being composed of mixed terms of different pole strengths. The terms are obtained from the expansion of the potential in a Taylor's series in inverse powers of the interatomic distance. If the atoms are different, the dipole-dipole and dipole-quadrupole first-order interaction energies are zero because of the odd parity of the dipole portions of their potential terms. That is to say the expression for the energy is the sum of pairs of integrals, each referring to one atom alone. The integrand of each contains the product of two atomic functions, which product is even under inversion since the functions belong to the same atomic configuration. In addition each integrand contains a linear or quadratic function of the electron coordinates, referred to the nucleus of the atom in question. For first-order dipole-dipole or dipole-quadrupole interactions at least one of the any pair of such integrals contains a linear factor in its integrand, which being odd under inversion causes the integral to vanish. Moreover if either atom has spherical symmetry (S state), the first-order quadrupole-quadrupole energy is zero. Nonvanishing first-order dipole energies are obtained only if the atoms are the same and are in states with different parity. Second-order interaction energies do not in general vanish. They are sometimes referred to as polarization or induced energies. Since for two neutral atoms the expanded potential begins with the inverse third power of the interatomic distance, second-order energies vary with the inverse sixth and higher inverse powers of the distance. These interactions are those which produce van der Waals forces. They were first discussed extensively on the basis of quantum mechanics by London.[1] The most careful studies have been made for hydrogen and helium.[2]

Many atoms are not spherically symmetrical in the ground state; for these the quadrupole moment does not vanish. If we have two such atoms, there will be, in general, a nonvanishing first-order interaction. The quadrupole-quadrupole potential term varies with the inverse fifth power of the distance. London has noted in this connection that for two rotating molecules the quadrupole-quadrupole interaction energy will depend on the relative orientation of the two angular momenta.[3] The diagonal terms of the energy of interaction of two rotating neutral systems have in fact their dependence on orientation given by

$$(1/R^5)\{J(J+1)-3M^2\}\{J^*(J^*+1)-3M^{*2}\},$$

where J, M; J^*, M^* are the angular momentum and magnetic quantum numbers describing in part the states of the two systems and R is the separation distance. As London has pointed out, the interaction vanishes on the average over all orientations. However nondiagonal terms must be considered in an accurate treatment of the problem.

2

Let us introduce for the two atoms parallel sets of Cartesian axes, one with its origin in each nucleus, and let each have the z axis along the internuclear line. We shall use an asterisk to distinguish quantities referring specifically to the second atom. Thus coordinates, quantum numbers, wave functions (or states) are written, for example, x, M, Ψ when they refer to the first atom and x^*, M^*, Ψ^* when they refer to the second. If we have but two electrons, one near each nucleus, the expression for the quadrupole-quadrupole potential energy is

$$(3e^2/4R^5)\{r^2r^{*2}-5r^2z^{*2}-5r^{*2}z^2-15z^2z^{*2} \\ +2(xx^*+yy^*-4zz^*)^2\}. \quad (1)$$

It is convenient to write this in terms of the following functions,

$$f(-2)=\tfrac{1}{2}(\tfrac{3}{2})^{\frac{1}{2}}(x-iy)^2, \quad f(-1)=(\tfrac{3}{2})^{\frac{1}{2}}(x-iy)z, \\ f(0)=\tfrac{1}{2}(3z^2-r^2), \quad f(1)=-(\tfrac{3}{2})^{\frac{1}{2}}(x+iy)z, \quad (2) \\ f(2)=\tfrac{1}{2}(\tfrac{3}{2})^{\frac{1}{2}}(x+iy)^2.$$

These functions have the property that they are partners belonging to the rows of the five-dimensional irreducible representation of the three-dimensional rotation group, which property

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[1] F. London, Zeits. f. Physik **63**, 245 (1930).

[2] Slater and Kirkwood, Phys. Rev. **37**, 682 (1931); H. R. Hassé, Proc. Camb. Phil. Soc. **27**, 66 (1931); H. Margenau, Phys. Rev. **38**, 747 (1931); Pauling and Beach, Phys. Rev. **47**, 686 (1935).

[3] F. London, Zeits. f. physik Chemie **B11**, 222 (1931).

is helpful in evaluating matrix elements. Expression (1) becomes

$$(e^2/R^5)\{f(-2)f^*(2)+4f(-1)f^*(1)\\+6f(0)f^*(0)+4f(1)f^*(-1)+f(2)f^*(-2)\}. \quad (1a)$$

We define for a given atom the functions

$$F(m)=\sum f(m), \quad (2a)$$

where the summation is over all the electrons $1\cdots N$ of the atom. These atomic functions have the same rotational properties as the one electron functions. Summing (1a) over the electrons $1\cdots N$ of the first atom and $N+1\cdots N^*$ of the second atom, we obtain for the quadrupole-quadrupole interaction potential energy

$$\begin{aligned}&e^2W/R^5\equiv(e^2/R^5)\sum_m a(m)F(m)F^*(-m),\\&a(-2)=a(2)=1, \qquad (3)\\&a(-1)=a(1)=4,\quad a(0)=6.\end{aligned}$$

3

The calculation of the energy of interaction of atoms at large separation distances is complicated by the fact that the atomic spin-orbit energy differences may be of the same order of magnitude. The doublet separation is only 0.0018 ev in the lowest term of boron but in the lowest term of thallium it is 0.94 ev. The limiting cases in which the energy differences are very small or very large compared to the interaction energy are most easily treated. For some atoms the atomic splitting is so small that it is negligible over a rather wide range of R. For other atoms it is at large distances much larger than the interaction; then at smaller distances the interaction becomes comparable to the splitting; at still smaller distances the molecular interaction is the dominant portion of the energy. We distinguish therefore the cases that the splitting in both of the atoms is negligible, the splitting in the first atom is large and in the second is negligible, and the splitting in both is large. Whether one of these cases is applicable to a pair of atoms depends of course on the value of R. Transition cases involve very complicated treatment except in the very simplest cases.

Let us suppose that Russell-Saunders coupling to exist in the states of the atoms. We restrict our attention to the states of an atom belonging to a definite term, distinguished by a symbol γ indicating the configuration of which it is a part and definite L and S indicating the total orbital and spin angular momenta.[4] Even or odd parity we distinguish by $\omega=\pm 1$. If the spin-orbit splitting is neglected, all the levels of a term fall together and the atomic states are best described in the SLM_SM_L coupling scheme. On the other hand if the levels of a term are widely separated, we need consider only states of a given level, indicating the total angular momentum by J; under such circumstances the $SLJM$ coupling scheme is most suitable.

Let us now consider the case in which the atomic spin-orbit splitting is negligible. The characteristic values of the observables of the widely separated system are $\gamma\omega SLM_SM_L$; $\gamma^*\omega^*S^*L^*M^*{}_SM^*{}_L$. Let $\Psi(M_SM_L)$ be the Schrödinger representation of the state of the first atom and $\Psi^*(M^*{}_SM^*{}_L)$ be that of the second. We choose the relative phases so that the functions are partners belonging to the rows of the direct product of the Sth and Lth irreducible representations of the three-dimensional rotation-reflection group.[5] In neglecting exchange we we could very well use as our functions for the system simple products of the atomic functions. It is however almost as easy to use functions antisymmetrical in all the electrons. Such a presentation has the advantage that the correlation between atomic and molecular states is more apparent.

We first note that the original interaction energy was symmetrical in all $N+N^*$ electrons of the system while (3) is not. An unsymmetrical expression has been obtained from a symmetrical interaction by assuming particular electrons to belong to a given atom; a specific assignment is necessary if we are to expand the potential at this point of the treatment. If we use completely antisymmetrical wave functions, the expansion cannot be made until the functions have been substituted in the matrix integral and the latter reduced to expressions in which there are specific assignments of the electrons in each function. Those terms in which electrons are assigned to

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[4] We use for the most part the atomic terminology of Condon and Shortley, *Theory of Atomic Spectra.*

[5] More accurately of the "unitary group" or the group of the two-dimensional unitary matrices of determinant 1; see. for instance, Wigner, *Gruppentheorie.*

different atoms will be small under the assumption of small overlapping. We therefore retain only terms in which the assignment is the same for each atom. It is then possible at this final stage to substitute expressions like (3) for the interaction.

It is simpler, however, to define from the start a function similar to (3) but having the desired property of symmetry and giving the same result for the energy as obtained by the process outlined above. We add to the definition of W the restriction that it vanish when the electrons $1\cdots N$ are not associated with the first atom and then sum over all exchanges Q, that is all permutations which lead to an ordered assignment in each atom. We obtain the symmetrical interaction

$$(e^2/R^5)T=(e^2/R^5)\sum_Q QW. \tag{3a}$$

As before, in computing energy matrices we finally obtain elements in which the electrons are assigned to specific atoms; we retain only those parts in which the assignment is the same for both functions for each atom. On introducing T there is only one term in the sum over Q which does not give zero, namely that which has the same assignment.

The symmetries of the system are those of rotations around the internuclear line, reflections in planes through this line, and in the case of like nuclei of inversion, that is reflections in the midpoint between the nuclei holding the nuclei fixed. The states of the system will, correspondingly, have quantum numbers Λ and Σ for the total orbital angular momentum and spin along the axis, be positive or negative (of importance only in Σ states), and for like nuclei be g or u. The possible molecular states and their relation to the states of the atoms when widely separated have been considered in detail by Wigner and Witmer.[6]

Let $\mathbf{S}$ be the total spin of the system. Its possible values are $S+S^*$, $S+S^*-1,\cdots$, $|S-S^*|$. We define the functions

$$\varphi(\mathbf{S}\Sigma M_L M^*{}_L)=\sum_{M_S}\Psi(M_S M_L)$$
$$\times\Psi^*(\Sigma-M_S M^*{}_L)(SS^*M_S\Sigma-M_S|SS^*\mathbf{S}\Sigma), \tag{4}$$

which have been built up out of simple products by use of the vector model and belong to the $\mathbf{S}$th irreducible representation of the three-dimensional rotation group. The coefficients on the right are the elements of the usual transformation matrices for angular momenta.

Take first unlike atoms and $\Lambda\neq 0$. Let $c=\omega\omega^*(-)^{L+L^*}$. The two antisymmetrized functions

$$\begin{aligned}\psi(\mathbf{S}\Sigma\Lambda M_L)&=A'\varphi(\mathbf{S}\Sigma M_L,\ \Lambda-M_L),\\ c(-)^\Lambda&\psi(\mathbf{S}\Sigma,\ -\Lambda,\ -M_L)\end{aligned} \tag{5}$$

are partners belonging to the two rows of the Λth representation of the two-dimensional rotation-reflection group. The operator A' is defined as[7]

$$A'=(N!N^*!/(N+N^*)!)^{\frac{1}{2}}\sum_Q(-)^qQ,$$

where Q, as before, is a permutation which leads to an ordered assignment of electrons in each atom and q is the parity of Q. For a given Λ, M_L takes on the following values $(L\geqslant L^*)$

$$\begin{aligned}&L+L^*\geqslant\Lambda\geqslant L-L^*+1,\\ &\qquad\qquad M_L=L,\ L-1,\ \cdots,\ \Lambda-L^*;\\ &L-L^*\geqslant\Lambda>0,\\ &\qquad\qquad M_L=\Lambda+L^*,\ \Lambda+L^*-1,\ \cdots,\ \Lambda-L^*.\end{aligned} \tag{6}$$

This can be seen either by constructing a diagram or by calculating the character of the reducible representation. In addition we have for $\Lambda=0$

$$\begin{aligned}\psi\left(\mathbf{S}\Sigma\,{}^{a}_{b}\,M_L\right)&=\frac{1}{\sqrt{2}}A'\{\varphi(\mathbf{S}\Sigma M_L,\ -M_L)\\ &\qquad\mp\varphi(\mathbf{S}\Sigma,\ -M_L,\ M_L)\},\\ &\qquad M_L=L^*,\ L^*-1,\ \cdots>0,\end{aligned} \tag{5a}$$

$$\psi(\mathbf{S}\Sigma\ b0)=A'\varphi(\mathbf{S}\Sigma\ 00).$$

The functions $\psi(a)$ are positive (Σ^+) if $c=-1$, negative (Σ^-) if $c=1$. On the other hand the functions $\psi(b)$ are positive if $c=1$, negative if $c=-1$. For a given c these functions belong to different irreducible representations. The matrix T is diagonal in $\mathbf{S}$, Σ, and Λ (also a and b) and moreover elements in which both states are replaced by partners will have the same values. The diagonality in $\mathbf{S}$ results from the fact that T is independent of the spin and therefore is

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[6] Wigner and Witmer, Zeits. f. Physik **51**, 859 1928; also R. S. Mulliken, Phys. Rev. **36**, 1440 (1930); F. Hund, Zeits. f. Physik **63**, 723 (1930). For a good discussion see H. Sponer, *Molekülspektrum*, II pp. 132–137.

[7] Condon and Shortley, reference 4, p. 215.

symmetrical under all rotations of the spin axes alone.

Let us compute the matrix of W using the functions (4). It is no longer necessary to carry the quantum numbers $\boldsymbol{S}\Sigma$. We find, because of the unitary nature of the transformation coefficients and the fact that the spin is not contained in W,

$$
\begin{aligned}
(M_L'M^*{}_L'|W|M_LM^*{}_L)&=\sum_m a(m)(LM_L'|F(m)|LM_L)\\
&\quad\times(L^*M^*{}_L'|F^*(-m)|L^*M^*{}_L). \qquad (7)
\end{aligned}
$$

Now the functions F belong to the representation 2 of the three-dimensional rotation group. The product $F(m)\Psi(M_L)$ occurring in the first of the elements on the right can be resolved by the vector model into a sum of functions χ belonging to representations L' according to the relation

$$
\begin{aligned}
\Psi(M_L)F(m)=\Sigma\chi(L2L'M_L+m)&\\
\times(L2L'M_L+m|L2M_Lm),&\qquad (8)
\end{aligned}
$$

where again we have as coefficients the transformation functions for angular momenta. The summation is over the values $L'=L+2,\cdots,|L-2|$. Except for the case $L=0$ (S state), there is a χ in the sum belonging to the Lth representation. We have

$$
\begin{aligned}
(LM_L'|F(m)|LM_L)=A(L)\delta(M_L',M_L+m)&\\
\times(L2M_Lm|L2LM_L'),&\qquad (9)
\end{aligned}
$$

using the orthogonality theorems for the scalar product. $A(L)$ is the scalar product of $\Psi(M_L)$ and $\chi(M_L)$ and is therefore independent of M and m. In this way we obtain for (7)

$$
\begin{aligned}
&(M_L'M^*{}_L'|W|M_LM^*{}_L)=A(L)A^*(L^*)\\
&\times\delta(M_L'+M^*{}_L',M_L+M^*{}_L)a(M_L'-M_L)\\
&\times(L2M_LM_L'-M_L|L2LM_L')\\
&\qquad\times(L^*2M^*{}_LM^*{}_L'-M^*{}_L|L^*2L^*M^*{}_L'). \qquad (7a)
\end{aligned}
$$

The non-zero elements of T for the states of (5) and (5a) (unlike atoms) are found to be

$$
\begin{aligned}
&(\Lambda M_L'|T|\Lambda M_L)=(M_L',\Lambda-M_L'|W|M_L,\Lambda-M_L),\\
&\left({}^{a}_{b}\,M_L'|T|\,{}^{a}_{b}\,M_L\right)=(M_L',-M_L'|W|M_L,-M_L)\mp(M_L',-M_L'|W|-M_L,M_L), \qquad (10)\\
&(bM_L'|T|b0)=\sqrt{2}(M_L',-M_L'|W|00),\\
&(b0|T|b0)=(00|W|00).
\end{aligned}
$$

Take next like atoms. The additional symmetry gives a reduction of the energy determinant, for g and u states do not mix. We define the functions

$$
\begin{aligned}
\psi\left(\boldsymbol{S}\Sigma\,{}^{e}_{f}\,\Lambda M_L\right)=\frac{1}{\sqrt{2}}A'\{&\varphi(\boldsymbol{S}\Sigma M_L,\Lambda-M_L)\\
&\mp\varphi(\boldsymbol{S}\Sigma,\Lambda-M_L,M_L)\}, \qquad (11)\\
&M_L=L,L-1,\cdots>\tfrac{1}{2}\Lambda,
\end{aligned}
$$

and in addition if Λ is even

$$
\psi(\boldsymbol{S}\Sigma f\Lambda\tfrac{1}{2}\Lambda)=A'\varphi(\boldsymbol{S}\Sigma\tfrac{1}{2}\Lambda\tfrac{1}{2}\Lambda). \qquad (11a)
$$

$\psi(e)$ is g if $\boldsymbol{S}$ is odd (molecular triplets, etc.), u if $\boldsymbol{S}$ is even (molecular singlets, quintets, etc.). On the other hand $\psi(f)$ is g if $\boldsymbol{S}$ is even, u if $\boldsymbol{S}$ is odd. Moreover the states $\psi(e0M_L)$ are negative and the states $\psi(f0M_L)$ are positive. We have then the correlation ($\Lambda=0$) that negative states are g if $\boldsymbol{S}$ is odd and u if $\boldsymbol{S}$ is even, while positive states are g if $\boldsymbol{S}$ is even and u if $\boldsymbol{S}$ is odd. These functions belong to different representations of the group of inversions in the midpoint between the atoms. When $\Lambda\neq 0$, they belong to the second row of the Λth representation of the two-dimensional rotation-reflection group, their partners being the functions obtained by changing the signs of Λ and M_L and multiplying by $(-)^{\Lambda}$. The non-zero elements of T for the states of (11) and (11a) are

$$
\begin{aligned}
&\left({}^{e}_{f}\,\Lambda M_L'|T|\,{}^{e}_{f}\,\Lambda M_L\right)=(M_L',\Lambda-M_L'|W|M_L,\Lambda-M_L)\mp(M_L',\Lambda-M_L'|W|\Lambda-M_L,M_L), \qquad (12)\\
&(f\Lambda M_L'|T|f\Lambda\tfrac{1}{2}\Lambda)=\sqrt{2}(M_L',\Lambda-M_L'|W|\tfrac{1}{2}\Lambda\tfrac{1}{2}\Lambda),\\
&(f\Lambda\tfrac{1}{2}\Lambda|T|f\Lambda\tfrac{1}{2}\Lambda)=(\tfrac{1}{2}\Lambda\tfrac{1}{2}\Lambda|W|\tfrac{1}{2}\Lambda\tfrac{1}{2}\Lambda).
\end{aligned}
$$

4

Let us next consider briefly the case of two different atoms in one of which the atomic spin-orbit splitting is large and in the other it is negligible. We describe the states of the first atom in the $SLJM$ coupling scheme, keeping the second in the SLM_SM_L scheme, and consider only molecular states arising from a given J level. Introducing the new function

$$\varphi(JS^*M^*{}_SMM^*{}_L)=\Psi(JM)\Psi^*(M^*{}_SM^*{}_L), \qquad (13)$$

we have at large distances the molecular states represented by the functions

$$\psi(JS^*M^*{}_S\Gamma M)=A'\varphi(JS^*M^*{}_SM,\ \Gamma-M), \qquad (14)$$

for $\Gamma\neq 0$. If J is an integer, Γ can in addition have the value zero, for which value we define the functions

$$\psi\left(JS^*M^*{}_S \genfrac{}{}{0pt}{}{a}{b} M\right)=\frac{1}{\sqrt{2}}A'\{\varphi(JS^*M^*{}_SM,\ -M)$$
$$\mp\varphi(JS^*M^*{}_S,\ -M,\ M)\},\quad M\neq 0; \qquad (14a)$$
$$\psi(JS^*M^*{}_S\ b\ 0)=A'\varphi(JS^*M^*{}_S00).$$

The possible values of M in these expressions depend on whether L^* is larger or equal to or less than J. We shall not write down the detailed expressions, for they are quite similar to the corresponding restrictions of the last section in any given case. There is one peculiarity which we note. The simultaneous rotation of spin and position axes does not give us a transformation group that is particularly useful. Instead we might introduce an artificial type of spin transformation depending on the space state of the particle in question. This is not necessary however, for one readily sees that T is diagonal in Γ and $M^*{}_S$. We define the expression

$$\begin{aligned}(JM'M^*{}_L{}'|W|JMM^*{}_L)&\\ =\sum_m a(m)(JM'|F(m)|JM)&\\ \times(L^*M^*{}_L{}'|F^*(-m)|L^*M^*{}_L)&\\ =C(J)A^*(L^*)\delta(M'+M^*{}_L{}',\ M+M^*{}_L)&\\ \times a(M'-M)(J2MM'-M|J2JM')&\\ \times(L^*2M^*{}_LM^*{}_L{}'-M^*{}_L|L^*2L^*M^*{}_L{}').&\qquad (15)\end{aligned}$$

$C(J)$ is a scalar product independent of M and is zero if J is zero or one-half. In terms of this expression the non-zero elements of T are

$$\begin{aligned}&(J\Gamma M'|T|J\Gamma M)=(JM',\ \Gamma-M'|W|JM,\ \Gamma-M),\\ &\left(J\genfrac{}{}{0pt}{}{a}{b}M'|T|J\genfrac{}{}{0pt}{}{a}{b}M\right)=(JM',\ -M'|W|JM,\ -M)\mp(JM',\ -M'|W|J,\ -M,\ M),\\ &(JbM'|T|Jb0)=\sqrt{2}(JM',\ -M'|W|J00),\\ &(Jb0|T|Jb0)=(J00|W|J00).\end{aligned} \qquad (16)$$

5

We come finally to the case in which the spin-orbit splitting of the atomic term energies is large in both atoms. All atomic states are represented in the $SLJM$ scheme. The molecule has a quantum number Ω for the total angular momentum along the internuclear line. The components of the orbital angular momentum and spin are not defined separately. We introduce the function

$$\varphi(JJ^*MM^*)=\Psi(JM)\Psi^*(J^*M^*). \qquad (17)$$

Consider unlike atoms and $\Omega\neq 0$. Let

$$d=\omega\omega^*(-)^{J+J^*}.$$

The two antisymmetrized functions

$$\begin{aligned}&\psi(JJ^*\Omega M)=A'\varphi(JJ^*M,\ \Omega-M),\\ &d(-)^\Omega\psi(JJ^*,\ -\Omega,\ -M),\end{aligned} \qquad (18)$$

are partners belonging to the two rows of the Ωth representation of the two-dimensional rotation-reflection group in which the rotation of the spin as well as the position axes is carried out. For a given Ω, M takes on the values ($J\geqslant J^*$)

$$\begin{aligned}&J+J^*\geqslant\Omega\geqslant J-J^*+1,\\ &\qquad M=J,\ J-1,\ \cdots,\ \Omega-J^*;\\ &J-J^*\geqslant\Omega>0,\\ &\qquad M=\Omega+J^*,\ \Omega+J^*-1,\ \cdots,\ \Omega-J^*.\end{aligned} \qquad (19)$$

If J and J^* are integers or are half-integers, Ω

can in addition have the value zero. We define in case $\Omega=0$ the two sets of functions

$$\psi\left(JJ^*\genfrac{}{}{0pt}{}{a}{b}M\right)=\frac{1}{\sqrt{2}}A'\{\varphi(JJ^*M,\,-M)\mp\varphi(JJ^*,\,-M,\,M)\},\quad M=J^*,\,J^*-1,\,\cdots>0,\tag{18a}$$

including if J and J^* are integers,

$$\psi(JJ^*b0)=A'\psi(JJ^*00).\tag{18b}$$

The functions $\psi(a)$ are positive (0^+) if $d=-1$, negative (0^-) if $d=1$ while the functions $\psi(b)$ are positive if $d=1$, negative if $d=-1$. The matrix T is diagonal in Ω (and a and b). We can express the results in terms of the expression

$$\begin{aligned}(JJ^*M'M^{*\prime}|W|JJ^*MM^*)&=\sum_m a(m)(JM'|F(m)|JM)\\&\quad\times(J^*M^{*\prime}|F^*(-m)|J^*M^*)\\&=C(J)C^*(J^*)\delta(M'+M^{*\prime},\,M+M^*)\\&\quad\times a(M'-M)(J2MM'-M|J2JM')\\&\quad\times(J^*2M^*M^{*\prime}-M^*|J^*2J^*M^{*\prime}).\end{aligned}\tag{20}$$

The non-zero elements of T for unlike atoms are found to be

$$\begin{aligned}&(JJ^*\Omega M'|T|JJ^*\Omega M)=(JJ^*M',\,\Omega-M'|W|JJ^*M,\,\Omega-M),\\&\left(JJ^*\genfrac{}{}{0pt}{}{a}{b}M'|T|JJ^*\genfrac{}{}{0pt}{}{a}{b}M\right)=(JJ^*M',\,-M'|W|JJ^*M,\,-M)\mp(JJ^*M',\,-M'|W|JJ^*,\,-M,\,M),\\&(JJ^*bM'|T|JJ^*b0)=\sqrt{2}(JJ^*M',\,-M'|W|JJ^*00),\\&(JJ^*b0|T|JJ^*b0)=(JJ^*00|W|JJ^*00).\end{aligned}\tag{21}$$

For like atoms in states of the same configuration and term $(\gamma^*=\gamma,\,S^*=S,\,L^*=L,\,\omega^*=\omega)$ and the same J values, we define the functions

$$\psi\left(JJ\genfrac{}{}{0pt}{}{e}{f}\Omega M\right)=\frac{1}{\sqrt{2}}A'\{\varphi(JJM,\,\Omega-M)\mp\varphi(JJ\Omega-M,\,M)\},\quad M=J,\,J-1,\,\cdots>\tfrac{1}{2}\Omega.\tag{22}$$

If J is an integer and Ω is even or if J is an half-integer and Ω is odd, we have in addition the function

$$\psi(JJf\Omega\tfrac{1}{2}\Omega)=A'\varphi(JJ\tfrac{1}{2}\Omega\tfrac{1}{2}\Omega).\tag{22a}$$

$\psi(e)$ is u if J is an integer, g if J is a half-integer. $\psi(f)$ is g if J is an integer, u if J is a half-integer. When $\Omega\neq0$, these functions belong to the second row of the Ωth representation of the two-dimensional rotation-reflection group, their partners being the functions obtained by changing the signs of Ω and M and multiplying by $(-)^{2J+\Omega}$. For $\Omega=0$, g functions are positive and u functions are negative. The non-zero elements of T for like atoms with $J^*=J$ are found to be

$$\begin{aligned}&\left(JJ\genfrac{}{}{0pt}{}{e}{f}\Omega M'|T|JJ\genfrac{}{}{0pt}{}{e}{f}\Omega M\right)=(JJM',\,\Omega-M'|W|JJM,\,\Omega-M)\mp(JJM',\,\Omega-M'|W|JJ\Omega-M,\,M),\\&(JJf\Omega M'|T|JJf\Omega\tfrac{1}{2}\Omega)=\sqrt{2}(JJM',\,\Omega-M'|W|JJ\tfrac{1}{2}\Omega\tfrac{1}{2}\Omega),\\&(JJf\Omega\tfrac{1}{2}\Omega|T|JJf\Omega\tfrac{1}{2}\Omega)=(JJ\tfrac{1}{2}\Omega\tfrac{1}{2}\Omega|W|JJ\tfrac{1}{2}\Omega\tfrac{1}{2}\Omega).\end{aligned}\tag{23}$$

The remaining possibility of like atoms in states belonging to the same configuration and term but with different J values leads to expressions which are somewhat more complicated than those considered because the coefficients involve both J and J^*. Since we are primarily interested in the lowest states of the atoms, we shall not discuss this case.

6

The elements of the matrix T in the cases discussed have as a common factor the product of

TABLE I. $\lambda(hh^*\delta)$ *for integral* δ. *If* δ *is not zero there are two states for each number listed. If the atomic term splitting is negligible in both atoms* ($h=L$, $h^*=L^*$, $\delta=\Lambda$), *the letters mean the following: Let* $c=\omega\omega^*(-)^{L+L^*}$. *If the atoms are different, an a after a number means that the state is positive* (Σ^+) *if* $c=-1$, *negative* (Σ^-) *if* $c=1$, *while b means that the state is positive if* $c=1$, *negative if* $c=-1$. *If the atoms are the same, an e means the state is g if the molecular spin is odd, u if it is even. An f means that the state is g if the spin is even, u if it is odd. Also for* $\Lambda=0$ *states with e are negative and states with f are positive. For other cases see the text.*

δ	$h=1$ $h^*=1$	2 1	3 1	4 1	1.5 1.5	2 2
0	0 *ea*	−1.014 *a*	−1.225 *a*	−1.305 *a*	2.4 *ea* 0 *ea*	2.774 *ea* −1.060 *ea*
	3.6 *fb* 0 *fb*	2.324 *b* −0.295 *b*	2.096 *b* −0.382 *b*	2.013 *b* −0.418 *b*	3.2 *fb* −0.8 *fb*	3.261 *fb* 1.508 *fb* −0.484 *fb*
1	0 *e*	2.456 0.047 −1.489	2.061 −0.170 −1.401	1.972 −0.289 −1.392	−1.6 *e*	1.202 *e* −0.917 *e*
	−2.4 *f*				1.2 *f* −0.8 *f*	1.127 *f* −1.413 *f*
2		0.356 −2.891	2.199 0.230 −1.939	1.367 0.347 −1.424	0.4 *e*	−2.000 *e*
	0.6 *f*				−2.8 *f*	0.857 *f* −1.857 *f*
3		1.014	0.646 −3.096	2.032 −0.032 −1.710		0.857 *e*
					1.2	−2.571 *f*
4			1.225	0.853 −3.222		
						1.714 *f*
5				1.354		

two atomic coefficients. Dividing by this common factor we obtain the elements of a dimensionless determinant the roots of which are needed to describe the quadrupole-quadrupole interaction between atoms.

In general let h, h^* be a pair of numbers, integers or half-integers, corresponding to L, L^*; J, L^*; or J, J^*. Let δ stand for Λ, Γ, or Ω as the case may be. The range of the remaining parameter (M_L or M) is essentially the same in all three cases. A comparison of (7a), (15) and (20) shows that for the same numerical values h, h^* the elements of W are the same aside from the atomic coefficients. If h^* is numerically different from h, we see from (10), (16) and (21) that on dividing out the atomic coefficients the dimensionless determinants are the same. For unlike atoms with $h^*=h$ there is one further simple reduction of the determinant possible. In this case ($L^*=L$, $L^*=J$, or $J^*=J$) we can form linear combinations $\psi(e)$ and $\psi(f)$ which are formally the same as for like atoms. It can be shown that T has no cross terms between these two groups and that the determinant is the same as obtained from the expressions for like atoms, that is from (12) or (23) on dividing out the coefficients. Thus we have the simplifying result that the dimensionless determinant depends only on the numerical values of the pair of numbers h, h^*. We shall designate the roots of a subdeterminant by $\lambda(hh^*\delta)$. How many roots there are for a given δ depends in general on how many times the δth representation is contained in the reducible representation obtained from the transformation under two-dimensional rotations and reflections of all the possible simple product functions of the atomic states.

Roots of the dimensionless determinant for some values of h and h^* are given in Tables I and II.

7

The atomic coefficients $A(L)$ and $C(J)$ are defined by the relations

$$A(L)(L2M_L0\,|\,L2LM_L)=(LM_L\,|\,F(0)\,|\,LM_L), \quad (24)$$
$$C(J)(J2M0\,|\,J2JM)=(JM\,|\,F(0)\,|\,JM).$$

To obtain explicit expressions, we transform to the zero-order representation scheme characterized by the one-electron quantum numbers $a=nlm_sm_l$. If we let A stand for the collection of

TABLE II. $\lambda(hh^*\delta)$ *for half-integral* δ.

δ	$h=1.5$ $h^*=1$	2 1.5	4.5 1
0.5	2.746 0 −1.049	2.864 1.551 −0.377 −1.168	1.977 −0.399 −1.345
1.5	0.176 −2.722	0.916 −1.195 −1.872	1.916 −0.206 −1.476
2.5	0.848	0.619 −2.770	1.883 0.125 −1.774
3.5		1.434	2.054 0.518 −2.339
4.5			0.934 −3.270
5.5			1.401

such quantum numbers in a zero-order state of the atom, we have for $A(L)$ the relation

$$A(L)(L2M_L0|L2LM_L)=\sum_{A,B}(\gamma SLM_SM_L|A)\times(A|F|B)(B|\gamma SLM_SM_L). \qquad (25)$$

But only $A=B$ terms occur or are different from zero. For $(A|F|B)$ vanishes if A differs from B by more than one individual electron quantum number set and has the value $\pm(a|f|b)$ if all sets but $a\neq b$ are the same. But even this term is ruled out since if all but one of the m_l are the same, they must all be the same because of the condition $\Sigma m_l=M_L$ for both A and B. We have therefore for (25) the expression

$$\sum_A\{(\gamma SLM_SM_L|A)^2\sum_a(a|f|a)\}. \qquad (26)$$

But

$$(a|f|a)=(-)\left[\frac{l(l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}}\times(l2m_l0|l2lm_l)\langle r^2\rangle_{\text{Av}}, \qquad (27)$$

where

$$\langle r^2\rangle_{\text{Av}}=\int_0^\infty drr^2R(nl)^2, \qquad (28)$$

$R(nl)/r$ is the radial part of the wave function for an electron in an nl state. We note that since the coefficient

$$(l2m_l0|l2lm_l)=\frac{3m_l^2-l(l+1)}{[(2l-1)l(l+1)(2l+3)]^{\frac{1}{2}}} \qquad (29)$$

when summed over the electrons in complete shells gives zero, contributions to $A(L)$ will come only from incomplete shells. All atoms whose normal states are not S states have one incomplete shell having angular momentum. We can write

$$A(L)=B(L)\langle r^2\rangle_{\text{Av}}, \quad C(J)=D(J)\langle r^2\rangle_{\text{Av}}. \qquad (30)$$

The second factor in each case is the average value of r^2 for electrons in that shell. We have

$$B(L)=(-)\left[\frac{l(l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}}\sum_A\left\{(\gamma SLM_SM_L|A)^2\sum_{m_l}\frac{(l2m_l0|l2lm_l)}{(L2M_L0|L2LM_L)}\right\}. \qquad (31)$$

Likewise if we start in the $SLJM$ scheme we obtain

$$D(J)=(-)\left[\frac{l(l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}}\sum_A\left\{(\gamma SLJM|A)^2\sum_{m_l}\frac{(l2m_l0|l2lm_l)}{(J2M0|J2JM)}\right\}. \qquad (32)$$

TABLE III. *Atoms with incomplete p-shells. A star after an element means the spin-orbit splitting of the lowest energy term is less than 0.036 ev. Abbreviations (s.c) and (s.c.f) are used to distinguish numbers obtained using shielding constant and self-consistent field wave functions, respectively.*

ELEMENT	GROUND LEVEL		$B(L)$	$D(J)$	r_m IN BOHR RADII		$\langle r^2\rangle_{\text{Av}}$(np) IN (BOHR RADII)^2	
	np				(s.c)	(s.c.f)	(s.c)	(s.c.f)
B*	$2p$	$^2P^0_{1/2}$	-0.6325	0	1.54	1.80	4.4	9.12
Al*	$3p$	"	"	"	2.57		10	
Ga	$4p$	"	"	"	2.74		11	
In	$5p$	"	"	"	3.20		14	
Tl	$6p$	"	"	"	3.53		17	
C*	$2p^2$	$^3P_0$	$+0.6325$	0	1.23	1.26	2.8	4.882
Si*	$3p^2$	"	"	"	2.17		7.3	
Ge	$4p^2$	"	"	"	2.42		8.5	
Sn	$5p^2$	"	"	"	2.83		11	
Pb	$6p^2$	"	"	"	3.12		14	
0*	$2p^4$	$^3P_2$	-0.6325	-0.3743	0.88	0.85	1.4	2.440
S	$3p^4$	"	"	"	1.65		4.2	
Se	$4p^4$	"	"	"	1.97		5.6	
Te	$5p^4$	"	"	"	2.30		7.5	
F	$2p^5$	$^2P^0_{3/2}$	$+0.6325$	$+0.4472$	0.77	0.73	1.1	1.82
Cl	$3p^5$	"	"	"	1.48		3.4	
Br	$4p^5$	"	"	"	1.80		4.7	
I	$5p^5$	"	"	"	2.11		6.2	

The transformation coefficients to the zero-order scheme are usually simplest for extreme values of $M_S M_L$ or M. They can often be obtained for extreme values by inspection. Otherwise they are readily obtainable with the help of the angular momentum operators as used by Gray and Wills.[8]

8

We come now to the problem of obtaining the numerical values of $\langle r^2\rangle_{\mathrm{Av}}$. In Tables III and IV we have listed most of the elements for which these considerations are of interest. The second column in the tables gives the nature of the lowest level of the atoms. We restrict our discussion to the lowest term or level.

The average value of r^2 has been estimated for each atomic valence l electron by using the shielding constants and effective principal quantum numbers of Slater.[9] Such a method gives unreliable values, however, especially for light atoms. This is because the major contribution to the average value comes in the expression (28) from values of r out beyond the maximum of the density function. In this range it is well known that simple functions with shielding constants are poor approximations. The error is presumably less for an electron with a large principal quantum number, n, since the peak of the density function is sharper and the value obtained more nearly the square of the radius at the maximum, r_m. The magnitude of the error for small n is shown by the values which we have calculated for B, C, O and F using wave functions obtained from the self-consistent field.[10] The numbers so obtained are approximately twice those calculated from shielding constants.

The self-consistent field probably gives wave functions which are too large at large distances. Electrons are kept away from the neighborhood of the nucleus because of the static nature of the electron field which the method uses. This tendency to favor a more diffuse distribution is more clearly the case when no account is taken of exchange. The value of $\langle r^2\rangle_{\mathrm{Av}}$ is a very sensitive function of such effects. For the chlorine negative ion the value of $\langle r^2\rangle_{\mathrm{Av}}(3p)$ has been calculated with exchange to be[11] $5.137a_0^2$ (a_0 = Bohr radius). The closely related diamagnetic susceptibility is calculated to be $-30.4\cdot10^{-6}$. Without exchange the diamagnetic susceptibility is calculated to be $-41.3\cdot10^{-6}$ which corresponds to a value of $\langle r^2\rangle_{\mathrm{Av}}(3p)$ of about $7.4a_0^2$. The self-consistent field functions for oxygen and carbon were obtained without exchange and hence the values for $\langle r^2\rangle_{\mathrm{Av}}$ obtained for these atoms are probably much too large, judging from the effect of exchange on Cl$^-$. The importance of exchange in neutral atoms may be slightly less however. The function for F (also Ne and F$^-$, Table V) was calculated with exchange between the $2p$ electrons. Boron has but one $2p$ electron. The values for these atoms are probably quite good.[12]

TABLE IV. *Atoms with incomplete d shells. Numbers in parentheses are positions of maximum radial density of the two electrons in the s shell lying outside the incomplete d shell, which electrons are most effective in determining the radius of the atoms.*

ELEMENT	GROUND LEVEL				r_m IN BOHR RADII (s.c)	$\langle r^2\rangle_{\mathrm{Av}}$(nd) IN (BOHR RADII)^2 (s.c)
	nd		$B(L)$	$D(J)$		
Sc*	$3d4s^2$	$^2D_{3/2}$	-0.5345	-0.4472	3.00(4.55)	14
Y	$4d5s^2$	"	"	"	4.55(5.33)	30
La	$5d6s^2$	"	"	"	5.33(5.88)	40
Ti	$3d^24s^2$	$^3F_2$	-0.2213	-0.1833	2.47(4.35)	9.5
Zr	$4d^25s^2$	"	"	"	3.75(5.08)	20
Hf	$5d^26s^2$	"	"	"	4.38(5.60)	27
V	$3d^34s^2$	$^4F_{3/2}$	$+0.2213$	$+0.1533$	2.09(4.15)	6.8
W	$5d^45s^2$	$^5D_0$	$+0.5345$	0	3.23(5.11)	15
Fe	$3d^64s^2$	$^5D_4$	-0.5345	-0.4006	1.44(3.65)	3.2
Co	$3d^74s^2$	$^4F_{9/2}$	-0.2213	-0.1935	1.32(3.51)	2.7
Ni	$3d^84s^2$	$^3F_4$	$+0.2213$	$+0.2003$	1.21(3.38)	2.3
Ir	$5d^9$	?$^2D_{5/2}$	$+0.5345$	$+0.4782$	2.58	9.4

Additional information is obtainable from the diamagnetic susceptibility of closely related atoms. The diamagnetic susceptibility of a gas of atoms in singlet states is given by Van Vleck's expression, $-0.79\cdot10^{-6}\Sigma\langle r^2\rangle_{\mathrm{Av}}$, where the sum is over all the electrons of an atom. In Table V we have some experimental values for Ne and A obtained by Havens and in addition some values

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[8] Gray and Wills, Phys. Rev. **38**, 248 (1931).

[9] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[10] Self-consistent field data have been calculated from functions given by the following: B, Brown, Bartlett and Dunn, Phys. Rev. **44**, 296 (1933); C, C. C. Torrance, Phys. Rev. **46**, 388 (1934); O, Hartree and Black, Proc. Roy. Soc. **139**, 311 (1933); F, F$^-$, and Ne, with exchange between p electrons, F. W. Brown, Phys. Rev. **44**, 214 (1933).

[11] Hartree and Hartree, Proc. Roy. Soc. **156**, 60 (1936); Cl$^-$ with exchange. The value of 7.4 for $\langle r^2\rangle_{\mathrm{Av}}(3p)$ without exchange is only approximate since the numbers for inner electrons without exchange are not given.

[12] Unfortunately some doubt as to the accuracy of the functions is cast by Brown's result for the electron affinity of fluorine. He obtained a negative number for the electron affinity when effects due to the change in the function on removal of the electron were included.

for the negative halogen ions obtained by Brindley and Hoare from salt crystals using the assumption of additivity of the susceptibilities of the two ions of the salts.[13] The magnetic susceptibility of Ne obtained from the self-consistent field with exchange between the $2p$ electrons is only five percent greater than the experimental value. If we calculate back from the experimental values using Slater values for the inner electrons, which contribute only a small fraction of the sum, we obtain the numbers for $\langle r^2\rangle_{\text{Av}}$ listed in the fifth column (the numbers in parentheses have been obtained from self-consistent field values for the inner electrons). We see that for Ne the difference is about ten percent. However with ions the agreement is not so good. The experimental values are much smaller than the values from the self-consistent field. This result is not surprising since each ion is in the disturbing field of its neighbors. The crystals are not completely ionic; Ewing and Seitz have shown by the application of the Hartree approximation to LiH and LiF crystals that there is considerable charge in the neighborhood of the metallic ion.[14] The picture of the valence electrons localized in a region about the electron-negative atoms is not a very accurate one.

We have a lower bound for $\langle r^2\rangle_{\text{Av}}$ for chlorine in the number 2.88 for argon and an upper bound in the number 5.137 for the chlorine negative ion.

9

If one of the three cases discussed in Sections 3, 4, and 5 is applicable, the quadrupole-quadrupole interaction energy between two atoms is given by one of the expressions

$$\begin{aligned}&(e^2/R^5)A(L)A^*(L^*)\lambda(LL^*\Lambda),\\&(e^2/R^5)C(J)A^*(L^*)\lambda(JL^*\Gamma),\\&(e^2/R^5)C(J)C^*(J^*)\lambda(JJ^*\Omega).\end{aligned}\tag{33}$$

TABLE V. *Data for some closely related atoms.*

	Magnetic Susceptibility 10^6			$\langle r^2\rangle_{\text{Av}}(np)$ in (Bohr Radii)^2		
	Expt.	(s.c)	(s.c.f)	From Expt.	(s.c)	(s.c.f)
Ne	-7.651 ± 0.008	-5.58	-8.08	1.20(1.23)	0.88	1.32
A	-19.23 ± 0.20	-18.5		2.88	2.77	
F^-	-9.4	-8.13	-17.1	1.48(1.50)	1.28	3.12
Cl^-	-24.2	-25.2	-30.4	3.64(3.82)	3.81	5.137
Br^-	-34.5	-39.3		4.38	5.14	
I^-	-50.6	-58.6		5.58	6.84	

The results would be of more significance if we knew at what distances other forces begin to be of equal strength. It is not easy to say however. At large distances the Heitler-London method gives the repulsive forces to a good approximation. From Sugiura's formula[15] we obtain for hydrogen at a separation distance of $4a_0$ for the lowest singlet and triplet states -0.27 ev and 0.20 ev, respectively. The induced polarization or van der Waals attraction is slightly smaller at this distance. Using the coefficients of Pauling and Beach,[2] we obtain for the first three terms (terms in the inverse sixth, eighth and tenth powers of R) the numbers of the expression $-(0.0429+0.0513+0.0293)$ ev $=-0.124$ ev.[16] For purposes of comparison let us find the distance at which the Heitler-London repulsion between two helium atoms is 0.2 ev. Slater has calculated this energy[17] and has obtained the expression 484 exp $(-2.43R/a_0)$ ev. For 0.2 ev we find $R=3.2a_0$. At $R=4r_m\cong2.2a_0$ the repulsive energy is 2.3 ev (r_m is the position of the maximum of the radial density function). Using Margenau's coefficients we find for the van der Waals energy of two helium atoms $-(0.039+0.030+0.011)$ ev $=-0.080$ ev at $R=3.2a_0$. The Heitler-London energy, being essentially a penetration energy, builds up and falls off faster than an inverse power energy. As pointed out in the preceding section, for heavy atoms the electron distribution function dies off more rapidly beyond the last maximum than for light atoms. If for comparison we use a distance of twice the sum of the atomic radii, that is twice the sum of r_m, the exchange forces should be relatively smaller at such distances for heavy atoms than for light. For atoms with incomplete d shells the situation is complicated by the presence of an outside s shell.

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[13] G. G. Havens, Phys. Rev. **43**, 992 (1933). Brindley and Hoare, Proc. Roy. Soc. **152**, 342 (1935).

[14] Ewing and Seitz, Phys. Rev. **50**, 760 (1936).

[15] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927); see H. Bethe, *Handbuch der Physik*, Vol. 24, p. 537.

[16] In hydrogen the van der Waals energies are more important than exchange energies for R greater than about $7a_0$. For $R=7a_0$ the three van der Waals terms are in the proportion 1, 1/2, 1/8. The approximations made in calculating the coefficients are poor for smaller distances.

[17] J. C. Slater, Phys. Rev. **32**, 349 (1928).

TABLE VI. *Energies of attraction at distances of twice the sum of the atomic radii. The atomic radius is defined as the position of the last maximum in the electron density function. The spin-orbit coupling has been neglected and the values for* $\langle r^2 \rangle_{\mathrm{Av}}$ *taken from the last column of Table III. The last four molecules have in addition attractive* Δ *states at this distance with energies one-sixth the energies of the* Σ *states and the same multiplicities (neglecting other forces). The known states listed are those which have been observed and which on dissociation go into normal states of the atoms.* $2r_e$ *is for the equilibrium position of the lowest observed state.*

	KNOWN STATES	$2r_e\ 10^8$ cm	$R\ 10^8$ cm	E′EV	STATES
B_2			3.80	−0.112	$^1\Pi_g$, $^3\Pi_u$
BO	$^2\Sigma^+$, $^2\Pi$	2.4	2.80	−0.139	$^2\Pi$, $^4\Pi$
C_2	$^3\Pi_u$?	2.62	2.66	−0.190	$^1\Pi_g$, $^3\Pi_u$, $^5\Pi_g$
CF			2.10	−0.231	$^2\Pi$, $^4\Pi$
O_2	$^3\Sigma_g^-$, $^1\Sigma_g^+$, $^3\Sigma_u^+$	2.4	1.80	−0.341	$^1\Pi_g$, $^3\Pi_u$, $^6\Pi_g$
F_2	$^1\Pi$?		1.54	−0.406	$^1\Pi_g$, $^3\Pi_u$
BC			3.23	−0.202	$^2\Sigma^-$, $^4\Sigma^-$
BF			2.67	−0.195	$^1\Sigma^+$, $^3\Sigma^+$
CO	$^1\Sigma^+$, $^3\Pi$, $^1\Pi$	2.26	2.23	−0.347	$^1\Sigma^+$, $^3\Sigma^+$, $^5\Sigma^+$
OF			1.67	−0.549	$^2\Sigma^-$, $^4\Sigma^-$

If we have two atoms in P states and neglect the atomic multiplet splitting, we see from the first column of Table I that the states of the system fall into four energy levels due to the quadrupole-quadrupole interaction of the two atoms. In Table VI are given the energies for the lowest (attractive) levels at distances of twice the sum of the atomic radii for the molecular pairs obtainable from B, C, O and F. Consider B_2 and F_2. The atoms have spin $\frac{1}{2}$, which give $S=0$, 1. Also $c=1$. From Table I we see that the lowest states ($\lambda=-2.4$) are f states. This means that $^1\Pi$ and $^3\Pi$ are g and u, respectively. Similarly we find that for the next level, which has zero energy, the states are $^1\Sigma_u^-$, $^3\Sigma_g^-$, $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^1\Pi_u$, $^3\Pi_g$. The third level has the states $^1\Delta_g$, $^3\Delta_u$ and an energy $-\frac{1}{4}$ that given in Table VI, that is it is repulsive. The fourth level has the states $^1\Sigma_g^+$, $^3\Sigma_u^+$ and an energy -1.5 that of the lowest level.

For C_2 and O_2 since the spins are both 1, $S=0$, 1, 2. The lowest level has the states $^1\Pi_g$, $^3\Pi_u$, $^5\Pi_g$ for which the energy is given in Table VI. The states $^1\Sigma_u^-$, $^3\Sigma_g^-$, $^5\Sigma_u^-$, $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^1\Pi_u$, $^3\Pi_g$, $^5\Pi_u$ have zero energy. The states $^1\Delta_g$, $^3\Delta_u$, $^5\Delta_g$ are repulsive, the energy being $-\frac{1}{4}$ that of the lowest level, and the states $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$ are also repulsive, having energy -1.5 that of the lowest level. For BO and CF since the atomic spins are $\frac{1}{2}$, 1, $S=\frac{1}{2}$, $\frac{3}{2}$. Also $c=-1$. AA^* is positive. The lowest level has the states $^2\Pi$, $^4\Pi$. The states $^2\Sigma^+$, $^4\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^-$, $^2\Pi$, $^4\Pi$ have zero energy; the states $^2\Delta$, $^4\Delta$ have energy $-\frac{1}{4}$ that of the lowest level; the states $^2\Sigma^-$, $^4\Sigma^-$ have energy -1.5 that of the lowest level.

For BC and OF the atomic spins are $\frac{1}{2}$, 1 and therefore $S=\frac{1}{2}$, $\frac{3}{2}$. We see that $c=-1$ and that AA^* is negative. The lowest level is therefore given by $\lambda=3.6$. Its states are $^2\Sigma^-$, $^4\Sigma^-$. The next energy is also attractive, $\frac{1}{6}$ that of the lowest level, and has the states $^2\Delta$, $^4\Delta$. The states $^2\Sigma^+$, $^4\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^-$, $^2\Pi$, $^4\Pi$ have zero energy; the states $^2\Pi$, $^4\Pi$ are repulsive and have an energy $-\frac{2}{3}$ that of the lowest energy. For CO the spins are 1 and $S=0$, 1, 2. $C=1$ and AA^* is negative. The lowest level has the states $^1\Sigma^+$, $^3\Sigma^+$, $^5\Sigma^+$. The next has $\frac{1}{6}$th the energy and the states $^1\Delta$, $^3\Delta$, $^5\Delta$. The states $^1\Sigma^-$, $^3\Sigma^-$, $^5\Sigma^-$, $^1\Sigma^+$, $^3\Sigma^+$, $^5\Sigma^+$, $^1\Pi$, $^3\Pi$, $^5\Pi$ have zero energy. The states $^1\Pi$, $^3\Pi$, $^5\Pi$ are repulsive with an energy $-\frac{2}{3}$ that of the lowest level. The level scheme of BF is the same as CO except that both spins are $\frac{1}{2}$ and therefore there are no molecular quintets.

The writer takes pleasure in acknowledging his indebtedness to Professor Wigner, who brought the problem to his attention, for advice and stimulating discussion. He wishes to thank the Wisconsin Alumni Research Foundation for its support of this work.