PHYSICAL REVIEW VOLUME 123, NUMBER 5 SEPTEMBER 1, 1961

Theory of Long-Range Interatomic Forces. I. Dispersion Energies between Unexcited Atoms*

PETER R. FONTANA†
Sloane Physics Laboratory, Yale University, New Haven, Connecticut

(Received February 2, 1961)

A general theory of second-order dispersion forces between atoms in nondegenerate ground states is first developed by using an irreducible tensor formalism and the theory of angular momentum. This forms the basis for calculations of forces between excited systems, which are the subject of later publications. Attention is given to the interaction of two noble gas atoms where it is assumed that each electron oscillates with simple harmonic motion, and the interaction between two alkali atoms is calculated by considering the electrons to be moving in a Coulomb field. The dominant terms of the dispersion energy between a number of atoms and molecules are tabulated. The results indicate that the hitherto neglected dipole-octupole contributions are in many cases larger than the quadrupole-quadrupole terms.

I. INTRODUCTION

THE calculation of interaction energies between atoms in ground and excited states has become of considerable interest. The recent advances in molecular beam techniques make it possible to determine the energy curves over a large range of internuclear separations. So far, however, precise experimental data are only available in the short-range region where the exchange forces are dominant. These experiments also show that many of the empirical formulas which describe the interaction energies between atoms or molecules are inadequate. The interaction energy curves at large internuclear separations have not yet been investigated systematically. One reason for the scarcity of data in this region is the need for an extremely small aperture and high resolution of the detecting apparatus to test the long-range behavior of the energy curves. Increasing interest in these problems, however, promise that such difficulties are about to be overcome. All the macroscopic measurements involving viscosity, index of refraction, and transport coefficient give only qualitative information around the Van der Waals minimum, a region where the charge distributions already overlap appreciably, and where the exchange forces make a considerable contribution to the interaction energy. From the theoretical point of view, this region is very difficult to investigate, and the approximation methods needed to perform a reasonable calculation very often obscure the basic concepts. The interaction energies at large separations, on the other hand, are mainly due to electrostatic interactions, and they can be calculated exactly.

The present method is designed to generalize previous approaches, thus enabling one to investigate the interactions between atoms in higher excited states and to determine the effects of spin-orbit coupling on the interaction energies.[1] This generalization is obtained by combining the theory of angular momentum with the formalism of irreducible tensors.

II. CLASSICAL ELECTROSTATIC INTERACTION ENERGY

The long-range interatomic forces are mainly governed by the electrostatic interaction between the charge distributions of the two atoms or molecules. Margenau[2] has calculated this interaction energy by expanding the potential between two sets of point charges in a Taylor series. The terms in this series correspond to different multipoles, the leading one being the dipole-dipole term. Margenau has expanded the electrostatic interaction energy up to the quadrupole-quadrupole term, and Heller[3] has extended this approach up to the sixteenth pole.

A different approach to this problem has recently been made by Rose[4] who expresses the complete interaction as a sum of coupling terms between the multipole moments by making use of the algebra of irreducible tensors.[5] We shall use his results since they can be very conveniently combined with the theory of angular momentum. The interaction energy is written as a double contraction of irreducible tensors to form the scalar V. Specifically:

$$V=\sum_{i,j}\sum_{a,\alpha}\sum_{b,\beta}\frac{16\pi^2 e_i\epsilon_j}{(2a+1)[(2b+1)!!]}\mathcal{Y}_a{}^{\alpha*}(\mathbf{r}_i)\mathcal{Y}_b{}^{\beta*}(\mathbf{r}_j)\times\mathcal{Y}_b{}^{\beta}(\nabla)\Upsilon_a{}^{\alpha}(\mathbf{R}).\quad(1)$$

The vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ originate at the centers of the two nonoverlapping charge distributions, and point to the charges e_i and ϵ_j, respectively. $\mathbf{R}$ extends from the center of charge distribution A (described by the $\mathbf{r}_i$) to the one in B (characterized by the $\mathbf{r}_j$). $\mathcal{Y}_a{}^{\alpha*}(\mathbf{r})$ is a

---

* Part of a dissertation presented to the faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

† Present address: Physics Department, The University of Chicago, Chicago, Illinois.

[1] The second paper of this series deals mainly with first-order interactions between atoms in excited states and the third one considers the effects of spin-orbit coupling.

[2] H. Margenau, Phys. Rev. **38**, 747 (1931); Revs. Modern Phys. **11**, 1 (1939).

[3] R. Heller, J. Chem. Phys. **9**, 156 (1941).

[4] M. E. Rose, J. Math. Phys. **37**, 215 (1958).

[5] B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. **46**, 626 (1950). R. J. Buehler and J. O. Hirschfelder, Phys. Rev. **83**, 628 (1951); **85**, 149 (1952).

regular solid spherical harmonic defined as

$$\mathcal{Y}_a^{\alpha*}(\mathbf{r}) = r^a Y_a^{\alpha*}(\mathbf{r}^{(1)}) = (-)^\alpha r^a Y_a^{-\alpha}(\mathbf{r}^{(1)}), \tag{2}$$

and $\Upsilon_a^\alpha(\mathbf{R})$ the irregular solid harmonic

$$\Upsilon_a^\alpha(\mathbf{R}) = R^{-a-1} Y_a^\alpha(\mathbf{R}^{(1)}). \tag{3}$$

$\mathbf{r}^{(1)}$ and $\mathbf{R}^{(1)}$ denote unit vectors in the direction of $\mathbf{r}$ and $\mathbf{R}$. The ∇ in (1) operates on $\mathbf{R}$.

It is seen that all the information about charge distribution A is contained in $\mathcal{Y}_a^{\alpha*}(\mathbf{r}_i)$, and similarly $\mathcal{Y}_b^{\beta*}(\mathbf{r}_j)$ contains all the knowledge about charge distribution B. The summation over α and β comes from the contraction of the irreducible tensors and corresponds physically to a coupling of the respective systems.

The $\mathbf{R}$ dependence in (1) can be rewritten in the following form:

$$\frac{\mathcal{Y}_b^\beta(\nabla)\Upsilon_a^\alpha(\mathbf{R})}{(2a+1)[(2b+1)!!]} = \frac{(-)^b}{(2a+1)(2b+1)} \times\left[\frac{(2a+1)(2b+1)(a+b-\alpha-\beta)!(a+b+\alpha+\beta)!}{4\pi(2a+2b+1)(a-\alpha)!(a+\alpha)!(b-\beta)!(b+\beta)!}\right]^{\frac{1}{2}} \times\Upsilon_{a+b}^{\alpha+\beta}(\mathbf{R}). \tag{4}$$

If the two coordinate systems with origins A and B are rotated so that their Z axes coincide with $\mathbf{R}$, then

$$\Upsilon_{a+b}^{\alpha+\beta}(\mathbf{k}R) = R^{-a-b-1}\left[\frac{2a+2b+1}{4\pi}\right]^{\frac{1}{2}} \delta_{\alpha,-\beta}. \tag{5}$$

By substituting (5) and (4) into (1), we can write the classical interaction energy between two nonoverlapping charge distributions as

$$V = \sum_{i,j} \sum_{a,b,\alpha} \frac{(-)^b 4\pi e_i \epsilon_j (a+b)!\delta_{\alpha,-\beta}}{R^{a+b+1}[(2a+1)(2b+1)(a-\alpha)!(a+\alpha)!(b-\alpha)!(b+\alpha)!]^{\frac{1}{2}}} \mathcal{Y}_a^{\alpha*}(\mathbf{r}_i)\mathcal{Y}_b^{\beta*}(\mathbf{r}_j). \tag{6}$$

The phase factor $(-)^b$ which seems to destroy the symmetry of the result with respect to systems A and B arises from the direction of $\mathbf{R}$. This phase factor will play an important role in the evaluation of resonance matrix elements between two identical atoms. It will be shown later that the delta condition in (6) quantizes the total angular momentum of the system along the internuclear axis. As a consequence of this, all first-order secular determinants are factorized into subdeterminants which are distinguished by different molecular designations.

III. DISPERSION ENERGIES BETWEEN ALKALIS AND NOBLE GAS ATOMS

The forces arising from the mutual polarization of the two atoms are usually calculated by perturbation theory. For atoms in nondegenerate S states, the first order perturbation vanishes, and at large internuclear separations, the interaction is governed by the first term of the second order formula. The second order, as well as all higher order perturbation approximations, give results which can be expressed as an infinite series in R^{-1}. This series, however, diverges for all R and many attempts have been made to remove the divergence.

Brooks[6] has pointed out that Margenau's series expansion is an asymptotic one and that the divergence arises from the integration over portions of configuration space in which the expansion of the electrostatic energy is not valid. He obtains convergent results by arbitrarily limiting the range of integration in the matrix elements. In the case of the hydrogen molecule ion, there still remains a substantial disagreement, however, between the corrected perturbation calculation and the exact results of Hylleraas.[7] Roe[8] attributes this difference to the neglect of the exchange forces in Brooks' calculation. Starting from the calculation of Roe who did not expand the electrostatic interaction energy in a Taylor series, Dalgarno and Lewis[9] have shown that the divergence of the results is not due to the use of the interaction energy in regions of space where it is not valid. They claim that the divergence is a fundamental property of such series.

Despite these remarks the expansion of V in a power series of R^{-1} is a very convenient one, and we shall show that some truncation methods will give reliable results.

In the following derivations, we shall not include the correction factors due to retardation effects,[10] nor the adiabatic coupling between electronic and nuclear motion. It has been shown[11] that the nuclear-electronic coupling is negligible for atoms in nondegenerate S states.

A. Dispersion Energy between Two Noble Gas Atoms

We assume that the eigenvalue problem

$$\{\mathcal{H}_o - E_o\}\psi_o = 0,$$

has been solved and that a true perturbation V is applied on the system. The first-order perturbation formula requires only the knowledge of the unperturbed state function, whereas all higher order equations

---

[6] F. C. Brooks, Phys. Rev. **86**, 92 (1952).

[7] E. A. Hylleraas, Z. Physik **71**, 739 (1931).

[8] G. M. Roe, Phys. Rev. **88**, 659 (1952).

[9] A. Dalgarno and J. T. Lewis, Proc. Phys. Soc. (London) **A69**, 57 (1956).

[10] H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948).

[11] T. Y. Wu and A. B. Bhatia, J. Chem. Phys. **24**, 48 (1956). T. Y. Wu, *ibid.* **24**, 444 (1956). A. Dalgarno and R. McCarroll, Proc. Roy. Soc. (London) **A237**, 383 (1956); **239**, 413 (1957).

involve summation over the discrete spectrum, as well as an integration over the continuum.

Since only a small number of atomic wave functions are known, it is assumed at this point that the state functions can be represented by three-dimensional harmonic oscillators with a single frequency. This means that all excited states have an energy equal to the ionization energy of the noble gas atom. Thus atom 1 is characterized by one-electron state functions $\psi_{n_1l_1m_1}(\mathbf{r}_i)$ with frequency ν_1 and likewise atom 2 by $\psi_{n_2l_2m_2}(\mathbf{r}_i)$ with frequency ν_2.

The normalized state function of the harmonic oscillator in spherical polar coordinates is[12]

$$\psi_{nlm}(\mathbf{r})=\left[2\gamma^{\frac{3}{2}}\frac{\Gamma(\frac{1}{2}n-\frac{1}{2}l-\frac{1}{2})}{[\Gamma(\frac{1}{2}n+\frac{1}{2}l+1)]^3}\right]^{\frac{1}{2}}(\gamma r^2)^{\frac{1}{2}l}\exp(-\tfrac{1}{2}\gamma r^2)$$
$$\times L_{\frac{1}{2}n-\frac{1}{2}l-\frac{1}{2}}{}^{l+\frac{1}{2}}(\gamma r^2)Y_l{}^m(\theta,\varphi),\quad(7)$$

where the Laguerre polynomial $L_a{}^b(z)$ is defined by[13]

$$L_a{}^b(z)=\frac{[\Gamma(a+b+1)]^2}{\Gamma(a+1)\Gamma(b+1)}\,{}_1F_1(-a;b+1;z),\quad(8)$$

${}_1F_1(-a;b+1;z)$ being the Kummer confluent hypergeometric series.[14,15]

$${}_1F_1(\alpha;\beta;z)=\sum_{\lambda=0}\frac{\Gamma(\alpha+\lambda)\Gamma(\beta)}{\Gamma(\alpha)\Gamma(\beta+\lambda)\Gamma(1+\lambda)}z^\lambda.\quad(9)$$

The argument γ in (7) is related to the oscillator strength f and polarizability α of the noble gas atom,[16]

$$\gamma=fe^2/\alpha h\nu.\quad(10)$$

The first-order contribution to the interaction energy is zero since the electrostatic perturbation V does not connect S states. The first nonvanishing terms come from the second-order formula,

$$E^{(2)}=\sum_{p'}{}'\frac{|(o|V|p')|^2}{E_o-E_{p'}}.\quad(11)$$

It is not necessary to antisymmetrize the state functions in (11) since the formula for V is only valid for nonoverlapping charge distributions.

The interaction energy is first computed by using product state functions of one-electron state functions. The contributions of all the other electrons are then added up to give the final result.

Using (1) we can rewrite (11) as

$$\sum_{p'}{}'\left[\sum_{a,b}\sum_{\alpha,\beta}\frac{16\pi^2e^2}{(2a+1)[(2b+1)!!]}\mathcal{Y}_b{}^\beta(\nabla)\Upsilon_a{}^\alpha(\mathbf{R})\right.$$
$$\left.\times(o|\mathcal{Y}_a{}^{\alpha*}(\mathbf{r}_1)\mathcal{Y}_b{}^{\beta*}(\mathbf{r}_2)|p')\right]^2\frac{1}{E_o-E_{p'}}.\quad(12)$$

Since $\mathcal{Y}_a{}^{\alpha*}(\mathbf{r}_1)$ depends only on atom 1 and $\mathcal{Y}_b{}^{\beta*}(\mathbf{r}_2)$ only on atom 2, (12) can be factored:

$$\sum_{p'}{}'\frac{|(o|V|p')|^2}{E_o-E_{p'}}$$
$$=\sum_{p'}{}'\left[\sum_{a,b}\sum_{\alpha,\beta}\frac{16\pi^2e^2}{(2a+1)[(2b+1)!!]}\mathcal{Y}_b{}^\beta(\nabla)\Upsilon_a{}^\alpha(\mathbf{R})\right.$$
$$\times(n_1l_1m_1|\mathcal{Y}_a{}^{\alpha*}(\mathbf{r}_1)|n_1'l_1'm_1')$$
$$\left.\times(n_2l_2m_2|\mathcal{Y}_b{}^{\beta*}(\mathbf{r}_2)|n_2'l_2'm_2')\right].\quad(13)$$

The matrix elements on the right of (13) are evaluated as follows:

$$(nlm|\mathcal{Y}_a{}^{\alpha*}(\mathbf{r})|n'l'm')$$
$$=(-)^\alpha(nl|r^a|n'l')(lm|Y_a{}^{-\alpha}(\theta,\varphi)|l'm'),\quad(14)$$

where $(nl|r^a|n'l')$ is the radial matrix element of the 2^a-pole interaction. The matrix element involving angles can be readily evaluated by using the Clebsch-Gordan series and introducing the Clebsch-Gordan or Wigner coefficients C.[17,18]

$$(lm|Y_a{}^{-\alpha}(\theta,\varphi)|l'm')$$
$$=\left[\frac{(2l'+1)(2a+1)}{4\pi(2l+1)}\right]^{\frac{1}{2}}C(l'al;m',-\alpha,m)C(l'al;000)$$
$$=\left[\frac{(2l+1)(2a+1)}{4\pi(2l'+1)}\right]^{\frac{1}{2}}C(lal';m,\alpha,m')C(lal';000)(-)^\alpha$$
$$=(-)^\alpha(l'm'|Y_a{}^\alpha(\theta,\varphi)|lm).\quad(15)$$

It should be noted that $C(l'al;m',-\alpha,m)$ is zero unless the conditions $m'=m+\alpha$ and $l'=l+a,\ l+a-l\cdots|l-a|$ are satisfied. Furthermore $C(l'al;000)$ is zero unless $l'+a+l$ is even. This means that for given l' and l only even *or* odd multipoles can give nonvanishing matrix elements.

The integration over the Laguerre polynomials yields

---

[12] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 1663.

[13] The normalization factor in the square bracket of (8) depends, of course, on the definition of the Laguerre polynomials. There has been considerable confusion in the use of these functions, and a number of different definitions can be found in the literature. The definition of $L_a{}^b(z)$ in reference 12 differs from the ones in the references 14 and 15 by a factor of $\Gamma(a+b+1)$. Equation (8) will be used throughout this paper.

[14] H. Buchholz, *Die Konfluente Hypergeometrische Funktion* (Springer-Verlag, Berlin, 1953), p. 4, 135.

[15] A. Erdélyi, W. Magnus, F. Oberhettinger, and G. F. Tricomi, *Higher Transcendental Functions*, Bateman Manuscript Project, (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 1, p. 248.

[16] H. Margenau, J. Chem. Phys. **6**, 896 (1938).

[17] E. P. Wigner, *Group Theory* (Academic Press, Inc., New York, 1959), p. 189.

[18] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 62.

for the radial part of the matrix element:

$$(10|r^a|n'l')=\left[\frac{(2a+1)!!}{(2\gamma)^a}\right]^{\frac{1}{2}}\delta_{n'-1,a}\delta_{n'-1,l}. \qquad (16)$$

Combining (16) and (15), and making use of the delta conditions of (16) in the evaluation of the C coefficients, we can rewrite (13) as

$$\sum_{p'}{}' \frac{|(o|V|p')|^2}{E_o-E_{p'}}$$

$$=\sum_{a,b}\sum_{\alpha,\beta}\frac{(2a+1)!!(2b+1)!!}{(2\gamma_1)^a(2\gamma_2)^b}$$

$$\times\left[\frac{(-)^{\alpha+\beta}4\pi e^2}{(2a+1)[(2b+1)!!]}\mathcal{Y}_b{}^\beta(\nabla)\Upsilon_a{}^\alpha(\mathbf{R})\right]^2\frac{1}{E_o-E_{p'}}. \qquad (17)$$

The reason for taking the summation over the different multipoles outside the square bracket is the following: The dipole-dipole term of V connects only doubly excited states with the ground state of the system; the dipole-quadrupole only triply excited states, etc., and thus no cross terms appear in the end result.

Finally, summing up all the contributions of the other electrons, we find for the dispersion energy between two noble gas atoms

$$E^{(2)}=-\sum_{a,b=1}^{\infty}\sum_{\alpha,\beta}\frac{f_1f_2(2a+1)!!(2b+1)!!}{(2\gamma_1)^a(2\gamma_2)^b}$$

$$\times\left[\frac{(-)^{\alpha+\beta}4\pi e^2}{(2a+1)[(2b+1)!!]}\mathcal{Y}_b{}^\beta(\nabla)\Upsilon_a{}^\alpha(\mathbf{R})\right]^2$$

$$\times\frac{1}{ah\nu_1+bh\nu_2}, \qquad (18)$$

where we have set

$$E_o-E_{p'}=\tfrac{3}{2}h\nu_1+\tfrac{3}{2}h\nu_2-h\nu_1(n_1{}'+\tfrac{3}{2})-h\nu_2(n_2{}'+\tfrac{3}{2})$$
$$=-[ah\nu_1+bh\nu_2].$$

So far we have not restricted ourselves to any special direction of $\mathbf{R}$. For the evaluation of (18), however, it is more convenient to have $\mathbf{R}$ along the positive Z axis of the aligned coordinate systems. Substituting (4) and (5) into (18) yields

$$E^{(2)}=-\sum_{a,b=1}^{\infty}\sum_{\alpha}\frac{f_1f_2e^4(2a-1)!!(2b-1)!!(a+b)!(a+b)!}{R^{2a+2b+2}(2\gamma_1)^a(2\gamma_2)^b(a-\alpha)!(a+\alpha)!(b-\alpha)!(b+\alpha)!}\frac{1}{ah\nu_1+bh\nu_2}. \qquad (19)$$

Specific evaluation of (19) gives for the first six terms

$$E^{(2)}=-\frac{\frac{3}{2}e^4f_1f_2}{(h\nu_1+h\nu_2)\gamma_1\gamma_2R^6}-\frac{(45/8)e^4f_1f_2}{(h\nu_1+2h\nu_2)\gamma_1\gamma_2{}^2R^8}$$
$$-\frac{(45/8)e^4f_1f_2}{(2h\nu_1+h\nu_2)\gamma_1{}^2\gamma_2R^8}-\frac{(315/8)e^4f_1f_2}{(2h\nu_1+2h\nu_2)\gamma_1{}^2\gamma_2{}^2R^{10}}$$
$$-\frac{(210/8)e^4f_1f_2}{(h\nu_1+3h\nu_2)\gamma_1\gamma_2{}^3R^{10}}$$
$$-\frac{(210/8)e^4f_1f_2}{(3h\nu_1+h\nu_2)\gamma_1{}^3\gamma_2R^{10}}-\cdots. \qquad (20)$$

The terms correspond, respectively, to dipole-dipole, dipole-quadrupole, quadrupole-dipole, quadrupole-quadrupole, dipole-octupole, and octupole-dipole interaction.[19]

Margenau[16] has evaluated a similar expression for two identical noble gas atoms. If we set in (20), $\nu_1=\nu_2=\nu$, and $\gamma_1=\gamma_2=\gamma$, then

$$E^{(2)}=-\frac{\frac{3}{2}e^4f^2}{2h\nu\gamma^2R^6}-\frac{(45/4)e^4f^2}{3h\nu\gamma^3R^8}-\frac{(735/8)e^4f^2}{4h\nu\gamma^4R^{10}}-\cdots, \qquad (21)$$

which agrees with the expression given by Margenau up to quadrupole-quadrupole contributions. In the last term of (21) we have included the dipole-octupole and octupole-dipole interactions since they also vary as R^{-10}. These additional terms make it desirable to augment the table in reference 2, which has often been considered to contain all terms up to R^{-10}. To conform with Margenau's notation, we write $E^{(2)}=C_1R^{-6}+C_2R^{-8}+C_3R^{-10}$. The coefficient C_3 now includes the dipole-octupole, as well as the quadrupole-quadrupole contributions. In Table I we have also included for completeness the coefficients for the dispersion energies between alkali atoms.

B. Dispersion Energy between Two Alkali Atoms

The simple harmonic oscillator model is not very useful for atoms with incomplete outer shells, since the requirements that all electrons oscillate with the same frequency is then very unrealistic. We, therefore, change the previous approach by using hydrogenic functions instead of oscillator functions. The central potential is modified by introducing different screening parameters for different orbitals. The effective nuclear charge Z^* which accounts for the screening by the inner shells is determined by comparing the theoretical expression for the energy with the experimental value.

The method for obtaining the dispersion energy is analogous to the one described in Sec. A. However, in this case one has to sum over all excited states of both atoms and it turns out that the partial sums converge

---

[19] The first four terms of (20) agree with the ones given by J. F. Hornig and J. O. Hirschfelder, J. Chem. Phys. **20**, 1812 (1952), except for their dipole-quadrupole term which should read $(45/8)h^2\alpha_a\alpha^2{}_b\nu_a\nu_b{}^2/[e^2R^8(\nu_a+2\nu_b)]$.

TABLE I. Interaction constants of dispersion energies between similar ground-state atoms and molecules.

	$h\nu$ (ev)	$\alpha\times10^{24}$ (cm³)	f	$-C_1\times10^{60}$ (erg−cm⁶)	$-C_2\times10^{76}$ (erg−cm⁸)	$-C_3\times10^{92}$ (erg−cm¹⁰)
He	24.5	0.207[a]	1.1	1.26	2.02	3.96
Ne	25.7	0.39	2.37	4.70	6.90	12.4
A	17.5	1.63	4.58	55.9	121	320
Kr	14.7	2.46	4.90	107	274	860
Xe	12.2	4.0	5.61	236	708	2622
H_2	∼14.5	0.81	∼1.5	11.4	31.1	104
N_2	15.8	1.74	4.61	57.5	119	302
O_2	13.6	1.57	3.11	40.3	96.0	280
CO_2	15.5	2.86	5.70	152	411	1361
CH_4	14.1	2.58	4.60	113	310	1044
NH_3	11.7	2.24	2.72	71	236	967
Cl_2	12.7	4.60	6.55	323	1000	3795
HCl	13.4	2.63	4.25	111	321	1131
HBr	12.1	3.58	4.71	186	595	2329
HI	10.5	5.4	5.30	368	1367	6221
Li	1.85	15[b]	∼0.75[c]	500	6430	101 200
Na	2.10	18[b]	0.975[d]	817	11 000	181 500
K	1.61	29[b]	0.987[d]	1630	26 700	537 800
Rb	1.57	29[b]	0.996[d]	1590	25 200	489 800
Cs	1.41	36[b]	∼0.98	2200	39 500	870 200

[a] L. Essen, Proc. Phys. Soc. (London) **B66**, 189 (1953).
[b] G. E. Chamberlain and J. C. Zorn, Bull. Am. Phys. Soc. **5**, 241 (1960).
[c] G. Stephenson, Nature **167**, 156 (1951).
[d] G. Stephenson, Proc. Phys. Soc. (London) **A64**, 458 (1951).

rather slowly to the correct value. This indicates that the continuous spectra of the two atoms contribute appreciably to the dispersion energy. It is possible to eliminate this sum by using an approximate second-order formula. The first-order matrix element $(0|V|0)$ is zero and the lowest order nonvanishing terms are given by

$$E^{(2)}=(o|V^2|o)/\epsilon_2, \tag{22}$$

where o stands for $n_1l_1m_1$, $n_2l_2m_2$, the quantum numbers of the ground-state system, ϵ_2 is an appropriate average energy, and

$$V^2=(16\pi^2e^2)^2\Bigg[\sum_{a,b}\sum_{\alpha,\beta}\frac{1}{(2a+1)[(2b+1)!!]}\mathcal{Y}_a^{\alpha*}(\mathbf{r}_1)\mathcal{Y}_b^{\beta*}(\mathbf{r}_2)\times\mathcal{Y}_b^{\beta}(\nabla)\Upsilon_a^{\alpha}(\mathbf{R})\Bigg]\Bigg[\sum_{c,d,\gamma,\delta}\frac{1}{(2c+1)[(2d+1)!!]}\times\mathcal{Y}_c^{\gamma*}(\mathbf{r}_1)\mathcal{Y}_d^{\delta*}(\mathbf{r}_2)\mathcal{Y}_d^{\delta}(\nabla)\Upsilon_c^{\gamma}(\mathbf{R})\Bigg]. \tag{23}$$

Substitution of (23) into (22) yields

$$\frac{(o|V^2|o)}{\epsilon_2}=\frac{(16\pi^2e^2)^2}{\epsilon_2}\times\sum_{a,b,\alpha,\beta}\sum_{c,d,\gamma,\delta}\frac{\mathcal{Y}_b^{\beta}(\nabla)\Upsilon_a^{\alpha}(\mathbf{R})\mathcal{Y}_d^{\delta}(\nabla)\Upsilon_c^{\gamma}(\mathbf{R})}{(2a+1)[(2b+1)!!](2c+1)[(2d+1)!!]}\times(n_1l_1|r^{a+c}|n_1l_1)(n_2l_2|r^{b+d}|n_2l_2)(l_1m_1|Y_a^{\alpha*}Y_c^{\gamma*}|l_1m_1)\times(l_2m_2|Y_b^{\beta*}Y_d^{\delta*}|l_2m_2). \tag{24}$$

The factors of the matrix elements in (24) which involve angles can be calculated by using the coupling rule for spherical harmonics:

$$Y_a^{\alpha*}Y_c^{\gamma*}\doteq(-)^{\alpha+\gamma}\sum_{k_1}\left[\frac{(2a+1)(2c+1)}{4\pi(2k_1+1)}\right]^{\frac{1}{2}}\times C(ack_1;-\alpha,-\gamma)C(ack_1;00)Y_{k_1}^{-\alpha-\gamma}. \tag{25}$$

Thus

$$(l_1m_1|Y_a^{\alpha*}Y_c^{\gamma*}|l_1m_1)=(-)^{\alpha+\gamma}\sum_{k_1}\frac{1}{4\pi}[(2a+1)(2c+1)]^{\frac{1}{2}}\times C(ack_1;-\alpha,-\gamma)C(ack_1;00)\times C(l_1k_1l_1;m_1,-\alpha-\gamma)C(l_1k_1l_1;00). \tag{26}$$

Since in our case $l_1=m_1=0$, the sum rule and Δ condition of the C coefficients require that $-\alpha-\gamma=0$, $k_1=0$, and $a=c$. These conditions simplify (26) appreciably. By using the explicit expression for the C coefficients, we get

$$(00|Y_a^{\alpha*}Y_c^{\gamma*}|00)=\frac{(-)^{\alpha}}{4\pi}\delta_{a,c}\delta_{\alpha,-\gamma}. \tag{27}$$

A similar equation holds for the second matrix element.

So far we did not need to know the exact form of the atomic functions. In spherical polar coordinates we have for the normalized hydrogenic state function

$$\psi_{nlm}(\mathbf{r})=\left[\gamma^3\frac{\Gamma(n-l)}{2n[\Gamma(n+l+1)]^3}\right]^{\frac{1}{2}}\times(\gamma r)^le^{-\frac{1}{2}\gamma r}L_{n-l-1}^{2l+1}(\gamma r)Y_l^m(\theta,\varphi),$$

$$n=1,2,\cdots l=n-1,n-2,\quad -l\leq m\leq l, \tag{28}$$

where γ stands for $2me^2Z^*/\hbar^2n$.

With (28) the evaluation of the radial matrix element in (24) gives

$$(10|r^{2a}|10)=\frac{(2a+2)!}{2(2Z_1^*/a_o)^{2a}}, \qquad (29)$$

where a_o is the Bohr radius.

As in Sec. A, it is more convenient to let the internuclear distance **R** coincide with the Z axis. Furthermore, the final result takes on a particularly simple form if atomic units are used. Substitution of (4), (5), (27), and (29) into (24) yields for the dispersion energy between two alkali atoms in their ground states[20]

$$E^{(2)}=-\sum_{a,b,\alpha}\frac{2(a+b)!(2a+2)!(2b+2)!}{(2R)^{2a+2b+2}(2a+1)(2b+1)(a-\alpha)!(a+\alpha)!(b-\alpha)!(b+\alpha)!}\,\frac{1}{(Z_1^*)^{2a}(Z_2^*)^{2b}[Z_1^{*2}+Z_2^{*2}]}. \qquad (30)$$

If in (30) we let $Z_1^*=Z_2^*=1$, then we get for the dispersion energy between two hydrogen atoms

$$E^{(2)}=-\frac{6}{R^6}-\frac{135}{R^8}-\frac{3937.5}{R^{10}}-\cdots. \quad \text{(a.u.)} \qquad (31a)$$

The last term in (31) includes dipole-octupole, as well as quadrupole-quadrupole terms.[21] Comparison with other results again shows that the sum of the coefficients of the dipole-octupole and octupole-dipole contributions is larger than the quadrupole-quadrupole term.[22]

Hirschfelder and Linnett[23] have shown that for $R>3a_o$ the effective nuclear charges are slightly less than one. Setting $Z_1^*=Z_2^*=0.99$, Eq. (30) yields

$$E^{(2)}=-\frac{6.4}{R^6}-\frac{146}{R^8}-\frac{4350}{R^{10}}-\cdots, \quad \text{(a.u.)} \qquad (31b)$$

which compares favorably with the variational calculation of Hirschfelder and Löwdin.[24]

TABLE II. Comparison of theoretical and experimental values for alkali polarizabilities.

	α theoretical (cm^3)	α experimental (cm^3)
Li	$(21\pm3)\times10^{-24}$	$(15\pm2.7)\times10^{-24}$
Na	$(16.5\pm2.5)\times10^{-24}$	$(18\pm3.2)\times10^{-24}$
K	$(28\pm4)\times10^{-24}$	$(29\pm5.2)\times10^{-24}$
Rb	$(29\pm4)\times10^{-24}$	$(29\pm5.2)\times10^{-24}$
Cs	$(36\pm5)\times10^{-24}$	$(36\pm6.5)\times10^{-24}$

Some care has to be taken in the use of (30). As already mentioned, this series diverges for all R's, and one has to find means to cut the series off so that the inclusion of the last result still improves the result. Dalgarno and Lewis[21] have outlined a truncation method which is quite useful.

Furthermore, a more precise calculation must also take into account the contributions of the higher order perturbations. For instance the third-order perturbation introduces terms of odd power of R^{-1}, the lowest one being R^{-11}.

The usefulness of (30) depends also on the accuracy with which the effective nuclear charges Z^* can be determined. The comparison of the theoretical expression for the energy with the corresponding experimental value has already been mentioned. Another method is the use of experimentally determined polarizabilities α. Recently Chamberlain and Zorn[25] measured α for all the alkalis by molecular beam methods.

An approximate calculation based on hydrogen-like state functions and effective nuclear charges determined from optical spectra compares with the experimental values as shown in Table II.[26] The agreement is gratifying.

One can show by using methods which will be more fully described in the third paper, that the inclusion of spin does not alter the final result for the interaction energy between two alkali atoms in their ground states.

---

[20] P. Fontana, Bull. Am. Phys. Soc. 4, 318 (1959).

[21] A. Dalgarno and J. T. Lewis, Proc. Phys. Soc. (London) **A69**, 57 (1956).

[22] L. Pauling and J. Y. Beach, Phys. Rev. **47**, 686 (1935).

[23] J. O. Hirschfelder and J. W. Linnett, J. Chem. Phys. **18**, 130 (1950).

[24] J. O. Hirschfelder and P. O. Löwdin, Molecular Phys. **2**, 229 (1959).

[25] G. E. Chamberlain and J. C. Zorn, Bull. Am. Phys. Soc. **5**, 241 (1960).

[26] J. C. Zorn and P. R. Fontana, Bull. Am. Phys. Soc. **5**, 242 (1960).