SUMMARY

Symposium on MOLECULAR PHYSICS

Kanaya Hotel, Nikko
11—12 Sept. 1953

Held on the Occasion of
The International Conference on
Theoretical Physics
Kyoto-Tokyo, September, 1953

PROGRAMME

Friday, September 11, 1953

at 2.00 p.m.

ELECTRONIC STRUCTURE OF SIMPLE MOLECULES

Discussion Chairman:	R. S. Mulliken	
Co-Chairman:	M. Kotani	
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at 3.40 p.m.

tea

at 4.00 p.m.

π -ELECTRON SYSTEMS

Discussion Chairman:	J. C. Slater	
Co-Chairman:	I. Oshida	
B1. C. A. Coulson	Introductory Lecture	
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at 6.00 p.m.

dinner

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at 8.00 p.m.

INTERMOLECULAR INTERACTIC

at 9.40 p.m.

Saturday, September 12, 1953

at 9.00 a.m.

MOLECULAR COLLISIONS

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at 10.30 a.m.

MICROWAVE STUDY OF MOLECULES

at 0.20 p.m.

A1.

Work on Molecular Theory in the Solid-State and

Molecular Theory Group, M.I.T.

J. C. Slater

(Massachusetts Institute of Technology)

The primary interest of the M.I.T. group is solid-state theory, and the molecular problems which we have undertaken have been with the object of clarifying certain problems in the theory of solids. The first one of these was the work of Meckler on O_2, the only one of the problems which has yet been completed. We knew that a simple molecular orbital theory indicated that the energy of the triplet state should lie below that of the singlet state, but would indicate an energy difference between the two states which got greater with increasing internuclear distance, staying finite at infinite distance, a clearly wrong result. This situation was like that in the theory of ferromagnetism, where the energy hand theory indicates that the energy difference between ferromagnetic and non-ferromagnetic states should persist to infinite distances. It seemed to me that the case of O_2 was the simplest example of the same situation, and that a calculation which would indicate how to get around the problem for O_2 would point the way to the same thing for the case of ferromagnetism. It was clear that what was needed was a configuration interaction, just as a configuration interaction is necessary in the case of H_2 to get a correct solution at infinite internuclear distance, provided we start with molecular orbitals.

Meckler carried out such a configuration interaction, including enough configurations so that he could correctly describe the state of two separated atoms in their ground states. This involved using nine configurations for the triplet state, twelve for the singlet. He solved the resulting secular equation at a number of internuclear distances, and found in fact that his singlet and triplet states came together at infinite distance. He further found that the dissociation energy, internuclear distance, and vibration frequency which he computed were in surprisingly good agreement with experiment. The energy level curves showed one very interesting feature: They showed a maximum at intermediate nuclear distances, the energy at these distances being higher than at infinity, or at the equilibrium distance. There does not seem to be any experimental evidence for or against this situation.

These results were encouraging enough so that we have looked for additional problems where a calculation of configuration interaction might throw light on wider problems than the structure of a single molecule. In any molecular orbital or energy band calculation, a single determinantal function for the ground state gives quite improper behavior at infinite internuclear separation, for it does not take proper account of correlation, the tendency of electrons of opposite spin to stay apart from each other on account of electrostatic repulsion, the effect which keeps atoms in their ground states at infinite internuclear distance. Clearly a configuration interaction, which corrects this situation, must be carried out if we wish to get good results at large internuclear distance. Meckler's work on oxygen indicates that at least in that case, though the ground state at the equilibrium distance consists of about 92 percent of one molecular orbital state, nevertheless the mixture of the other states, or the configuration interaction, has a large effect on the energy. We may expect, then, that it is rather necessary to carry out a configuration interaction even at the equilibrium distance, in order to get good results.

Accordingly we have studied the magnitude of the problem of carrying out configuration interactions. What we find is that the number of interacting configurations rapidly becomes enormous, as the complication of the molecule increases. For instance, we have studies methane, setting up all configurations in which the electrons are distributed between the 2s, 2p states of carbon (the ls states are assumed always occupied), and the ls states of the hydrogen, in all possible combinations of ionized and non-ionized states. The number of such states is enormous. We have eight spin-orbital functions on the carbon, eight on the hydrogen, or 16 in all, to which we are to assign eight electrons. We can do this in 16!/(8!) 12,870 different ways. Out of these, we can show that 104 have the symmetry required for the ground state. We

should, then, have to solve a 104 x 104 secular equation to do a job on methane comparable with what Meckler has done on oxygen. This, with present numerical methods, is too formidable a task to undertake. And yet we really should solve such problems, not only for our interest in molecules, but in crystals. Methane is the simplest example of the tetrahedral binding which occurs in diamond, silicon, and germanium. All existing studies of these important crystals are made on the basis of the energy band method, which is the analog in crystal theory of the molecular orbital method without configuration interaction. It is very important to know how good the result is, and what is the nature of the modification of the results produced by configuration interaction.

At this point, we began to look around to see whether there was not some way to reduce the order of the secular equation required for configuration interaction; in order words, can we not conclude in advance that certain interacting configurations are less important than others? We may give an example of the sort of simplification which might plausibly be expected. In methane, we may set the problem up in terms of directed orbitals, and interms of bonding and antibonding combinations of the carbon and hydrogen orbitals. These are essentially the equivalent orbitals of Lennard-Jones and his collaborators; We have four bonding orbitals of each spin, four antibonding. The lowest configuration comes if all eight electrons are located in the bonding orbitals, just filling them. Now if we consider just one bond, with two electrons in it, we have relatively few configurations: a singlet where both electrons are in the bonding orbital, a singlet and a triplet if one is in the bonding, one in the antibonding orbital, a singlet when both are in the antibonding orbital. The configuration interaction required to describe the bond correctly in the limit of infinite internuclear distance is the 3 x 3 secular problem between the three singlets (in the case of a symmetrical bond between like atoms, this factors to a 2 x 2 and a 1 x 1 problem, for the case where one electron is bonding, one antibonding, does not combine with the others). In a case like methane, with several bonds, we could set up just those configurations which had two electrons in each bond, but arranged in all these possible ways. This is a good deal less than the total number of configurations, for that includes cases where individual bonds contain all the way from zero to four electrons. In methane, for instance, there are 22 out of the 104 configurations leading to the ground state which have this character. By combination of these 22 states, we can get a wave function which goes to states of the neutral atoms at infinite separation, though it will not go to the ground state of carbon, but rather to that state of the $2s2p^3$ configuration known as the valence state. We may hope that a combination of these 22 configurations will be a good deal more accurate at small internuclear distances than a singlet configuration would be.

We can hardly accept this reduction of the configuration interaction problem, without testing its correctness by direct calculation. There have been altogether too many cases in the literature where terms were neglected on the basis of intuition, without calculation, and when later it was found that the neglected terms are really large. If we could solve the complete 104 x 104 problem for methane, then the reduced 22 x 22 problem, and show that the lowest states so derived were essentially equivalent, then we should have verified the method, at least in this case. But this is too hard to do. Therefore we have looked for even simpler problems where we might be able to carry through the calculations, and we have hit one the H_2O molecule as the most likely one for the purpose. In H_2O, we can do a configuration interaction, somewhat similar to the complete methane interaction, with only 18 configurations. Out of these, 12 correspond to configurations with just two electrons in each bond. These are numbers which we can manage. Accordingly Drs. Koster and Schweinler are carrying out the calculation of a configuration interaction between these 18 states of water. When this is done, they will set up the simplified case of the 12 configurations, and see how well this represents the function. We shall also be in position to make other sorts of checks of our wave function, since we shall have presumably a pretty good wave function involving two separate covalent bonds. The real question under consideration is, how much do the electrons in the two bonds affect each other? And water is the simplest molecule having two such bonds.

There is one important question which comes up in connection with simplified configuration interaction problems of this sort. If we carry out a complete configuration interaction, as Meckler did for O_2, it does not make any difference whether the one-electron orbitals from which we construct our determinantal function are correct mole-

cular orbitals or not; that is, whether they are solutions of a one-electron self-oncsistent Schrödinger problem or not. As the extent of our configuration interaction is reduced, it becomes important to have good molecular orbitals, until finally in the limit where we use only a single configuration, the success of the method depends entirely on having good molecular orbitals. We are thus led to the need of solving a self-consistent LCAO problem, such as has been outlined by Roothaan, or possibly with a simplified method of handling the exchange. This is a very diffuclt problem, which has been carried out, aside from diatomic molecules, in only a very few cases. Mulligan's calculation of CO_2 is probably the best example. We are therefore facing the problem of finding molecular orbitals in more complicated cases, and Dr. Meckler and Dr. Kaplan are working on this problem. There are two aspects of such a calculation. One is the evaluation of certain integrals, including three-center integrals. Koster and Schweinler are facing this problem, and solving it straightforwardly, in the case of the H_2O calculation, and Meckler and Kaplan are taking advantage of this work. The calculations are being made essentially by the method of Bernett and Coulson. The other part of the problem is that of making the solution self-consistent: that is, finding the coefficients in the linear combinations of atomic orbitals which best represent molecular orbitals in a self-consistent field. Formally, the problem can be solved by the method set up by Roothaan, by using successive approximations: but this calculation is so tedious that it has rarely been carried through, except in a few cases such as Mulligan's CO_2. Meckler has now approached the problem of mechanizing the problem of self-consistency. He has been able to set up a program for the Whirlwind digital computer, which will carry through a stage of this calculation as a single operation, so that we can feed in an initial estimate of the values of these coefficients, come out at the end with final values. Some judgment must then be exercised, in deciding the best initial conditions to use for the next step of the calculation: but we hope in this way to get a usable method applicable to more complicated molecules than have been attempted so far. The molecule on which Meckler and Kaplan are working is ammonia.

There are a number of other molecular problems now under way in the group, but the ones which have been described are enough to indicate the general scope and aim of the investigations. We have been interested, not so much in investigating molecules of chemical interest, as in studying those whose method of calculation leads to increased understanding of the application of quantum mechanics to problems of molecular structure. We feel that quantum chemistry has still not advanced far enough so that we even know what are the best approximate methods to use for molecules, and can estimate their accuracy. We are trying by well-chosen examples to learn as much as we can about these methods.

A2.

Researches on Electronic Structures of Some Simple Molecules

Eiichi Ishiguro

(Department of Physics, Ochanomizu University)

1. Introduction.

Researches on the electronic structures of some simple molecules, now in progress in this country, will be reported below.

2. The scheme of the calculations relating to the Li_2 and O_2 molecules.

M. Kotani, E. Ishiguro, T. Arai, K. Takayanagi, Y. Mizuno and K. Kayama are now investigating the electronic structures of the Li_2 and O_2 molecules by the LCAO-MO and Heitler-London methods, in which the interactions of all electrons are explicitly considered.

(1) They chose the following forms of the AO's for the basis of their calculations:

$$(1s) = (\xi^3/\pi)^{\frac{1}{2}}\exp(-\xi r),$$

$$(2s) = (\zeta'^5/3\pi)^{\frac{1}{2}}\exp(-\zeta' r),$$

$$(2p\sigma) = (\zeta'^5/\pi)^{\frac{1}{2}}\, r\cos\vartheta\, \exp(-\zeta' r),$$

$$(2p\pi) = (\zeta'^5/\pi)^{\frac{1}{2}}\, r\sin\vartheta\cos\varphi\, \exp(-\zeta' r),$$

$$(2p\pi') = (\zeta'^5/\pi)^{\frac{1}{2}}\, r\sin\vartheta\sin\varphi\, \exp(-\zeta' r).$$

(2) All the molecular integrals occurring in the calculations are calculated rigorously for several sets of parameters $\alpha = \xi R$ and $\beta = \zeta' R$, where R denotes the internuclear distance.

(3) The following methods of constructing the molecular wave functions are used for the calculations of the electronic energies at various internuclear distances: a) the ASMO method including the interactions among several configurations; b) the HLSP method including the interactions among several structures; c) the LCAO-SCF method; d) Moffit's method[1], which is the generalization of the method of the interaction operator. Further, some simplified calculations, in which, for example, the effect of the inner shells are neglected, are carried out.

(4) The wave functions obtained by the above calculations will serve to discuss the following physical quantities of these molecules; a) the gradient of the electric field at the nucleus, q (in the case of Li_2 molecule)[2]; b) the quadrupole moment of molecule, Q; c) the electron density at the nucleus for the electrons with unpaired spins, $Y^2(0)$ (in the case of O_2)[3]. The quantities a) and c) are of particular interest in connection with the theory of hyperfine structures in radio frequency or microwave spectroscopy.

3. The calculation of the molecular integrals for Li_2 and O_2 molecules.

We choose the sets of parameters (α, β) as shown in Tab. I. In order to examine the method of the calculations of the molecular integrals we made the rather luxurious calculations.

Table I.

	Li_2	Li_2	Li_2	O_2
α	14.00	13.25	14.00	17.75
β	3.00	3.25	3.50	5.25

The method of integrals are as following.

(1) The one electron integrals, mono-atomic integrals and Coulomb integrals are calculated as usual. 4) - 7)

(2) The exchange integrals are calculated by M. Kotani et alii's method.[4)5)6)8)] For that purpose we have calculated the following functions for several sets of values α and β.

$$W_\tau^{\nu}(m,n,\alpha,\beta) = \int_1^\infty\int_1^\infty Q_\tau^{\nu}(\lambda_1) P_\tau^{\nu}(\lambda_2)\, e^{-\alpha\lambda_1-\beta\lambda_2} \lambda_1^m \lambda_2^n (\lambda_1^2-1)^{\frac{\nu}{2}} (\lambda_2^2-1)^{\frac{\nu}{2}} d\lambda_1 d\lambda_2$$

(3) The ionic integrals are calculated by the Barnett and Coulsons' method.[9] The Kotani et alii's method 4) - 6) or the Brennan and Mulligan's method[10] are also used for checking and thus we obtained the values of ionic integrals correct to 7 decimals in atomic units

4. Li_2 molecule

The ground state is a $^1\Sigma_g^+$ state, and we have 8 configurations as shown in Tab. 2. We do not at present consider the configurations which correspond to the excitation of the inner shell electrons. The number of these configurations amounts to abount 300 even in our frame work and we will consider some of those configurations in a later work. Accordingly the correlation of the inner shell electrons are not taken into account in our present calculations.

Table 2

	M. O.	H. L.
1.	$\sigma_{1g}^2 \quad \sigma_{1u}^2 \quad \sigma_{2g}^2$	1. $(1s_a)^2\,(1s_b)^2 \quad (2s_a)(2s_b)$
2.	" " $\sigma_{2g}\ \sigma_{2g}$	2. " " $(2s_a)(2p\sigma_b) + (2s_b)(2p\sigma_a)$
3.	" " σ_{2g}^2	3. " " $(2p\sigma_a)(2p\sigma_b)$
4.	" " σ_{2u}^2	4. " " $(2s_a)^2 + (2s_b)^2$
5.	" " $\sigma_{2u}\ \sigma_{2u}$	5. " " $(2s_a)(2p\sigma_a) + (2s_b)(2p\sigma_b)$
6.	" " σ_{2u}^2	6. " " $(2p\sigma_a)^2 + (2p\sigma_b)^2$
7.	" " $\pi_{+g}\ \pi_{-g}$	7. " " $\pi_{+a}\pi_{-b} + \pi_{-b}\pi_{+a}$
8.	" " $\pi_{+u}\ \pi_{-u}$	8. " " $\pi_{+a}\pi_{-a} + \pi_{-b}\pi_{+a}$

The configurations 1 - 6 contain the radial correlations of the valency electrons and the configurations 7 - 8 include also its angular correlations[11]. The M.O. calculations are being made by Y. Mizuno and K. Kayama, the H.L.S.P. calculations are being done by T. Arai and the L.C.A.O.S.C.F. calculations are being endeavoured by K. Takayanagi and Miss M. Aoyagi.

The results of our preliminary calculations together with other results obtained hitherto are listed in Table III.

author	method	No. of electrons considered.	internuclear distance (Å)	parameters used	total energy (a.u.)	dissociation energy (e.V)
a) Bartlett & Furry	H. L. Nodeless 2s	2	2.28	$\zeta = 0.63$		1.09
b) Tomita & Ishiguro	H. L. $2s + \lambda(2p\sigma)$ $\lambda = 0.2$ Nodeless 2s	2	2.70	$\zeta = 0.637$		0.9
c) James	H. L. Single conf.	4	3.18	$\xi = 2.68$ $\zeta = 0.670$	-14.8457	(0.27)
	Variation	4	2.98	$\alpha = 15$ $\beta = 4$		$(0.51)^{2)}$
d) Coulson & Dancanson	M. O. 2s with Node Interaction between core and valency eletrons are neglected	2 + (+2)	2.65	Hartree / Fock: ξ=2.7 / 2.7; ζ=0.766 / 0.81; ξ=1.042 / 1.008	-14.807 (Hartree) -14.817 (Fock)	
Mizuno & Kayama	M.O. with single conf.	4	2.38	α=14.00, β=3.50	-14.445	
		4	2.65	" "	-14.800	
	M.O. including conf. 1 - 6	4	2.91	" "	-14.793	
		4	2.65	" "	-14.835	
Observed value			2.67		-15.001	1.14 e.V

a) J. H. Bartlett & W. H. Furry P. R. 38 (1931) 1615
b) K. Tomita & E. Ishiguro unpublished (1951)
c) H. M. James J. C. P. 2 (1934) 794
d) C. A. Coulson & W. E. Dancanson P. R. S. 181 (1943) 378

5. O_2 molecule

The ground state of the O_2 molecule is $^3\Sigma_g^-$. Just as Meckler[12], M. Kotani, Y. Mizuno and K. Kayama consider at present the following 9 configurations.

1	σ_{1g}^2	σ_{1u}^2	σ_{2g}^2	σ_{2u}^2	σ_{3g}^2	π_{+u}^2	π_{-u}^2	π_{-g}	π_{+g}
2	-	-	-	-	σ_{3g}^2	π_{+g}^2	π_{-g}^2	π_{+u}	π_{-u}
3	-	-	-	-	σ_{3u}^2	π_{+u}^2	π_{-u}^2	π_{+g}	π_{-g}
4	-	-	-	-	σ_{3u}^2	π_{+g}^2	π_{-u}^2	π_{+u}	π_{-u}
5	-	-	-	-	σ_{3g}^2	σ_{3u}^2	π_{+u}	π_{-u}	π_{+g} π_{-g}
6									
7	-	-	-	-	$(\pi_{-g})^2$	$(\pi_{+u})^2$	σ_{3g}	σ_{3u}	π_{-u} π_{+g}
8	-	-	-	-	$(\pi_{+g})^2$	$(\pi_{-u})^2$	σ_{3g}	σ_{3u}	π_{+u} π_{-g}
9									

More over they have 21 configurations which lack at least one σ_{3g} or σ_{3u} electron. They will take into account these configurations by the parturbation method if the difference of the diagonal elements of the energy operator corresponding to these configurations from those corresponding to the above 9 configurations turn out to be large as compared to the off diagonal elements. The calculations using the H. L. S. P. method are being examined by T. Arai.

6. The calculations relating to the LiH and N_2 molecules

For the treatment of the LiH molecule see the Abstract by K. Tomita and K. Fukui.

The research on the electronic structures of the N_2 molecule has been planned by T. Nakamura. He is treating this molecule in the ground and excited electronic states by the LCAO-MO method with configuration interactions. He is also interested in the study of the natures of various approximations usually used in the molecular theory. The parameters α and β used here (see 2.) are: $\alpha = \frac{1}{2} R = 14.00$ and $\beta \propto \frac{1}{2} R = 4.00$. The numerical computations of the molecular integrals may be carried out in the same way as explained in 3. He has also examined the evaluation of the hetero-nuclear hybrid integrals in terms of the auxiliary function

$$F_{\kappa,mn}(a,b) = \int_1^\infty\int_{-1}^{1} e^{-a\lambda - b\mu} \frac{(\lambda^2-1)^\kappa}{(\lambda+\mu)^{\kappa+1}} \lambda^m \mu^n \, d\lambda \, d\mu ,$$

first introduced by Kotani, Amemiya and Simose.

1) W. Moffitt: Proc. Roy. Soc. 210(1951) 245
2) E. G. Harris and D. S. Martin: P. R. 90(1953) 585
3) S. L. Miller, C. H. Townes and M. Kotani: P. R. 90 (1953) 542
4) M. Kotani, A. Amemiya and T. Simose: Proc. Phys. Math. Soc. Japan 20 Extra No. 1 (1938)
M. Kotani, and A. Amemiya: 22 Extra No. 1 (1940)
M. Kotani, E. Ishiguro, K. Hijikata, T. Nakamura and A. Amemiya: J. Phys. Soc. Japan 8 (1953) 463
5) G. Araki and W. Watari: Prog. Theore. Phys. 6 (1951)961
6) H. J. Kpineck: Zeit. f. Naturforsch. 5a (1950) 420 , 6a (1951)177, 7a (1952)785
7) C. C. J. Roothaan: J. C. P. 19 (1951) 1445
8) K. Rüdenberg: J. C. P. 19 (1951) 1459
9) M. P. Barnett & C. A. Coulson, Phil. Trans. Roy. Soc. London 243 (1951) 221
10) R. O. Brennan and J. F. Mulligan: J. C. P. 20 (1952) 1635
11) L. C. Green, M. M. Mulder & P. C. Milner: P. R. 91(1953) 35
12) A. Meckler: Quarterly Progress Report July 15 (1952) 62

On the Electronic Structure of LiH

Atomic Orbital Approach with Configurational Interaction

Kazuhisa Tomita and Kiyoshi Fukui

(Department of Physics, University of Kyoto)

An atomic orbital calculation on the ground state of LiH was carried out including all the electrons. This is the case which was left untouched by Fischer[1].

Supposing that the ground state of LiH is $^1\Sigma$, we adopted the following six lowest configurations

$$\Psi_{\mathrm{I}} = (N_{\mathrm{I}}/\sqrt{48})\{|\chi_1\alpha, \chi_1\beta, \chi_2\alpha, \chi_4\beta| + |\chi_1\beta, \chi_1\alpha, \chi_2\beta, \chi_4\alpha|\}$$

$$\Psi_{\mathrm{II}} = (N_{\mathrm{II}}/\sqrt{48})\{|\chi_1\alpha, \chi_1\beta, \chi_3\alpha, \chi_4\beta| + |\chi_1\beta, \chi_1\alpha, \chi_3\beta, \chi_4\alpha|\}$$

$$\Psi_{\mathrm{III}} = (N_{\mathrm{III}}/\sqrt{24})\,|\chi_1\alpha, \chi_1\beta, \chi_4\alpha, \chi_4\beta|$$

$$\Psi_{\mathrm{IV}} = (1/\sqrt{24})\,|\chi_1\alpha, \chi_1\beta, \chi_2\alpha, \chi_2\beta|$$

$$\Psi_{\mathrm{V}} = (1/\sqrt{24})\,|\chi_1\alpha, \chi_1\beta, \chi_3\alpha, \chi_3\beta|$$

$$\Psi_{\mathrm{VI}} = (1/\sqrt{48})\{|\chi_1\alpha, \chi_1\beta, \chi_2\alpha, \chi_3\beta| + |\chi_1\beta, \chi_1\alpha, \chi_2\beta, \chi_3\alpha|\}$$

where χ_1, χ_2 and χ_3 represent the 1s-, 2s- and 2pσ-orbital of Li atom and χ_4 the 1s-orbital of H atom. α and β are the spin eigenfunctions. The same forms of χ's were used as in the case of Fischer:

$$\chi_1 = \sqrt{a^3/\pi}\; e^{-ar}$$

$$\chi_2 = [1-(\chi_1,\chi_2')^2]^{-1/2}\{\chi_2' - (\chi_1,\chi_2')\chi_1\}; \qquad \chi_2' = \sqrt{b^5/3\pi}\; r e^{-br}$$

$$\chi_3 = \sqrt{c^5/\pi}\; r e^{-cr}\cos\theta ,$$

$$\chi_4 = \sqrt{d^3/\pi}\; e^{-dr} ,$$

with $a = 2.69$, $b = 0.658$, $c = 0.545$, and $d = 1.0$.

By using the linear combination of the type

$$\Psi = \sum_{\kappa}^{\mathrm{VI}} C_\kappa \Psi_\kappa$$

the total energy was minimized to give the ground state for the three values of internuclear distance R(2.64, 3.02 and 3.4 a.u.). Higher configurations were taken into account successively and we obtained the results shown in Fig. 1, where the atomic reference state was taken as the calculated total energy of infinite nuclear separation.

The binding energy 0.0725 a.u., which is expected as an underestimation, amounts to 75% of the observed values. The first three configurations prove dominant in lowering the energy. This involves the presense of s, p-hybridization in the ratio $C_{\mathrm{II}}N_{\mathrm{II}}/(C_{\mathrm{I}}N_{\mathrm{I}}) \sim 0.5$ and also non-neigligible importance of the ionic structure Li^+H^- ($C_{\mathrm{II}} \sim 0.3$). The fundamental frequency $1.13 \times 10^{-3}\mathrm{cm}^{-1}$ is near but smaller than the experimental values $1.4 \times 10^3\mathrm{cm}^{-1}$, which is considered reasonable in tendency.

Having found some errors in Fischer's table of integrals in the course of calculation, we corrected them and re-examined the valence shell treatment. (Cf. Fig.2) Inclusion of polar structure gives too big binding energy and too small nuclear distance. Fundamental frequency is far from the observation in any case. This type of treatment, therefore, seems far less reliable than expected higherto.[2]

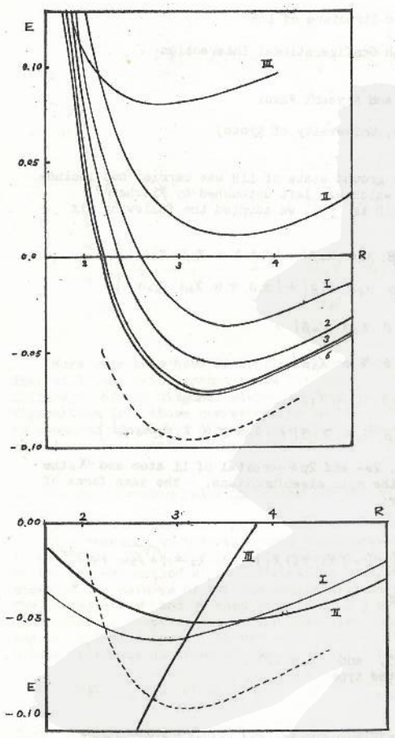

Fig. 1.

Energy curves for the ground state of LiH (in atomic unit).

I, II, III : diagonal energy of single configuration ψ_I, ψ_{II} or ψ_{III}.

2, 3, 6 : result when 2, 3 or 6 configurations are included.

dotted curve: observed energy (only in this case the origin of the scale is taken to be the true atomic state which lies 0.066 a.u. below the calculated reference state.)

Fig. 2.

Energy curves in 2-electron case.

(I, II and III correspond to those in Fig. 1.)

Further increase of the number of configurations amplifies the difficulty of calculation, but will give little improvement. Therefore a more practical way seems to limit ourselves to the first few configurations and to deform the component atomic orbitals in order to reach a better result.

1) Inga Fischer, Arkiv för Fysik, 5, 349(1952)
2) Hutchisson and Muscat, Phys. Rev. 40, 340(1932)

a2.

Correlational Energy in Atoms and Molecules

T. Arai

(Kyoto University)

In the usual treatments of the electronics structure of moelcules, the molecular wavefunction MWF is constructed from the MO or AO, and even though the configuration interaction is taken into account, we take only several configurations which are interesting for molecules. From this function, we have, at the infinite internuclear separations, an approximate (or SCF, at the best) wavefunctions of the constituent atoms.

However, the atomic energy calculated by these functions has the error, whose magnetude is usually greater than the excitation energy or the dissociation energy of molecules, and has the difference comparable with excitation energy and dissociation energy according to the states of atoms, because of the difference of the correlation energy.

Therefore from these functions we cannot have the satisfactory results not only for the excitation energy of atoms, at infinite nuclear distance, but also for the excitation energy and dissociation energy of molecules. Because the MWF which contains the configuration interaction, is constructed from the wavefunctions of several states of atoms, which have the different errors.

To avoid this difficulty, we construct the MWF from the constituent atomic eigenfunctions.

$$\Psi = \sum_{k\ell}^{\infty} \chi_{k\ell}^{mn} \Psi_{k\ell}^{mn} \qquad \Psi_{k\ell}^{mn} = \mathcal{A}\, \phi_{ak}^{m} \phi_{b\ell}^{n} \tag{1}$$

ϕ_{ak}^{m} and $\phi_{b\ell}^{n}$ are the kth and ℓth eigenfunctions of atoms or ions A and B which have m and n electrons respectively. Then we have the secular equation.

$$\det \left| (E - \bar{E}) S + V \right| = 0 \tag{2}$$

From the equation we can calculate the total energy.

$$E_I = \frac{\int \Psi H \Psi}{\int \Psi \Psi} = \frac{\int \sum \chi_{k\ell}^{mn} \chi_{k'\ell'}^{m'n'} \Psi_{k\ell}^{mn} H \Psi_{k'\ell'}^{m'n'}}{\int \sum \chi_{k\ell}^{mn} \chi_{k'\ell'}^{m'n'} \Psi_{k\ell}^{mn} \Psi_{k'\ell'}^{m'n'}} = \frac{\sum \chi^{\alpha} \chi^{\beta} H^{\alpha\beta}}{\sum \chi^{\alpha} \chi^{\beta} S^{\alpha\beta}} \tag{3}$$

where

$$H^{\alpha\beta} = \int \Psi_{k\ell}^{mn} H \Psi_{k'\ell'}^{m'n'} = (E_{ak'}^{m'} + E_{b\ell'}^{n'}) S^{\alpha\beta} + V^{\alpha\beta}$$

$$S^{\alpha\beta} = \int \Psi_{k\ell}^{mn} \Psi_{k'\ell'}^{m'n'} \qquad V^{\alpha\beta} = \int \Psi_{k\ell}^{mn} V \Psi_{k'\ell'}^{m'n'}$$

α and β indicate $mn, k\ell$ and $m'n', k'\ell'$ respectively. For β function, there is no need to take into account of the antisymmetrization.

This result is compared with the usual AO method, in which wavefunction is constructed from approximate atomic function

$$F = \sum^{K} y_{k\ell}^{mn} F_{k\ell}^{mn} \qquad F_{k\ell}^{mn} = \mathcal{A}\, f_{ak}^{m} f_{b\ell}^{n} \tag{4}$$

In this case we usually consider only K configurations which are interesting for molecules. Then we have an approximate energy E_F.

$$E_F = \frac{\int F H F}{\int F F} = \frac{\int \sum^{K} y^{\alpha} y^{\beta} F^{\alpha} H F^{\beta}}{\int \sum^{K} y^{\alpha} y^{\beta} F^{\alpha} F^{\beta}} \tag{5}$$

which have the error $\Delta = E_I - E_F < 0$.

To estimate this error Δ, we expand f by the atomic eigenfunction ϕ.

$$f^m_{ak} = (1-\varepsilon^m_k)\phi^m_{ak} + \sum_{i\neq k} \varepsilon^m_{ki}\,\phi^m_{ai} \tag{6}$$

where $\varepsilon^m_k \ll 1 \quad \varepsilon^m_{ki} \ll 1$.

$$(1-\varepsilon^m_k)^2 + \sum_{i\neq k} (\varepsilon^m_{ki})^2 = 1 \qquad \text{or} \qquad 2\varepsilon^m_k = \sum_i (\varepsilon^m_{ki})^2 \tag{7}$$

From this function we have an approximate atomic energy, which has the error Δ^m_{ak}.

$$\mathcal{E}^m_{ak} = E^m_{ak} - \Delta^m_{ak}$$

$$\mathcal{E}^m_{ak} = \int f^m_{ak} H_a f^m_{ak} = (1-\varepsilon^m_k)^2 E^m_{ak} + \sum_{i\neq k} (\varepsilon^m_{ki})^2 E^m_{ai}$$

$$\therefore \Delta^m_{ak} = 2\varepsilon^m_k E^m_{ak} - \sum_i (\varepsilon^m_{ki})^2 E^m_{ai} = \sum_i (\varepsilon^m_{ki})^2 \epsilon^m_{aki} \tag{8}$$

where $\epsilon^m_{aki} = E^m_{ak} - E^m_{ai}$, Δ^m_{ak} will be 0.5% - 1% of the atomic energy.

If we put

$$\chi^\alpha\chi^\beta = \chi^\alpha\chi^\beta + \Delta(\chi^\alpha\chi^\beta) \tag{9}$$

$$\int F^\alpha H F^\beta = H^{\alpha\beta} + \Delta H^{\alpha\beta} \tag{10}$$

$$\int F^\alpha F^\beta = S^{\alpha\beta} + \Delta S^{\alpha\beta} \tag{11}$$

we get from (5)

$$E_F = E_I\left(1 + \frac{\sum \Delta^{\alpha\beta}}{\sum \chi^\alpha\chi^\beta H^{\alpha\beta}} - \frac{\sum \delta^{\alpha\beta}}{\sum \chi^\alpha\chi^\beta S^{\alpha\beta}}\right) \tag{12}$$

where

$$\Delta^{\alpha\beta} = \Delta(\chi^\alpha\chi^\beta)\cdot H^{\alpha\beta} + \chi^\alpha\chi^\beta \cdot \Delta H^{\alpha\beta}$$

$$\delta^{\alpha\beta} = \Delta(\chi^\alpha\chi^\beta)\cdot S^{\alpha\beta} + \chi^\alpha\chi^\beta \cdot \Delta S^{\alpha\beta}$$

By the expansion formulae (6), we can reduce (10) into the form

$$\int F^\alpha H_a F^\beta = \int F^\alpha H_a\{(1-\varepsilon^{m'}_{k'})\phi^{m'}_{ak'} + \sum_i \varepsilon^{m'}_{k'i'}\phi^{m'}_{ai'}\} f^{n'}_{b\ell'}$$

$$= \int F^\alpha \{(1-\varepsilon^{m'}_{k'})E^{m'}_{ak'}\phi^{m'}_{ak'} + \sum_i \varepsilon^{m'}_{k'i'} E^{m'}_{ai'}\phi^{m'}_{ai'}\} f^{n'}_{b\ell'}$$

We put $E^{m'}_{ai'} = E^{m'}_{ak'} - \epsilon^{m'}_{ak'i'}$

So

$$\int F^\alpha H_a F^\beta = \int F^\alpha E^{m'}_{ak'}\{(1-\varepsilon^{m'}_{k'})\phi^{m'}_{ak'} + \sum_i \varepsilon^{m'}_{k'i'}\phi^{m'}_{ai'}\} f^{n'}_{b\ell'}$$

$$- \int F^\alpha \sum_i \varepsilon^{m'}_{k'i'}\epsilon^{m'}_{ak'i'}\phi^{m'}_{ai'}\cdot f^{n'}_{b\ell'}$$

$$= E^{m'}_{ak'}(S^{\alpha\beta} + \Delta S^{\alpha\beta}) - \epsilon^{\alpha\beta}_a \tag{13}$$

where $\epsilon^{\alpha\beta}_a = \int F^\alpha \sum_i \varepsilon^{m'}_{k'i'}\epsilon^{m'}_{ak'i'}\phi^{m'}_{ai'}\cdot f^{n'}_{b\ell'}$

We put $\epsilon^{\alpha\beta} = \epsilon^{\alpha\beta}_a + \epsilon^{\alpha\beta}_b$

$$\int F^\alpha V F^\beta = V^{\alpha\beta} + \Delta V^{\alpha\beta}$$

$$\int F^\alpha H F^\beta = (E^{m'}_{ak'} + E^{n'}_{b\ell'})(S^{\alpha\beta} + \Delta S^{\alpha\beta}) - \epsilon^{\alpha\beta} + V^{\alpha\beta} + \Delta V^{\alpha\beta}$$

$$\therefore \Delta H^{\alpha\beta} = (E^{m'}_{ak'} + E^{n'}_{b\ell'})\Delta S^{\alpha\beta} - \epsilon^{\alpha\beta} + \Delta V^{\alpha\beta} \tag{14}$$

If we put $E_I - (E^{m'}_{ak'} + E^{n'}_{b\ell'}) = \epsilon^\beta$

We get $E_I S^{\alpha\beta} - H^{\alpha\beta} = \epsilon^\beta S^{\alpha\beta} - V^{\alpha\beta}$

and from (14) $E_I \Delta S^{\alpha\beta} - \Delta H^{\alpha\beta} = \epsilon^\beta \Delta S^{\alpha\beta} - \Delta V^{\alpha\beta} + \epsilon^{\alpha\beta}$

From the above relations and (12), we get the error $\Delta = E_I - E_F$

$$\Delta = \frac{E_I \sum \delta^{\alpha\beta} - \sum \Delta^{\alpha\beta}}{\sum \chi^\alpha\chi^\beta S^{\alpha\beta}}$$

$$= \frac{\sum \Delta(\chi^\alpha\chi^\beta)(\epsilon^\beta S^{\alpha\beta} - V^{\alpha\beta}) + \sum \chi^\alpha\chi^\beta(\epsilon^\beta \Delta S^{\alpha\beta} - \Delta V^{\alpha\beta} + \epsilon^{\alpha\beta})}{\sum \chi^\alpha\chi^\beta S^{\alpha\beta}} \tag{15}$$

$\epsilon^\beta S^{\alpha\beta} \approx V^{\alpha\beta}$ and ϵ^β, $V^{\alpha\beta}$ and $\epsilon^{\alpha\beta}$ will have the order of several eV.

When f functions are the reasonaole approximation to ϕ and the K configurations are suitable enough, we get

$$\sum \Delta(\chi^\alpha\chi^\beta) \ll 1 \qquad \sum \Delta S^{\alpha\beta} \ll 1 \tag{16}$$

So we can put

$$\Delta \approx \frac{\sum \chi^\alpha\chi^\beta \epsilon^{\alpha\beta}}{\sum \chi^\alpha\chi^\beta S^{\alpha\beta}} \tag{17}$$

From (13)

$$\epsilon^{\alpha\beta}_a = \sum_{i'} \mathcal{A}\{(1-\varepsilon^m_k)\phi^m_{ak} + \sum_i \varepsilon^m_{ki}\phi^m_{ai}\}\{(1-\varepsilon^n_\ell)\phi^n_{b\ell} + \sum_j \varepsilon^n_{\ell j}\phi^n_{bj}\}$$
$$\times \varepsilon^{m'}_{k'i'}\epsilon^{m'}_{ak'i'}\phi^{m'}_{ai'}\{(1-\varepsilon^{n'}_{\ell'})\phi^{n'}_{b\ell'} + \sum_{j'} \varepsilon^{n'}_{\ell' j'}\phi^{n'}_{bj'}\}$$

$$\approx \sum_{i'} \varepsilon^{m'}_{k'i'}\epsilon^{m'}_{ak'i'}(\mathcal{A}\phi^m_{ak}\phi^n_{b\ell})\phi^{m'}_{ai'}\phi^{n'}_{b\ell'}$$
$$+ \sum_{i'} \varepsilon^m_{ki}\varepsilon^{m'}_{k'i'}\epsilon^{m'}_{ak'i'}(\mathcal{A}\phi^m_{ai}\phi^n_{b\ell})\phi^{m'}_{ai'}\phi^{n'}_{b\ell'}$$

If $\alpha = \beta$, the second term becomes

$$\sum_i (\varepsilon^m_{ki})^2 \epsilon^m_{aki}(\mathcal{A}\phi^m_{ai}\phi^n_{b\ell})\phi^m_{ai}\phi^n_{b\ell}$$

Only in this case, the overlap become more than 1, and will be the dominant terms in (17). From (8), $\sum (\varepsilon^m_{ki})^2 \epsilon^m_{aki}$ is the error in atom. Therefore $\epsilon^{\alpha\beta}$ is connected with the errors in atoms, whose magnitudes differ according to the states of atoms.

If $\Delta_0 < \Delta$ where $\Delta_0 = \sum_a E^m_{ao} - \sum_a f^m_{ao} H_a f^m_{ao}$

(the error in the energies of the isolated atoms in the ground state) the dissociation energy will be diminished by the use of the approximate atomic functions f.

If $\Delta_0 > \Delta$, we have rather greater dissociation energy.

We caiculat the dissociation energy of Li_2 and O_2 by the ϕ method and show how much it will improve the situation.

a3.

The Electronic Energies of the CH_2, CH Radicals and the Carbon Atom.

Kiyosi O-ohata

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Recently, Moffitt[1] discussed the relation between the electronic energies of the atom and the molecule, and stressed the importance of the atomic spectrum in a molecular problem. We found the same relation in the calculations of the electronic energies of the CH_2, CH radicals and the carbon atom, and took a conventional method for the calculations of the molecular spectrum in which we used the values in the Hartree field for the intra atomic energy integrals.

The electronic energies of the carbon atom, as Moffitt suggested, are not correctly prdicted by the use of Zener's type atomic orbital functions in the single configuration s^2p^2 or sp^3. The order of the ^3S and ^5S states are reversed between the calculated and observed spectrum. And the same results were obtained in the Hartree calculations. This is not the case if we take into account the configurational interaction between s^2p^2 and p^4 configurations of the carbon atom, but the ratio $^1S - {}^1D_{p^2} - {}^3P$ is incorrectly given in both cases. These discrepancies and the difference between the observed and calculated binding energies compel us to take into consideration more configurations.

The electronic energies of the CH radical were calculated using the methods of atomic orbitals (H - L method) and SCF MO's. The results of these calculations are shown in the following table,

Electronic Energies of the CH radical

	H - L method[3] (1)	(2)	(3)	SCF MO method	Obs.
$^4\Sigma^-$	- 3.00 eV	- 2.10 eV	- 2.32 eV	- 2.43 eV	— eV
$^2\Pi$	- 2.95	- 2.19	- 2.50	- 2.26	- 3.60
$^2\Delta$	- 1.14	+ 0.81	+ 0.54	- 0.21	- 0.74
$^2\Sigma^-$	- 0.18	+ 1.16	+ 0.83	+ 0.05	- 0.42
$^2\Sigma^+$	+ 0.31	+ 2.19	+ 1.66	+ 0.84	+ 0.33

where in column (1) we assumed all atomic orbitals to be orthogonal to each other and considered s^2p^2 and sp^3 configurations of the carbon atom. In column (2) the overlap integrals and all the permutations of electrons are included and in column (3) the p^4 configuration of the carbon atom are also included. For the intra atomic integrals in the above calculations, we used throughout the values obtained in the Hartree field.

These calculations show that the ground state of the CH radical is the $^4\Sigma^-$ state which is not observed. This may be due to the reason that we obtained a particularly lower value for the ^5S state in the atomic spectrum of the carbon. We also calculated the electronic energies of the CH_2 radical under the assumption which corresponds to the first column in the calculation of the CH radical, and we obtained the $^3B_1$ state for the ground state of the CH_2 radical. This will have the same relation in the $^4\Sigma^-$ state of the CH radical. However, this is contradictory to the prediction of the molecular aspects.[5]

The calculation of the electronic energies of the CH_2 radical using the SCF MO method requires the values of the three center energy integrals. These integrals were computed by the same method that Barker and Eyring proposed.[6] And we found a good approximate formula analogous to Mulliken's method.

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1) W. Moffitt, Proc. Roy. Soc., A210 (1951), 245.
2) C. W. Ufford, Phys. Rev. 53 (1938), 568.
3) K. Niira and K. O-ohata, Jour. Phys. Soc. Japan. 7 (1952), 61.
J. Higuchi, Bull. Chem. Soc. Japan, 26 (1953), 1.
4) J. Higuchi, Private communication.
5) R. S. Mulliken, Private communication.
6) K. O-ohata, Busseiron Kenkyu 50 (1952), 38.
R. S. Baker and H. Eyring, Jour. Chem. Phys., 21 (1953), 912.

Electronic States of the Molecule $(FHF)^-$

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Although a large amount of descriptive data has accumulated on the subject of hydrogen bonding, this linkage has received slight theoretical consideration, and a number of problems regarding condition for its formation remain only partially answered, for example, is the hydrogen atom to be considered as being symmetrically placed in the bond ? etc(?)

Firstly, the electronic structure of the ground state of the molecule $(FHF)^-$ is being studied by using Roothaan's LCAO-SCF method. The interactions of all electrons have been explicitly considered (except only 1s electrons of fluorine) and no extra-geometrical empirical data have been used.

In the general LCAO-SCF method all the electrons of the molecule are represented by LCAO MO's

$$\phi_i = \sum_p a_{ip}\chi_p = \sum_n d_{in}\sigma_n$$

where i numbers the MO's, P the AO's, (Slater-type) n the symmetry orbitals, the a's and the d's are undetermined coefficients.

The condition that the MO's be orthonormal then reduces to

$$\int \bar{\phi}_i \phi_j \, d\nu = \sum_{pq} \bar{a}_{ip} S_{pq} a_{jq} = \delta_{ij}$$

where the overlap integral S_{pq} are defined by

$$S_{pq} = \overline{S_{pq}} = \int \bar{\chi}_p \chi_q \, d\tau$$

The total N-electron normalized wave function $\bar{\Phi}$ for the closed-shell ground state is then built up as an antisymmetrized product (AP) of these LCAO MO's, and the ground state electronic energy is given by

$$E = \int \bar{\Phi} \mathcal{H} \bar{\Phi} \, d\tau \qquad \mathcal{H} = \sum_\mu H^\mu + \sum_{\mu\nu} \frac{2}{r_{\mu\nu}}$$

To obtain the best LCAO MO's, a veriation procedure is carried out of minimize the ground state energy, subject to the orthonormality of the MO's. It can be shown that this variational process leads to the following matrix equation

$$(H+G)a_i = La_i = \varepsilon_i S a_i$$

Here the column vectors a_i give the coefficients of the AO's in the ith LCAO MO; H is the bare-nuclear-field orbital energy matrix with elements

$$H_{pq} = \bar{H}_{qp} = \int \bar{\chi}_p H \chi_q \, d\tau = -\int \bar{\chi}_p \Delta \chi_q \, d\tau - \gamma \int \bar{\chi}_p \frac{2}{r_p} \chi_q \, d\tau - \gamma \int \bar{\chi}_p \frac{2}{r_{p'}} \chi_q \, d\tau - \int \bar{\chi}_p \frac{2}{r_H} \chi_q \, d\tau$$
$$+2 \left(\int \frac{2}{r_{jq}} (\chi^2_{js}(j)) \bar{\chi}_p(q) \chi_q(q) \, d\tau + \int \frac{2}{r_{jq}} (\chi^2_{js}(j)) \bar{\chi}_p(q) \chi_q(q) \, d\tau \right)$$

and G is the electronic interaction matrix with elements

$$G_{pq} = \bar{G}_{qp} = \sum \bar{a}_{ir} G_{prqt} a_{it}$$
$$G_{prqt} = 2J_{prqt} - J_{prtq}$$
$$J_{prqt} = \int \frac{\bar{\chi}_p^\mu \bar{\chi}_r^\nu 2\chi_q^\mu \chi_t^\nu}{r_{\mu\nu}} \, d\tau^{\mu\nu}$$

We take the following values as the parameters in the above calculation

$$Z_1 = 8.69 \qquad Z_2 = 2.60 \qquad R(F\text{-}F) = 2.26\,A^\circ$$

Z_1, Z_2 : coefficients in the exponents in 1s and 2s, 2p orbitals of the fluorine atom, respectively.

The large number of integrals over atomic orbitals that occur, is calculated as exactly as possible (expect only two-electron three center integrals). The two-electron three-center integrals are approximated by the following formula

$$(ab|cd) = \Delta_{ab}\Delta_{cd}(TT|T'T')$$

where $$(ab|cd) = \int\int \chi_a(1)\chi_b(1)\frac{2}{r_{12}}\chi_c(2)\chi_d(2)\,d\tau_1 d\tau_2$$

$$\Delta_{ab} = \int \chi_a \chi_b \, d\tau$$

χ_T and $\chi_{T'}$ are atomic orbitals associated with the centers of gravity T and T', respectively, which have to be chosen in a suitable way. (here is found by maximizing the expression for the overlapping charge $\chi_a\chi_b d\tau$ along the internuclear axis.) Complete numerical calculations are in progress.

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1) W. S. Fyfe, J. C. P. 21(1953) 2
E. Westurm, K. Pitzer, J. Am. Chem. Soc. 71(1949) 1940

B1 The Present Tendencies in the Theory of Large Molecules

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Practically all attempts at calculations for large unsaturated molecules make use of the molecular orbital method (m.o.). This method depends on our ability to separate the descriptions of the σ and π electrons. Recent work shows that this is almost wholly justified, though there are still some uncertainties.

The calculations themselves may be divided into
(a) non-empirical, and
(b) empirical.
In (a) no assumptions are made except that the π electrons may be treated separately. The information which is obtained is essentially (i) excitation energies and (ii) identification of the symmetry of the various excited states. Good progress in the latter has been made, but it turns out to be very hard to calculate the transition energies sufficiently accurately. This arises on account of configuration interaction, which seems to play a large even in the ground state of large molecules. (Fortunately, with small molecules, the influence of C.I. is much smaller.)

Attempts have recently been made, by Moffitt and Others, to adapt the conventional M.O. method in such a way that it gives a more realistic account of the states which are largely ionic in character. This improves the agreement with experiment, but is not wholly satisfying since it requires us to make use of empirical energies, not always available.

In the empirical treatments (b), the information which is obtained consists of (i) charge distribution, (ii) bond orders (iii) free valences, and (iv) spectral energies. In some form or other perturbation methods play a large part. Considerable study, both in Japan and in Britain, has shown how conjugation may take place across a bond which is formally a single bond, as in the molecules Ph-X, where X is a halogen. The charge migrations, excitation energies and bond orders, have been calculated.

Calculations of the chemical reactivity which is associated with π electrons are almost all of the empirical type (b). A general type of 'localisation' approach has been used for ionic, and free radical and other reactions. More recently an analysis in terms of the distribution of charge in the top-occupied level has proved valuable.

Longuet-Higgins and Dewar have shown how, by using some very elementary properties of the non-bonding π orbital in odd-numbered hydrocarbon molecules, extremely simple accounts of the long wave absorption, and the variation in activation energy in a related series of molecules , may be given. No great claim to precise accuracy is made, but the results are surprisingly good. Methods of this kind are likely to become more important as time goes on.

B2.

A Review of Recent Works on the π-Electron System in Japan

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Introduction

Theoretical researches on the π-electron system were recently carried out by several authors in Japan. Titles or outlines of these researches are listed in this pre-print. They are not many, but the time given to me is too short to review all of them. I will therefore review not all works but only those which were carried out in my faculty.

The π-electron system in conjugated molecules have been discussed by two different methods, namely free electron and LCAO MO methods. As respective examples of the application of these methods I will mention researches on the absorption spectra of conjugated long molecules and on the chemical reactivity of conjugated cyclic molecules.

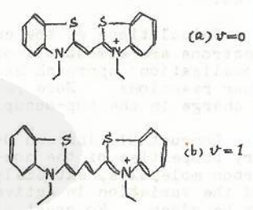
A characteristic property of conjugated long molecules is the so-called vinylene shift. It is the shift in the absorption maxima, to the longer wave length side, resulting from increasing the length of the conjugated chain by adding a vinylene group. Baylis,[1] Kuhn[2] and Simpson[3] first showed that the vinylene shift can roughly be interpreted by the one-dimensional free electron model without coupling. This model can be refined in two ways: modifying the one-electron field; and introducing the coupling of electrons. The effect of introducing a periodic field was studied assuming a simplified model by Fukui and coworkers[4] and the satisfactory result was obtained. I am now examining the effect of ionic field in the symmetric cyanine dye cation. I have just calculated the shift in the energy levels of the free electron model due to the Coulomb interaction.

On the other hand I[5] showed that, in case of asymmetric molecules such as carotenoids, the strong convergence of the observed shift of absorption maxima resulting from increasing the chain length can fully be accounted for by the Tomonaga model of free-electron gas with couplings of arbitrary strength.

A characteristic property of conjugated cyclic molecules is the special orientation of substituents. It was found by Wheland and Pauling[6] that in case of the substitution reaction of conjugated heterotype cyclic molecules the position of maximum total π-electron density, in LCAO MO sense, is most easily attacked. This fact was confirmed for electrophilic reagents and various heterotype reactants by Longuet-Higgins, Coulson and others and it was further found that the position of minimum π-density is most easily attacked by nucleophilic reagents. Fukui and coworkers[7] recently found that, in case of condensed aromatic hydrocarbons, the position of maximum π-electron density in the highest occupied level is most easily attacked by electrophilic reagents although the total π-density is uniform throughout the molecule.[8] This relation has recently been extended by Fukui and coworkers to the cases of electrophilic substitutions in heterocyclic molecules, nucleophilic and radical substitutions, and additions, including chain molecules.

I will explain the outline of these works in Japan in what follows.

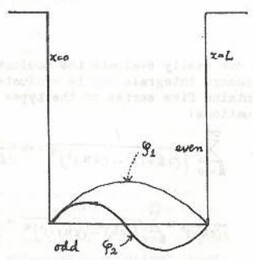
Fig.1 Cyanine dye cations
(ν=number of vinylene groups)



§1 Coulomb interactions in the free electron model

We consider a series of cyanine dye cations, shown in Fig.1, in which two N-ethylbenzothiazole rings are combined by vinylene groups. In the free electron model the potential energy of one-electron Hamiltonian is represented by a square well of very deep depth in one dimension (Fig.2). Since the molecule has a centre of symmentry the one-electron states can well be characterized by the parity. The orbitals (Fig.2) and energy levels are given by

Fig.2 Potential and orbitals



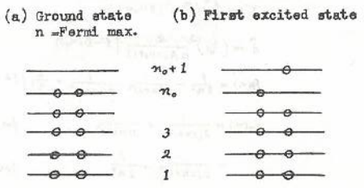
$$\varphi_n = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} n x$$

$$\varepsilon(n) = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n^2 \qquad (1.1)$$

$n = 1,2,3, \ldots\ldots$

If the number of π-electrons in the molecule is equal to N, the $n = 1,2,\ldots\ldots$ n_0 orbitals are occupied in the singlet ground state according to the Pauli principle where n_0 is equal to N/2 (Fig.3a) and it will be referred to as the Fermi maximum. In the first singlet excited state an electron in the n_0-orbital is excited to the (n_0+1)-orbital (Fig.3b). The energies of these states can be calculated by the standard method[9] taking into account the Pauli principle. The energy difference between these two states is the first excitation energy of the molecule which can be interpreted as corresponding to the absorption maxima. If we denote the one-dimensional interaction potential between two electrons by $J(x_1-x_2)$ this excitation energy is given by

Fig.3



$$\Delta E = \varepsilon(n_0+1) - \varepsilon(n_0) + W_c + W_{ex}$$

$$W_c = \sum_{n=1}^{n_0-1} 2\{C(n_0+1,n) - C(n_0,n)\} + C(n_0+1,n_0) - C(n_0,n_0)$$

$$W_{ex} = \sum_{n=1}^{n_0-1} \{D(n_0,n) - D(n_0+1,n)\} + D(n_0+1,n_0) \qquad (1.2)$$

where C and D denote the Coulomb and exchange integrals of J respectively.

In order to evaluate these integrals we expand the Coulomb potential between two electrons in the Fourier series in a parallelepiped of the length L and the sectional area A. We assume that $J(x_1-x_2)$ is given by its average over the sectional area. We have then

$$J(x_1-x_2)=\frac{2Le^2}{\pi A}\sum_{n=1}^{\infty}\frac{1}{n^2}\cos\frac{2\pi}{L}n(x_1-x_2) \qquad (1.3)$$

$$=\frac{Le^2}{\pi A}\sum_{n=1}^{\infty}\frac{1}{n^2}\cos\frac{\pi}{L}n(x_1-x_2)$$

We can easily evaluate the Coulomb integrals making use of the first expansion. The exchange integrals can be evaluated making use of the second expansion. The result contains five series of the types given by the left hand sides of the following equations:

$$\sum_{k=0}^{\infty}\frac{1}{\{(2k+1)^2-(2n)^2\}^2}=\frac{\pi^2}{16(2n)^2} \qquad n=1,2,3,\ \cdots$$

$$\frac{1}{2(2n+1)^4}+\sum_{k=0}^{\infty}\frac{1}{\{(2k)^2-(2n+1)^2\}^2}=\frac{\pi^2}{16(2n+1)^2} \qquad n=0,1,2,3,\cdots \qquad (1.4)$$

These series can be evaluated by expanding $\sin 2n|x|$ and $\sin(2n+1)|x|$ in the Fourier series. If we consider the norms of the functions we obtain Eqs.(1.4) by the Parseval theorem. Making use of these results we obtain

$$\begin{aligned}
&\Delta E=T(1+\delta)\\
&T=\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2(2n_0+1)\\
&\delta=\left(\frac{L}{\pi a}\right)^3\frac{2}{A(2n_0+1)}\{1-B(n_0)\}\\
&B(n)=\frac{9}{8n^2}-\frac{1}{2(n+1)^2}-\frac{1}{2(2n+1)^2}+\frac{6}{\pi^2}\{1+G(n)\}\\
&G(n)=\frac{1}{2(2n+1)^4}+\frac{1}{2(n+1)^4} \qquad \text{for } n=\text{even}\\
&\quad=\frac{1}{2(2n+1)^4}-\frac{1}{2n^4} \qquad \text{for } n=\text{odd}
\end{aligned} \qquad (1.5)$$

where a is the Bohr radius. The coupling effect is represented by δ. Its main part is due to the exchange integrals. If we neglect δ, ΔE is given by T. This term gives non-convergent vinylene shifts as was shown by Baylis, Kuhn and Simpson. The correction term δ can account for the convergence of the shift.

We assume that, for example, in the cyanine dye cation shown by (a) of Fig.1 the square well is extended over five carbon atoms and two nitrogen atoms (Fig.4) and the π-electrons contained in this well are six which associate with the three conjugated double bonds. Then the number of conjugated double bonds is equal to n_0 and L is equal to $(N+1)l$ where l is the mean length occupied by an atom. Although the observed bond length for C-N in pyridine is equal to 1.37Å, we assume, for the sake of simplicity, that l is equal to 1.4Å, (=2.646 atomic units) which is the bond length in benzene. The absorption maxima calculated on this value are compared with experiment [10] in Table 1. In order to agree with experiment we have to assume A to be equal to 1000 atomic units. This value is unreasonably large, but it has no real meaning. It only means the smallness of couplings. This unreasonable value may be due to neglecting the variation of wave functions in the lateral dimension.

Fig.4

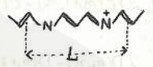


Table 1 Absorption maxima of cyanine dyes

n_0 = Fermi max. = number of conj. double bonds
$N = 2n_0$ = number of π-electrons
N-1 = number of carbon atoms in the chain
v = number of vinylene groups
λ = absorption maxima in mμ (solvent = MeOH)

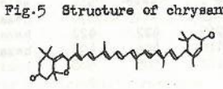
v	n_0	N	δ	λ_{calc}	λ_{obs}
0	3	6	0.0239	442	423
1	4	8	0.0533	552	558
2	5	10	0.0821	657	650
3	6	12	0.1164	753	758

§2 Convergence of shift in absorption maxima of carotenoids

In case of asymmetric molecules such as carotenoids the wave lengths of the absorption maxima are much shorter than those of cyanine dyes when we compare those of molecules with the same number of conjugated double bonds. Moreover the shift of the absorption maxima resulting from increasing the chain length is strongly convergent. As we have seen in the preceding calculation the effect of the Coulomb interaction gives rise to the convergence of the shift. If the coupling is strong we have to more completely take into account its effect. The Tomonaga model is most suitable for this purpose. I will mention an outline of the calculation in this line.[5]

In the present case the molecules have no symmetry, for example, as is shown in Fig.5. Therefore one-electron states can not be characterized by the parity. We adopt the basic one-electron orbitals and their levels as follows:

Fig.5 Structure of chrysanthemaxanthin



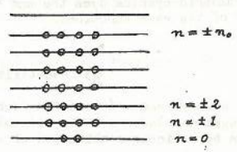
$$\varphi_n=\frac{1}{\sqrt{L}}\exp\left(\frac{2\pi i}{L}nx\right)$$

$$\varepsilon(n)=\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2n^2 \qquad (2.1)$$

$$n=0,\pm1,\pm2,\ \cdots\cdots$$

where the excited states are all doubly degenerate. If we compare these orbitals and levels with those given by (1.1) we see that the difference in these basic states can roughly account for the difference in absorption maxima of cyanine dyes and carotenoids. If the number of π-electrons is N, the $n=0, \pm1, \pm2, \cdots\cdots, \pm n_0$ orbitals are occupied in the ground state of the molecule where $n_0>0$ and $2n_0+1=N/2$ (Fig.6.) The total Hamiltonian including couplings of all electrons can be transformed into the diagonal form making use of the method of the second quantization. This transformation can be carried out even if the couplings are quite strong. The approximation included is that only states near the n_0-level are taking into account.

Fig.6 Ground state



The coupling of electrons is again assumed to be given by the lateral average of the Coulomb interaction as was done in the preceding calculation. The first excitation energy of the molecule is then given by

$$\Delta E = T\sqrt{1+\delta}$$

$$T = \left(\frac{k}{L}\right)^2 \frac{n_o}{m}$$

$$\delta = \left(\frac{L}{\pi}\right)^3 \frac{1}{aAn_o} \qquad (2.2)$$

where δ is nearly the same as the preceding one if we neglect a correction term given by B. If we assume that $L = N\ell$, $\ell = 1.4\text{Å} = 2.646$ atomic units, and $A = 724.288$ atomic units the calculated absorption maxima are in very good agreement with the observed values of 37 carotenoids. A few examples are shown in Table 2. We see that δ is very large for long molecules. In these cases the perturbation method by no means has its validity.

Table 2 Absorption maxima of carotenoids

j = number of conjugated double bonds
N = 2j = number of π-electrons
λ = absorption maxima in $m\mu$

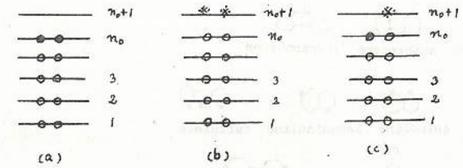
j	N	δ	λ_{calc}	λ_{obs}	solvent	dubstance
3	6	0.178	268	270	hexane	dibenzyl-hexatriene
8	16	0.965	422	422	hexane	chrysanthemaxanthin
13	26	2.416	493	493	hexane	rhodoviolascin
15	30	3.181	508	508	cyclohex,	decapreno-β-carotene

The real reason for the difference between wave lengths of the absorption maxima of symmetric cyanine dyes and carotenoids is not yet fully known. It may partly depend on the difference in the end structure, but the main reason may be that molecules of cyanine dyes discussed in the preceding section have a centre of symmetry whereas there is no centre of symmetry in carotenoid molecules. Such a phenomenon has often been interpreted as a resonance. As has been well known, the absorption maxima of asymmetric cyanine dyes are of shorter wave length than those of symmetric cyanine dyes with the same number of conjugated double bonds. This is well understood in the fact that a position of the absorption maxima of a cyanine dye with different terminal groups is generally in the shorter wave length side than a mean position of the absorption maxima of two symmetric cyanine dyes with the respective terminal groups. The deviation from a mean position varys with the nature of the terminal group. This may be due to the degree of asymmetry which determines the ratio of superposed parities. The case of carotenoids can be considered as parities are equally superposed, levels thus being completely degenerate. This fact may be understood on another view point, namely in case of carotenoids the periodic property of molecular structures is the predominant cause of determining the property of the wave function, whereas in case of symmetric cyanine dyes the end barriers of one-electron fields determine the property of the wave function.

§3 Reactivity of conjugated cyclic molecules

We next consider chemical substitution reaction of various reagents in cyclic conjugated molecules. The molecular orbital ψ_n of π-electrons in the molecule is given by a linear combination of atomic π-orbitals φ_r :

Fig.7 Frontier electrons and orbitals



$$\psi_n = \sum_{r=1}^{N'} C_r c_r(n) \qquad n = 1, 2, \ldots, N' \qquad (3.1)$$

The coefficients $c_r(n)$ are determined in the standard manner of the LCAO MO method. In the ground state of the molecule, the $n=1,2,\ldots,n_o$ orbitals are occupied by π-electrons. Fukui and coworkers referred to the electron in the n_o-orbital as the frontier electron and the (n_o+1)-orbital as the frontier orbital. They defined the frontier electron density f_r at the r-th atom as follows:

$$\text{(a)} \quad f_r = 2|c_r(n_o)|^2 \quad \text{for electrophilic reagents}$$

$$\text{(b)} \quad f_r = 2|c_r(n_o+1)|^2 \quad \text{for nucleophilic reagents} \qquad (3.2)$$

$$\text{(c)} \quad f_r = |c_r(n_o)|^2 + |c_r(n_o+1)|^2 \quad \text{for radical reagents}$$

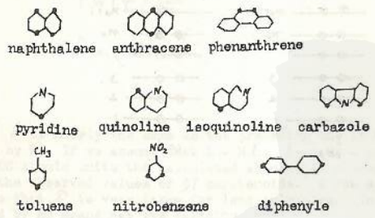
They calculated the frontier electron density for various molecules of condensed aromatic hydrocarbons, heterocyclic compounds, substituted condensed aromatics, and chain compounds. Several examples of the result are shown in Fig.8. If we compare the positions of maximum frontier electron density with experiment we see that these positions are most easily attacked by reagents in three cases of chemical reactions.

The true reason for these parallelism between the frontier electron density and the point of attack is not known.* It can be compared to the well-known theoretical interpretation on the directional valency of Slater and Pauling. This theory accounts for the directional property of valencies in carbon, nitrogen and oxygen by the angular density distribution of the valence electrons, or p and sp^3 atomic orbitals. If we consider that frontier electrons or orbitals correspond to these atomic orbitals then we can understand the orientation of substituents in the same way as the directional valency. Of course such a simple consideration does not mean explaining the mechanism of the observed fact. The true mechanism is much complicated.

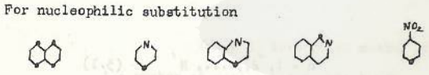
* Fukui and coworkers are considering a theoretical interpretation. Parr privately communicated me his own opinion on the theorstical reason.

Fig.8 Frontier electron density

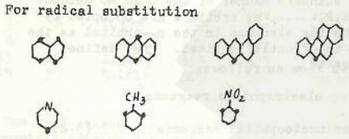
(a) For electrophilic substitution



(b) For nucleophilic substitution



(c) For radical substitution



(1) S.Baylis, J.Chem.Phys. 16 (1948), 287
(2) H.Kuhn, J.Chem.Phys. 16 (1948), 840
(3) W.T.Simpson, J.Chem.Phys. 16 (1948), 1124
(4) K.Fukui, C.Nagata and T.Yonezawa, J.Chem.Phys. 21 (1953), 186
(5) G.Araki and T.Murai, Prog.Theor.Phys. 8 (1952), 639
(6) G.W.Wheland and L.Pauling, J.Am.Chem.Soc. 57 (1935), 2086
(7) K.Fukui, T.Yonezawa, and H.Shingu, J.Chem.Phys. 20 (1952), 722
(8) C.A.Coulson and H.C.Longuet-Higgins, Proc.Roy.Soc. 191 (1947), 39
(9) E.U.Condon and G.H.Shortley, Theory of Atomic Spectra, p.169 (1935)
(10) L.G.S.Brooker, R.H.Sprague, C.P.Smyth and G.L.Lewis, J.Am.Chem.Soc. 62 (1940),1116
L.G.S.Brooker, G.H.Keyes and W.W.Williams, J.Am.Chem.Soc. 64 (1942), 199

σπ Interaction in Conjugated Organic Molecules

b1.

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The essential feature of "π-electron theory" is that in the molecules with conjugated double bonds the treatment of the π-electrons can be separated entirely from the treatment of the σ-electrons. It is assumed that the wave function of the π-electron spreads over the whole molecule and is well approximated by non-localized MO, while the wave function of each σ-electron is localized near the nucleus. But recent works by Coulson and others[1] show that in benzene the charge cloud of the σ-electrons extends over the whole molecule to the same extent as that of the π-electrons, and further according to Fujii and Shida[2] and to Itoh, Ohno and Yoshizumi[3] the diamagnetic anisotropy of benzene which may be one of the most direct experimental evidences for the streamer bonds cannot be interpreted quantitatively in terms of the usual π-electron theory.

Therefore, it would be desirable to examine the effect of σ-electrons more in detail. Roughly speaking, there are two ways of σπ interaction: (1) New levels which will be called σ-π levels should result from excitation of σ- (π-) electrons into unoccupied σ and π (σ) orbits. Altmann[4] discussed by VB method the lower excited electronic levels of ethylene which result from bonding between π- and σ-electrons, and he showed the importance of taking account of σ-π levels. But, for acetylene Ross[5] made a calculation by MO method which included only the CC bond σ-electrons and showed that σ-π levels are of high energies and interactions with the lower π-type levels are small. Further work by Maeda[6] which includes the CH σ-electrons shows low-lying σ-π levels, but in this case of acetylene there is no CI between the low-lying σ-π and π levels. The calculation by the MO method taking into account the CC σ-electrons and including all CI is now in progress for ethylene.

(2) The effect of σ- electrons on the π type levels through coulombic and exchange interactions between π- and σ-electrons should be taken into account even when the effect (1) is negligible. Of these interactions the exchange interaction has a greater effect on the excitation energy, disproving the assumption taken in the usual treatment of π-electrons[5-8]. For ethylene, for example,

		coulombic energy*	exchange energy
$^1A_{1g}$	(N)	148.99 ev	-8.85 ev
$^3B_{1u}$	(T)	0.49 **	1.24 **
$^1B_{1u}$	(V)	0.49	1.24
$^1A_{1g}$	(Z)	0.99	2.49

* the contribution from H atoms is omitted.
** the value relative to that of the normal configuration (N).

In this calculation electron pair bonds are assumed for CC and CH bonds. For acetylene[5,6] and benzene[8] the similar conclusion was obtained, and the assumption of the electron pair bonds for σ-electrons was found to be a fairly good approximation for the calculation of the excitation energy.

1) Coulson, March and Altmann, Proc. Nat. Acad. Sci. US 38 (1952) 372.
N. H. March, Acta Crystal. 5 (1952) 187.
2) Fujii and Shida, Bull. Chem. Soc. Japan 24 (1951) 242.
3) Itoh, Ohno and Yoshizumi, Progress Report No.2 (1953) 21.
4) A. L. Altmann, Proc. Roy. Soc. A210 (1952) 327, 343.
5) I. G. Ross, Trans. Farad. Soc. 48 (1952) 973.
6) S. Maeda, unpublished.
7) J. Van Dranen, Thesis, Amsterdam University (1951).
8) K. Niira, J. Chem. Phys. 20 (1952) 1498; J. Phys. Soc. Japan in press.

Errata

A Review of Recent Works on the π-Electron System in Japan

Gentaro Araki

The first line of right hand side of Eq. (1.3) should be omitted. For the next two sentences read "We can evaluate the Coulomb and exchange integrals making use of this expansion."

For "five series" in the next sentence read "series".

For Eq. (1.4) read

$$\sum_{k=0}^{\infty} \frac{1}{(2k+1)^4} = \frac{\pi^4}{96}$$

$$\left.\begin{aligned} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} \cdot \frac{1}{(2n)^2-(2k+1)^2} &= \frac{\pi^2}{32n^2} \\ \sum_{k=0}^{\infty} \frac{1}{(2n)^2-(2k+1)^2} \cdot \frac{1}{(2m)^2-(2k+1)^2} &= \frac{\pi^2}{64n^2}\delta_{nm} \end{aligned}\right\} \; n, m = 1, 2, 3, \cdots$$

$$\sum_{k=1}^{\infty} \frac{1}{(2n+1)^2-(2k)^2} \cdot \frac{1}{(2m+1)^2-(2k)^2} = \frac{\pi^2 \delta_{nm}}{16(2n+1)^2} - \frac{1}{2(2n+1)^2(2m+1)^2}$$

$$n, m = 0, 1, 2, 3$$

For $B(n)$ and $G(n)$ in Eq. (1.5) read

$$B = \frac{5}{8n_0^2} + \frac{1}{4n_0(n_0+1)} - \frac{1}{8(n_0+1)^2} - \frac{1}{2(2n_0+1)^2} + \frac{4}{\pi^2}(1-G)$$

$$G = \frac{1}{4(n_0+1)^2} + \frac{1}{4(n_0+1)^3} + \frac{1}{(2n_0+1)^2} - \frac{1}{2(2n_0+1)^4} + \frac{1}{4}\left\{\frac{1}{n_0^2} - \frac{1}{(n_0+1)^2}\right\}\sum_{k=0}^{n_0-1}\frac{1}{(2k+1)^2} + \frac{1}{4}\left\{\frac{1}{n_0^3} - \frac{1}{(n_0+1)^3}\right\}\sum_{k=0}^{n_0-1}\frac{1}{2k+1}$$

For the fourth and fifth columns of Table 1 read

δ	$\lambda_{calc.}$
0.0321	438
0.0550	551
0.0835	656
0.1177	752

For δ in Eq. (2.2) read

$$\delta = \left(\frac{L}{\pi}\right)^3 \frac{1}{4aAn_0}$$

62.

Non-Empirical Calculation of the Diamagnetic Anisotropy of Benzene

K. Ohno, H. Yoshizumi and T. Itoh

(Department of Physics, University of Tokyo)

The large anisotropy of Diamagnetic susceptibility of aromatic compounds, which is considered to be due to the free migration of π-electrons, has been investigated by F. London [1] and others from the semi-empirical point of view, and the calculated ratio of the anisotropies of various molecules to that of benzene is in fairly good agreement with experiment.

As to the absolute value of anisotropy of benzene, computation were made by K. Kambe [2] and S. Fujii and S. Shida [3] using the antisymmetrized L.C.A.O. M.O. method. We have extended this treatment by taking configuration interaction into account.

We included all the configurations obtained by excitation of one or two electrons from the lowest configuration, namely nine A_{1g} states (Ψ_i) and three A_{2g} states (Ψ_i'). It is to be noted that A_{1g} and A_{2g} states interact with each other in the presence of external magnetic field.

The hamiltonian is

$$\mathcal{H}\Psi = \sum_{\nu=1}^{6}\left\{\frac{\hbar^2}{8\pi^2 m}\left(i\vec{\nabla}_\nu + \vec{\alpha}_\nu\right)^2 + \sum_{k=1}^{6} V_{k\nu}\right\} + \sum_{\mu,\nu=1}^{6}\frac{e^2}{r_{\mu\nu}}$$

$\vec{\alpha}_\nu = \frac{2\pi e}{hc}\vec{A}_\nu$: $\vec{A}_\nu$ is the vector potential at the position of the ν-th electron.

As usual, we use the molecular orbitals of the following form in the construction of the energy matrix.

$$\phi_\ell = (6\sigma_\ell^2)^{-\frac{1}{2}}\sum_{k=1}^{6}\exp\left\{\frac{2\pi i}{6}k\ell + i(\vec{\alpha}_k\cdot\vec{r}_\nu)\right\}\cdot U_k(r_\nu)$$

$\ell = 0, \pm1, \pm2, 3 \qquad \phi_\ell^* \neq \phi_{-\ell}$

σ_ℓ : normalization factor

$\vec{\alpha}_k = \frac{2\pi e}{hc}\vec{A}_k$: $\vec{A}_k$ is the vector potential at the position of the K-th nucleus.

$U_k(r_\nu)$: the $2p\pi$ A.O. of the K-th carbon atom

In calculating the matrix element, the integrals containing the gauge factor $\exp[i(\vec{\alpha}_k\cdot\vec{r}_\nu)]$ were, for simplicity, approximated in the following manner:

$$\int \exp[i(\vec{\alpha}_k - \vec{\alpha}_m)\cdot\vec{r}_\nu)]\, U_k\cdot U_m\, d\tau \fallingdotseq \exp\left[i\left(\vec{\alpha}_k - \vec{\alpha}_m\right)\cdot\frac{\vec{R}_k+\vec{R}_m}{2}\right)\Big]\int U_k\cdot U_m\, d\tau$$

where $\vec{R}_k$ is the position vector of the K-th carbon atom. Then, all the necessary integrals have been given in the paper by Parr, Craig and Ross. [4]

In the case of the vanishing magnetic field, the ground state wave function can be written as a linear combination of nine A_{1g} functions

$$\psi_{g(H=0)} = \sum_{i=1}^{9} c_i\,\psi_{i(H=0)}$$

Coefficients c_i are obtained by solving the secular equation.

As we are concerned with the diamagnetic susceptibility, we need to know the energy under external field to the 2nd power of the field strength. Since A_{1g} matrix elements have no term proportional to 1st power of the field strength, the energy under the external field is written as

$$W_I = \int \psi_g^*\,\mathcal{H}\,\psi_g\, d\tau = \sum_{i=1}^{9} c_i^2 W_i + 2\sum_{i,j=1}^{9} c_i c_j H_{ij}$$

when only A_{1g} states are considered. Here $W_i = \int \psi_i^*\,\mathcal{H}\,\psi_i\, d\tau$, $H_{ij} = \int \psi_i^*\,\mathcal{H}\,\psi_j\, d\tau$.

If we denote by W_{2p}' the energy of a 2p electron of an isolated carbon atom in the magnetic field H, $W_0 = 6W_{2p}'$ is the energy of the molecule when H is applied parallel to the molecular plane. Then the anisotropy of the diamagnetic susceptibility is expressed as follows:

$$\chi_I = -\frac{\partial^2(W_I - W_0)}{\partial H^2}$$

The contribution from the interaction between A_{1g} and A_{2g} states was estimated by the second order perturbation calculation.

$$\chi_{II} = -\frac{\partial^2 W_{II}}{\partial H^2}\ , \text{ where } \quad W_{II} = \sum_{i'=1}^{3}\frac{|(\psi_g|\mathcal{H}|\psi_i')|^2}{W_g - W_{i'}}$$

The results of numerical computation are given in the following Table.

χ_I (Single Con.)	$-21.70\ \left(\frac{2\pi e\,\delta}{6Rc}\right)^2$	64.0 %
χ_I (with C.I.)	-21.58 "	63.6 %
χ_{II}	0.67 "	2.0 %
$\chi = \chi_I + \chi_{II}$	-20.91 "	61.6 %
$\chi_{exp.}$	-33.9 "	100.0 %

As is seen in the table, the final value is about 60 % of the observed value and the effect of configuration interaction is rather small, namely less than 1 % of the observed value.

The discrepancy between calculated value and experimented one might be due to the following 3 reasons,

(1) The L.C.A.O. approximation was made.

(2) The approximation for the integrals mentioned above was introduced solely for the purpose of the simplification of calculations.

(3) We did not consider σ-electrons. But, the hypothetical benzene molecule, from which all π-electrons are removed, might show some amount of diamagnetic anisotropy. Furthermore the contribution to the diamagnetic anisotropy through the $\sigma-\pi$ interaction may exist.

References

1) F.London, Journ. de Phys. et Rad., 8, (1937) 397
2) K.Kambe, Reports of the Univ. of Electro-Comunication No.1 (1950) 143 (in Japanese)
3) S.Fujii and S.Shida, Bulletin of the Chemical Soc. of Japan 24, (1951) 242
4) R.G.Parr, D.P.Craig and I.G.Ross, J. Chem. Phys., 18, (1950) 1562

Cl.

Interaction between Donors and Acceptors

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*

(1) A simple general quantum-mechanical theory is presented for the interaction of electron acceptors and donors (Lewis acids and bases) to form 1 : 1 or n : 1 molecular compounds ranging from loose complexes to stable compounds. This puts into more accurate or more general form ideas which have been in frequent use for some time. The theory involves resonance between no-bond structures (A,B) and dative structures (A^- - B^+), where A is an acceptor atom, molecule, or ion and B is a donor atom, molecule, or ion. Two classes of donors (π, and n or onium, bases) and three classes of acceptors (π, ν or vacant-orbital, and σ or dissociative) are particularly considered; i(ionic) donors and acceptors are also mentioned. General and specific factors governing the strengths of interaction between acceptors and donors of various classes are deduced from the theory. (2) A special class of intense electronic absorption spectra characteristic of molecular compounds A·B, and non-existent for either partner A or B alone, is predicted. These are called charge-transfer spectra. (3) The forces which lead to complex-formation may be called charge-transfer forces. They may be comparable importance to London's dispersion forces in accounting for van der Waals attractions. They have characteristic specific orientational properties of possible importance for the manner of packing of molecules in liquids, in molecular crystals, in heterogeneous systems, and in biological systems. They may also important in adsorption. They should increase under compression and thus contribute to compressibilities. The effect of charge-transfer forces in lowering activation barries for chemical reactions is briefly discussed. (4) The benzene-iodine and the $BX_3 \cdot NR_3$ types of molecular compound and the Ag^+ complexes are considered in detail. The characteristic absorption peak of the benzene-iodine and related complexes near $\lambda 3000$, discovered by Benesi and Hildebrand, is identified with the predicted charge-transfer absorption. Its position and intensity are in good agreement with the theory. Theoretical considerations based on symmetries of quantum-mechanical wave functions often favor unsymmetrical geometrical configurations of molecular complexes. For example, they point to an off-axis position for the Ag^+ in the Ag^+-benzene complex, a result which is supported also by empirical evidence.

**

Extending earlier work, a classification of electron acceptors and donors each into a number of types is given in Section II. In an extension of Sidgwick's nomenclature, donors D and acceptors A are here defined (see Section I) as all those entities during whose interaction transfer of negative charge from D to A takes place, with the formation as end-product either of an additive combination $A_m \cdot D_n$ or of new entities. In all cases of 1 : 1 interaction, the wave function ψ of A·D (and, formally at least, of the end-products also in the dissociative case) is of the approximate form given in equation (1) with appropriate ionic or covalent bonding (or no bonding) between D and A, and between D^+ and A^-, depending on whether A and/or D are closed-shell molecules or ions, or radicals. Donors and acceptors as here defined correspond closely to nucleophilic and electrophilic reagents as defined by Ingold or, except for the inclusion here of donor and acceptor radicals, correspond rather well to bases and acids as defined by G. N. Lewis. In Section III, the applicability of an extension of eq. (1) to crystalline molecular compounds is considered briefly. A brief discussion and listing of possible or probable known charge-transfer spectra of donor-acceptor molecular complexes are given in Section IV and Table VI. Sections V - VIII contain further elucidation of matters discussed in Sections I - II and in ref. 2

The energy U of interaction between a donor and acceptor as a function of a charge-transfer coördinate C (a kind of reaction coördinate, so defined as to increase from 0 to 1 with increasing transfer of electronic charge from D to A) is studied in Section IX for interactions between donor-acceptor pairs of the various calsses defined here. In many cases, there should be two important minima in the U(C) curve, namely, one for a loose "outer complex" for small C, and one for a tighter "inner complex" often of ion-pair character, for large C (see Figs. 1-2). In any particular case, one of these is the stable form, while the other is an excited or activated state (lower in energy, however, than the "activated complex" which usually intervenes between them). However, in many cases where the donor and acceptor form only a loose outer complex or none at all in the vapor state or in an inert solvent, the inner complex may become the stable form under the coöperative action of a suitable active solvent. The latter functions by solvation of the inner complex or its ions, either acting mainly electrostatically, or in some cases acting as (or, with the assistance of) an auxiliary acceptor or donor (double complex formation). The formation of ion-pair clusters or ionic crystals (e.g. $NH_3 + HCl \rightarrow NH_4^+ Cl^-$) can play the same role as that of an electrostatically functioning solvent in stabilizing the inner complex of a donor-acceptor pair. In a few interaction types, a "middle complex" is important (cf. Fig. 3), corresponding either to an activated complex or intermediate in a reaction such as those involving a Walden inversion, or to a stable association product as in I_3^- or HF_2^-. Section X contains improvements and errata for the previous papers of this series. The Appendix, consisting of Tables III-VI, contains detailed descriptions of the various donor and acceptor types and of their modes of functioning.

Recent results obtained on iodine complexes at the University of Chicago will also be reported, particularly on the change which occur at low temperatures and at high pressures.

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* Abstract of Mulliken's paper Molecular Compounds and their Spectra. II Jour. Am. Chem. Soc. 74, 811(1952)

** Abstract of Mulliken's paper Molecular Compounds and their Spectra. III Jour. Phys. Chem. 56, 801(1952)

Interaction between Long Conjugated Double-bond Systems

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INTRODUCTION-----Concerning to the interaction between long conjugated double-bond systems, there are three points supposed to give rise to anormalies. In the first place the dimensions cannot be ignored, but occasionally larger than the intermolecular distances. In 1942, London[1] has discussed the van der Waals force between long molecules, regarding them as an assembly of electric monopoles, and has found that the force shows much deviations from the ordinary one about atoms or small, nearly spherical molecules, and the additivity of the interaction potentials does not hold any longer.

Secondly, the electronic, excited states of the molecules containing long conjugated double bonds lie so close at hand above the ground states that such molecules absorb lights of longer wavelengths and are sometimes coloured. Besides the long conjugated double-bonds, cntaini ng many mobile π -electrons, are highly polarizable, and the large polarization causes large van der Waals or dispersion forces. According to London the rough estimation of the van der Waals energy between two similar atoms or small molecules at the mutual distance of R is given by

$$-K\alpha^2 \Delta E / R^6$$

where α is the polarizability and ΔE the energy difference between the first excited state and the ground state. The numerical factor K depends on the mutual orientation of the molecules. If the two molecules stand in a line, the direction being of the polarization, K=1 and if the two are parallel, just facing each other, K=1/2; whereas if the molecules are freely rotating, K takes the value of 1/3.

The polarizability α can be known, although being averaged with respect to all directions, from the molecular refraction through the firmula

$$\alpha = \frac{3}{4\pi N} \cdot \frac{n^2-1}{n^2+2} \cdot \frac{M}{\rho}$$

where N is Avogadro's number, n ,the refractive index, M, the molecular weight and ρ the density.

The refractive indices are, however, hardly known for such highly conjugated cmpounds owing to the lack of experimental data. We have to estimate them from the sum of atomic refractions.

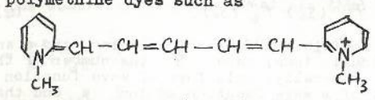
Generally, these compounds have rather high value of molecular refraction; they have some excess, called'exaltation', besides the sum of the atomic refractions with the characteristic cntribution of the double bonds called'increment'. If the molecular refraction of such a compound is as large as 40, the polarizability α becomes 1.8×10^{-23}cm^3. The dimensionless number $K\alpha^2/R^6$, which is the ratio of the van der Waals energy to the excitation energy, increases with decreasing R. For R=2.2 to 2.6 A the ratio amounts to unity. This means that for such short distances the role of the excited states become significant and the case cannot be trated only by a slight perturbation to the ground states.

If there exist electrostatic forces such as Coulombic attraction or repulsion between charged ions, or dipole-dipole interaction between polar molecules besides, the effect becomes more important for larger distances[2][3]For instance, the electrostatic energy between singly charged ions amounts to 2.2 electron volts at the distance of as large as 6.5A, the energy being equal to the light quantum of 5500A green light.

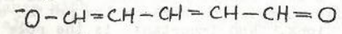
Lastly, when the molecules are almost in contact with each other, that is, the shortest distance between the molecules is smaller than about 3Å, the overlap of the electron clouds on the different molecules takes place. The prominent, streamer-like wave functions of the π-electrons play an important role. Hereby, the interaction at close proximity depends largely upon the delicate change in the configuration of the wave functions.

In this paper, the influences of the length, the mutual orientation, and the first excited levels of the long conjugated double-bond systems upon the interaction between them. The interaction between a pair of molecular ions, of polar molecules and of non-polar molecules are discussed. The degree of the anormalies is largest for the first and smallest for the last.

DIMINUTION OF THE COULOMBIC REPULSIVE FORCE BETWEEN SIMILAR IONS-----The polymethine dyes such as

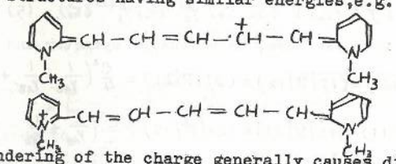


(I)



(II)

being monovalent ions,on which the positive or negative charge can move along the cnnjugated double-bonds by quantum mechanical resonance among similar structures having similar energies,e.g.



etc.

Such wandering of the charge generally causes diminution of the repulsive force between ions as shown in the following.

Before going through the details, let us deal with a simplified model to make the matter comprehensible. The molecular ion of the length L is considered to be resonating between the two extreme structures, each has the charge concentrated at one end or another. We denote the two structures by -1/2 and +1/2 respectively. If the energy of these structures are equally f and the interaction between the two is α, the energy E of the resonating molecular ion is, so far as the overlap of the wave functions is ignored, determined by the secular equation

$$\begin{vmatrix} f-E & \alpha \\ \alpha & f-E \end{vmatrix} = 0,$$

the two roots being $E^{(1)} = f+\alpha$ and $E^{(2)} = f-\alpha$, which express the ground and the excited states of the ion respectively.The corresponding orthogonally normalized wave functions are

$$\varphi^{(1)} = \frac{1}{\sqrt{2}}\{\varphi(-1/2) + \varphi(+1/2)\},$$
$$\varphi^{(2)} = \frac{1}{\sqrt{2}}\{\varphi(-1/2) - \varphi(+1/2)\}, \qquad (1)$$

$\varphi(-1/2)$ and $\varphi(+1/2)$ representing the wave functions of the two component structures. We presume that the wave functions concentrated at either end of the ion, namely

$$\varphi(-1/2) = \delta(x+L/2),$$
$$\varphi(+1/2) = \delta(x-L/2), \qquad (2)$$

where x is the coordinate on the molecule taking the centre as the origin and δ means Dirac's delta function.

The energy of interaction between two such ions is not difficult to estimate. Let the distance from an end, A or A', of an ion a to an end, B or B', of another ion r_{AB}, $r_{A'B}$ and so on, the mutual potential between the two structures, -1/2 and 1/2 and so on, are

$$\begin{aligned} V(-1/2, -1/2) &= e^2/r_{AB} \\ V(-1/2, +1/2) &= e^2/r_{AB'} \\ V(+1/2, -1/2) &= e^2/r_{A'B} \\ V(+1/2, +1/2) &= e^2/r_{A'B'} \end{aligned} \qquad (3)$$

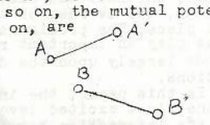


Fig. 1

We assume the wave function of the whole system composed of the pair of ions to be

$$\Phi = \sum_{i=1,2} \sum_{j=1,2} A_{ij}\, \varphi_a^{(i)}(s_a)\, \varphi_b^{(j)}(s_b), \qquad (4)$$

where A_{ij}'s are the proper coefficients determined later, and a and b designate the two individual ions, and S the number of the structures, -1/2 or 1/2. Generally, this form of wave function is not equivalent to a product of a wave function of ion a and that of b. This means that there exist correlation between the motion of the charges on the individual ions, and important is the role of this correlation as shown later.

Writing $(ij \mid V \mid kl)$ in place of the appearing sum

$$\sum_{s_a=-\frac{1}{2},+\frac{1}{2}} \sum_{s_b=-\frac{1}{2},+\frac{1}{2}} \varphi_a^{(i)}(s_a)\, \varphi_b^{(j)}(s_b)\, V(s_a, s_b)\, \varphi_a^{(k)}(s_a)\, \varphi_b^{(l)}(s_b), \quad (5)$$

where i, j, k and l are 1 or 2, we have, in virtue of symmetry and (2).

$$(11|V|11) = (22|V|22) = (12|V|12) = (21|V|21) = \frac{e^2}{4}\left(\frac{1}{r_{AB}} + \frac{1}{r_{AB'}} + \frac{1}{r_{A'B}} + \frac{1}{r_{A'B'}}\right),$$

$$(11|V|22) = (22|V|11) = (12|V|21) = (21|V|12) = \frac{e^2}{4}\left(\frac{1}{r_{AB}} + \frac{1}{r_{AB'}} - \frac{1}{r_{A'B}} - \frac{1}{r_{A'B'}}\right),$$

The two values are writtenas p and q respectively. The other $(ij|V|kl)$ including $(11|V|12)$ etc., vanish.

Then the energy E of the whole system is determined by the secular equation of the fourth order,

$$\begin{vmatrix} 2E^{(1)}+p-E & 0 & 0 & q \\ 0 & E^{(1)}+E^{(2)}+p-E & q & 0 \\ 0 & q & E^{(1)}+E^{(2)}+p-E & 0 \\ q & 0 & 0 & 2E^{(2)}+p-E \end{vmatrix} = 0, \qquad (6)$$

which is expressed by the produce of two quadratic equation, that is,

$$\{(2E^{(1)}+p-E)(2E^{(2)}+p-E) - q^2\}\{(E^{(1)}+E^{(2)}+p-E)^2 - q^2\} = 0 \qquad (7)$$

The four roots are, begining with the smallest,

$$\begin{aligned} E_1 &= E' - \sqrt{q^2 + (\Delta E)^2}, \\ E_2 &= E' - q, \\ E_3 &= E' + q, \\ E_4 &= E' + \sqrt{q^2 + (\Delta E)^2}, \end{aligned} \qquad (8)$$

where

$$\begin{aligned} E' &= E^{(1)} + E^{(2)} + p \\ \Delta E &= E^{(2)} - E^{(1)}. \end{aligned}$$

As the interaction between the ions becomes weaker, for instance owing to that the mutual distance become larger, p and q become smaller, and at last E_1 coincides with $2E^{(1)}$, E_2 and E_3 with $E^{(1)}+E^{(2)}$, and E_4 with $2E^{(2)}$. Then, to know the mode of interaction between two ions, both being in the ground state, we may observe the change of E_1. Accordingly, the energy of interaction U for the ions in the ground states is given by

$$U = E_1 - 2E^{(1)} = \Delta E + \frac{e^2}{4}\left(\frac{1}{r_{AB}} + \frac{1}{r_{AB'}} + \frac{1}{r_{A'B}} + \frac{1}{r_{A'B'}}\right) - \sqrt{(\Delta E)^2 + \frac{e^4}{16}\left(\frac{1}{r_{AB}} + \frac{1}{r_{A'B'}} - \frac{1}{r_{A'B}} - \frac{1}{r_{AB'}}\right)^2}$$

If ΔE is sufficiently large compared to q, we have (9)

$$U = \frac{e^2}{4}\left(\frac{1}{r_{AB}} + \frac{1}{r_{AB'}} + \frac{1}{r_{A'B}} + \frac{1}{r_{A'B'}}\right)$$

This is the same energy with the electrostatic one among the four ends of the two molecules, each supposed to have the averaged charge e/2. To the contrary, if ΔE is much less than q, we obtain

$$U = \frac{e^2}{2}\left(\frac{1}{r_{A'B}} + \frac{1}{r_{AB'}}\right) \quad \text{or} \quad \frac{e^2}{2}\left(\frac{1}{r_{AB}} + \frac{1}{r_{A'B'}}\right)$$

in accordance with $\frac{1}{r_{A'B}} + \frac{1}{r_{AB'}}$ is smaller or larger than $\frac{1}{r_{AB}} + \frac{1}{r_{A'B'}}$ respectively. For example, the two ions are fixed in a just parallel position, the distance being D, we have

$$\begin{aligned} r_{AB} &= r_{A'B'} = D \\ r_{A'B} &= r_{AB'} = \sqrt{D^2 + L^2} \end{aligned}$$

and

$$U = \Delta E + \frac{1}{2}\left(\frac{e^2}{D} + \frac{e^2}{\sqrt{D^2+L^2}}\right) - \sqrt{(\Delta E)^2 + \frac{1}{4}\left(\frac{e^2}{D} - \frac{e^2}{\sqrt{D^2+L^2}}\right)^2}, \qquad (10)$$

which tends to

$$U = \frac{1}{2}\left(\frac{e^2}{D} + \frac{e^2}{\sqrt{D^2+L^2}}\right) \quad \text{or} \quad U = \frac{e^2}{\sqrt{D^2+L^2}},$$

in accordance with $\Delta E \gg q$ or $\Delta E \ll q$.

If the two long ions are brought into a line, the distance between the centres being D, we have

$$U = \Delta E + \frac{e^2}{2D} + \frac{De^2}{2(D^2-L^2)} - \sqrt{(\Delta E)^2 + \left(\frac{e^2}{2D} - \frac{De^2}{2(D^2-L^2)}\right)^2}, \qquad (11)$$

which tends to

$$U = \frac{e^2}{2D} + \frac{De^2}{2(D^2-L^2)} \quad \text{or} \quad U = \frac{e^2}{2(D-L)} + \frac{e^2}{2(D+L)}$$

in accordance with $\Delta E \gg q$ or $\Delta E \ll q$ respectively.

The consideration above is, rather schematic and of qualitative nature. We can proceed to the more detailed calculation based on the theory of polymethine dyes, which we owe to Pauling, Foerster and Herzfeld.[4] According to this, for a polymethine dye the chromophore being a linear chain of 2N+1 carbon atoms, we have to take the resonance among 2N+1 structures into consideration. These are, for instance if N=2,

$$\overset{+}{C} - C - C - C - C,$$
$$C - C^{+} - C - C - C,$$
$$C - C - C^{+} - C - C,$$
$$C - C - C - C^{+} - C,$$
$$C - C - C - C - C^{+},$$

We name these structures as -N, -N+1, ...,+N respectively and designate any one of them by s. For the sake of simplicity we assume the energy of these structures are all equal, i. e.,

$$(s|H|s) = f \qquad s = -N, -N+1, \cdots\cdots, +N.$$

Moreover, the resonance (s | H | s') between the two structures, s and s are presumed to be

$$(s|H|s') = \alpha, \quad \text{if} \quad s - s' = \pm 1$$
$$(s|H|s') = 0, \quad \text{otherwise.}$$

Then the energy E of the molecule ion is determined by

$$\begin{vmatrix} f-E & \alpha & 0 & \cdots \\ \alpha & f-E & \alpha & \cdots \\ 0 & \alpha & f-E & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix} = 0.$$

The roots are

$$E = f + 2\alpha\cos\mu,$$

and the eigenfunctions,

$$\varphi(s) = \frac{1}{\sqrt{N+1}} \sin \mu s \quad \text{with} \qquad \mu = \frac{n\pi}{N+1} \quad (n = 1, 2, \cdots N),$$

and

$$\varphi(s) = \frac{1}{\sqrt{N+1}} \cos \mu s \quad \text{with} \qquad \mu = (n+\tfrac{1}{2})\frac{\pi}{N} \quad (n = 0, 1, \cdots N).$$

To determine the interaction between two such ions both in the ground states, we take the two states with the lowest energy only, the energies and the orthogonally normalized wave functions being

$$E^{(1)} = f + 2\alpha\cos\frac{\pi}{2(N+1)}, \qquad \varphi^{(1)}(s) = \frac{1}{\sqrt{N+1}} \cos\frac{\pi s}{2(N+1)}.$$

and

$$E^{(2)} = f + 2\alpha\cos\frac{\pi}{N+1}, \qquad \varphi^{(2)}(s) = \frac{1}{\sqrt{N+1}} \sin\frac{\pi s}{N+1},$$

respectively. For the two ions standing face to face with each other keeping the mutual distance D, the integrals, or better to say, the sums necessary to calculate the interaction are

$$(ij|V|kl) = \sum_{s_a=-N}^{N} \sum_{s_b=-N}^{N} \varphi^{(i)}(s_a)\varphi^{(j)}(s_b) V(s_a, s_b) \varphi^{(k)}(s_a)\varphi^{(l)}(s_b),$$

where

$$V(s_a, s_b) = \frac{e^2}{\sqrt{D^2 + \frac{L^2}{4N^2}(s_a - s_b)^2}}$$

and i, j, k, l = 1 or 2; s_a, s_b = -N, ...,+N. L means the distance between the two termnals of the conjugated double-bonds. If N is large, the sum with respect to s_a and s_b can be approximately replaced by integration with respect to the coordinates x and y, which are the distances from the middle point of each ion. Then the sums (ij | V | kl) are lead to the integrals

$$(11|V|11) = \int_{-L/2}^{L/2}\int_{-L/2}^{L/2} V(x,y)\left[\varphi^{(1)}(x)\right]^2\left[\varphi^{(1)}(y)\right]^2 dx\,dy,$$

$$(22|V|22) = \int_{-L/2}^{L/2}\int_{-L/2}^{L/2} V(x,y)\left[\varphi^{(2)}(x)\right]^2\left[\varphi^{(2)}(y)\right]^2 dx\,dy,$$

$$(12|V|12) = (21|V|21)$$
$$= \int_{-L/2}^{L/2}\int_{-L/2}^{L/2} V(x,y)\left[\varphi^{(1)}(x)\right]^2\left[\varphi^{(2)}(y)\right]^2 dx\,dy,$$
$$(11|V|22) = (21|V|12) = (12|V|21) = (22|V|11)$$
$$= \int_{-L/2}^{L/2}\int_{-L/2}^{L/2} V(x,y)\,\varphi^{(1)}(x)\varphi^{(2)}(x)\varphi^{(1)}(y)\varphi^{(2)}(y)\,dx\,dy,$$

where $$V(x,y) = \frac{e^2}{L^2}\cdot\frac{1}{\sqrt{D^2+(x-y)^2}}.$$

We call these integrals p_{11}, p_{22}, p_{12} and q respectively. All other integrals vanish in virtue of symmetry. Unfortunately these integrals cannot be expressed by a known function. So we have to carry out numerical calculation. The energy E of the whole system is given by

$$\begin{vmatrix} 2E^{(1)}+p_{11}-E & 0 & 0 & q \\ 0 & E^{(1)}+E^{(2)}+p_{12}-E & q & 0 \\ 0 & q & E^{(1)}+E^{(2)}+p_{12}-E & 0 \\ q & 0 & 0 & 2E^{(2)}+p_{22}-E \end{vmatrix} = 0. \qquad (12)$$

The four roots are

$$\left.\begin{matrix} E_1 \\ E_4 \end{matrix}\right\} = E^{(1)}+E^{(2)}+\frac{1}{2}(p_{11}+p_{22}) \mp \left[q^2+\left\{(E^{(2)}+\frac{p_{22}}{2})-(E^{(1)}+\frac{p_{11}}{2})\right\}^2\right]^{1/2}, \qquad (13)$$
$$\left.\begin{matrix} E_2 \\ E_3 \end{matrix}\right\} = E^{(1)}+E^{(2)}+p_{12} \pm q$$

The interaction between two ions in the ground states are

$$U = E_1 - 2E^{(1)} = \Delta E + \frac{1}{2}(p_{11}+p_{22}) - \left[q^2+\left\{\Delta E+\frac{1}{2}(p_{22}-p_{11})\right\}^2\right]^{1/2} \qquad (14)$$

The numerical calculation put forth for $\Delta E = 0$, 1 and infinity. The results are very similar to those of the simpler model above, the effective length L being taken as 1/2.8 of the real one.

For a pair of dissimilar ions, the energy levels being different for each ions, we have to use the mean value for ΔE in the results obtained above.

INCREASE OF ATTRACTIVE FORCE BETWEEN OPPOSITE IONS.------The similar consideration, when applied to the ion pair with opposing change, lead to an increase of the ordinary Coulombic attraction. If the two ions have long conjugated double bonds, for example they are (I) and(II), the last result obtained can be applied mutatis mutandis. That is, the inversion of the sign of the potentials (3) takes place, and p and q become negative, resulting the lowering of energy on approach. The interaction of the ions in the ground states are given by

$$U = E_1 - (E_a^{(1)}+E_b^{(1)}) = \frac{1}{2}(\Delta E_a + \Delta E_b) + p - \sqrt{\frac{1}{4}(\Delta E_a + \Delta E_a)^2 + q^2} \qquad (15)$$

and is always negative.

As an numerical example, we consider the just parallel position of the pair of ions, and put $L_a = L_b = L$ and $-e^2/L = K$, $D/L = \delta$, and calculated the ratio U : (e^2/D), the relative magnitude of the attraction taking the one between two point charges as the standard. The four cases of $(\Delta E_a + \Delta E_b)/2$: K are 0, 1, 2 and infinity were examined and the results are shown in Table I.

Table I.

δ	$\frac{1}{2}(\Delta E_a + \Delta E_b)$: K =	0	1	2	∞	Uniform rods
0.1		1	0.901	0.832	0.550	0.419
0.2		1	0.847	0.763	0.598	0.597
0.5		1	0.796	0.761	0.724	0.826
1		1	0.864	0.859	0.854	0.934
2		1	0.948	0.948	0.947	0.980
5		1	0.990	0.990	0.990	0.997
10		1	0.998	0.998	0.998	0.998

The last column shows the relative attractive potential between two rods opposite and uniformly charged calculated through

$$U = \frac{2e^2}{L}\left(\sinh^{-1}\frac{1}{\delta} - \sqrt{\delta^2+1} + \delta\right).$$

It is seen that the interaction energies are always larger than those between the rods as long as the ions and being equally charged. The effect is larger for shorter distances and for smaller ΔE. the attractive force approaching to that between two point chrges. Taking L= 5A, and then $e^2/L = 2.5$ eV, the energies are shown in Fig. 2. The curve for $\overline{\Delta E} = (\Delta E_a + \Delta E_b)/2 = 1$ approaches to the point-charge curve ($\Delta E = 0$) for shorter distances and to the curve $\overline{\Delta E} = \infty$ for larger distances, as is expected. As a result the repulsive force appears to vary with the power larger than two, say, three, of the distance

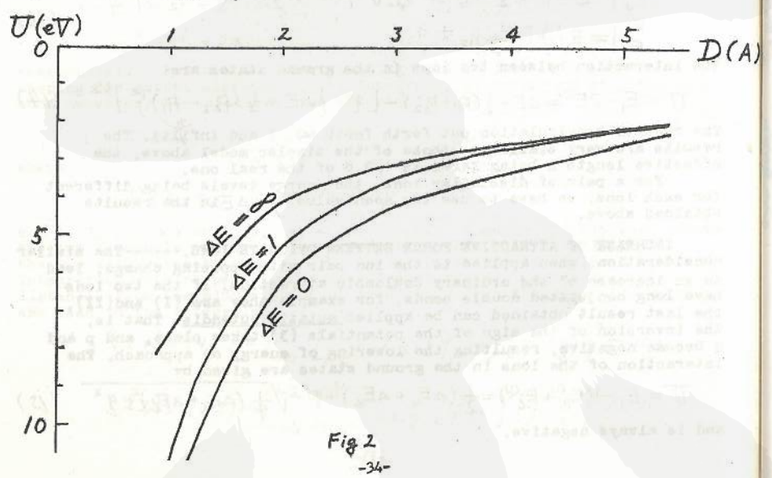


Fig 2

FORCES BETWEEN TWO POLAR MOLECULES ------- The similar procedure can be applied to two neutral polar molecules. Again it is presumed that the charges are concentrated at the both end of the molecule. Therefore, if the dipole moment of the molecule is μ, and the lengh, L, then the charges $+\epsilon = \mu/L$ and $-\epsilon = -\mu/L$ appear at the both ends of it. Now we deal with the configuration of Fig.3, which is expected to have the lowest energy.

Only the two lowest states of the molecule are taken into account. As hitherto it was so, these states are supposed to be the products of the resonance between two component structures, the energies being f_1 and f_2, the wave functions, φ_1 and φ_2, the charges at the ends, $\pm z\epsilon$ and $\pm\zeta\epsilon$ respectively and the interaction energy between the two structures, α.

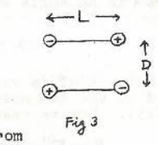


Fig 3

The energies of a free molecule are determined from

$$\begin{vmatrix} f_1 - E & \alpha \\ \alpha & f_2 - E \end{vmatrix} = 0 .$$

They are

$$E^{(1)} = \frac{1}{2}(f_1 + f_2) - \frac{1}{2}\left\{4\alpha^2 + (f_2 - f_1)^2\right\}^{\frac{1}{2}},$$

$$E^{(2)} = \frac{1}{2}(f_1 + f_2) + \frac{1}{2}\left\{4\alpha^2 + (f_2 - f_1)^2\right\}^{\frac{1}{2}},$$

corresponding to the ground and the excited atates respectively. The corresponding wave functions are

$$\varphi^{(1)} = \left(\frac{1}{2} + \frac{f_1 - f_2}{2\alpha}\right)^{\frac{1}{2}}\varphi_1 + \left(\frac{1}{2} - \frac{f_1 - f_2}{2\alpha}\right)^{\frac{1}{2}}\varphi_2,$$

$$\varphi^{(2)} = \left(\frac{1}{2} - \frac{f_1 - f_2}{2\alpha}\right)^{\frac{1}{2}}\varphi_1 - \left(\frac{1}{2} + \frac{f_1 - f_2}{2\alpha}\right)^{\frac{1}{2}}\varphi_2,$$

and the dipole moments,

$$\mu^{(1)} = \frac{1}{2}(z+\zeta)e L - \frac{f_2 - f_1}{2\alpha}(z-\zeta)e L,$$

$$\mu^{(2)} = \frac{1}{2}(z+\zeta)e L + \frac{f_2 - f_1}{2\alpha}(z-\zeta)e L.$$

Let V_{ij} the electrostatic potential between the first molecule in the i -th state and the second molecule in the j -th state, here i and j being 1 or 2. Then

$$V_{11} = -z^2e^2\left(\frac{1}{D} - \frac{1}{\sqrt{D^2+L^2}}\right)$$

$$V_{22} = -\zeta^2e^2\left(\frac{1}{D} - \frac{1}{\sqrt{D^2+L^2}}\right)$$

$$V_{12} = V_{21} = -z\zeta e^2\left(\frac{1}{D} - \frac{1}{\sqrt{D^2+L^2}}\right)$$

Denoting

$$\sum_{r=1}^{2}\sum_{s=1}^{2}\varphi^{(i)}(r)\,\varphi^{(j)}(s)\,V(r,s)\,\varphi^{(k)}(r)\,\varphi^{(l)}(s)$$

by $(ij\,|\,V\,|\,kl)$, we have

$$(11\,|\,V\,|\,11) = V_{11}\cos^4\frac{\chi}{2} + 2V_{12}\sin^2\frac{\chi}{2}\cos^2\frac{\chi}{2} + V_{22}\sin^4\frac{\chi}{2},$$

$$(22\,|\,V\,|\,22) = V_{11}\sin^4\frac{\chi}{2} + 2V_{12}\sin^2\frac{\chi}{2}\cos^2\frac{\chi}{2} + V_{22}\cos^4\frac{\chi}{2},$$

$$(12\,|\,V\,|\,12) = (21\,|\,V\,|\,21) = V_{11}\cos^2\frac{\chi}{2}\sin^2\frac{\chi}{2} + 2V_{12}\left(\cos^4\frac{\chi}{2} + \sin^4\frac{\chi}{2}\right) + V_{22}\cos^2\frac{\chi}{2}\sin^2\frac{\chi}{2}$$

$$(11|V|22) = (22|V|11) = (21|V|12) = (12|V|21)$$
$$= (V_{11} - 2V_{12} + V_{22}) \cos^2\frac{X}{2}\sin^2\frac{X}{2}$$

where X is an angle such as

$$\cos X = (f_2 - f_1)/\omega$$

Other $(ij|V|kl)$'s vanish. For the energy E of the whole system composed of the two molecules we have (12) again, and the roots expressed by (13). Now we examine the smallest root

$$E_I = E^{(1)} + E^{(2)} + \frac{1}{2}(P_{11}+P_{22}) - \left[q^2 + \left\{E^{(2)} - E^{(1)} + \frac{1}{2}(P_{22}-P_{11})\right\}^2\right]^{\frac{1}{2}}$$

At a small distance, such that

$$\left(E^{(2)} + \frac{P_{22}}{2}\right) - \left(E^{(1)} + \frac{P_{11}}{2}\right) \ll q$$

holds, we have

$$U = E_I - 2E^{(1)} = -\gamma\left(\frac{1}{D} - \frac{1}{\sqrt{D^2+L^2}}\right),$$

where

$$\gamma = e^2\left(Y^2\cos X\cos^2\frac{X}{2} + YZ\sin^2 X - Z^2\cos X\sin^2\frac{X}{2}\right).$$

So U is proportional to 1/D or 1/D according that $D \ll L$ or $D \gg L$,
At further distances it becomes

$$\left(E^{(2)} + \frac{P_{22}}{2}\right) - \left(E^{(1)} + \frac{P_{11}}{2}\right) \gg q$$

and we have

$$U = P_{11} - q^2/2\left\{\left(E^{(2)} + \frac{P_{22}}{2}\right) - \left(E^{(1)} + \frac{P_{11}}{2}\right)\right\}$$

The first term corresponds to the interaction of the permanent dipoles and the second to the van der Waals force. This can be known from the fact that when $D \gg L$, the former is proportional to the inversed third power and the latter to the inversed inversed sixth power of the distance D.

FORCES BETWEEN NON-POLAR LONG MOLECULES-------It seems to be the easiest way to have the intermolecular potentials between two non-polar molecules that we merely put $Z = -Z$ and $f_1 = f_2$ in the results of the last chapter. That is, to consider a non-polar molecules to be a mesomeric state of the two, oppositely oriented dipoles with equal intensities. Generally it is not the case, but to the ground state of such a molecule, the contribution of the non-polar structure; which has the lowest energy of all, is the largest. Some structures with higher energies being polar, however, in virtue of symmetry, make twins having opposed orientations. Even if we confine ourselves to the simplest case, we must take the normal non-polar structure and the two polar structures of higher energies and of equally and oppositely polarized, three in all. The former procedure can yet be applied but is more complicated. For instance, we have to deal with equations of the sixth order. Here we do not go further, but we may say that such interaction are rather small, owing to the weak interaction between non-polar structures.

However, even the structures are non-polar, they may have quadratic or higher electric momensts. With these, the non-polar structures can interact each other[5] and in some cases this type of interaction might be of some importance.

INTERACTION AT VERY SHORT DISTANCES--------The procedure above are applicable for moderate and large distance. But, for shorter distances, the assumption of the concentrated wave functions are not valid, owing to that the wave functions of π-electrons begin to overlap.

The limit lies at about 3A. We have to use the correct, spatially diffuse wave functions for the calculations of $(ij|V|kl)$. The exchange integrals become more important rather than the Coulombic integrals.

At this stage, there exist large anisotropies and selectivities of the intermolecular forces.[6] For the sake of simplecity, we consider that only two $2p\pi$ electrons exist in a molecule. If the molecule has V_h symmetry like ethylene, we have the two molecular orbitals, the symmetry being B_{3u} and B_{2g} restectively. considering the two electrons and their spins, we have the states ^1A_g, ^3B_u, ^1B_u and ^1A_g (excited), for the molecule as a whole.

When a pair of such molecules close together, the excited states affect the interaction as stated above. For very short distances, the effect of the triplet states becoles more important, owing to that they have a possibility of making chemical bonds between the two molecules by pairing the spins with each other. This is more distinguishable for the configuration (B) of Fig. 4, having the possible two σ-σ bonds between the molecule.

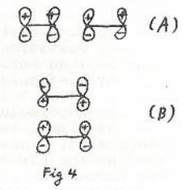


Fig 4

These will be of significant for the chemical reactivity. When the electron transfer from molecule to molecule takes place besides, we have to take the ionic structures as well as the neutral ones into account.

CONCLUSION-------- From the derivation above, the following effects are to be expected:

(1) The non-additivity of intermolecular potentials.
(2) The increment of the second virial coefficient in the pressure of gaseous state or in the osmotic pressure of solutions.
(3) Deviation from Coulombic law, affecting the theory of electrolytes.
(4) Bathochromic effects.
(5) Tendency of association of dye ions or molecules.
(6) Polar molecules, attracting each other, orientate so as to make the energy smallest. As a result, an electronegative atom in a molecule comes near an electropositive atom of the other molecule, and vice versa. Our effects help the orientation tendency as well as strengthen the electronegativity or the electropositivity respectively. This promotes the chemical reactivity. The sidelong predominated wave functions of the π-electrons may be of advantageous for the reaction.

LITERATURES

1) F. London : J. Phys. Chem., 46 (1942), 305.
2) F. London : Trans. Faraday Soc., 32 (1936), 8.
3) I. Oshida : Bulletin of the Kobayasi Institute of Physical Research, 1 (1951),240 ; 2 (1952), 175 (in Japanese).
4) e.g. K.F. Herzfeld: J. Chem. Phys., 10 (1942), 508
5) C. A. Coulson and P. L. Davis: Trans. Faraday Soc.,43 (1952),777.
6) M.Mizushima: Busseiron Kenkyu, No.5 (1947), 25 (in Japanese).

c1. Absorption Spectra of Dyes in Solutions

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The absorption specra of dyes in solutions are shifted from those in vapor and in inert solvents, both in wave-length and in intensities. These solvent effects are classified as follows,

1. dielectric effect
2. solvation effect
3. association (or micelle formation)
4. electrolytic dissociation equilibrium and salt effect
5. adsorption
6. intermolecular resonance

At first, the effects on absorption specra of polar solvents are considered, neglecting the solvation effect. That effect is treated with by the first and second order perturbation theory, and the following formula is obtained,

$$
\begin{aligned}
hc\,\Delta\sigma &= \left\{\frac{2(D-1)}{2D+1} - \frac{2(n^2-1)}{2n^2+1}\right\}\frac{M_g^2 - M_g\cdot M_e}{a^3} + \frac{3(n^2-1)}{2n^2+1}\frac{M_g^2 - M_e^2}{a^3} \\
&+ \frac{2(2D+1)(D-n^2)}{3(2D+n^2)D}\frac{kT}{a^3}\left\{\sum_{m\neq g}\frac{(g|M_0|m)^2}{\epsilon_m-\epsilon_g} - \sum_{m\neq e}\frac{(e|M_0|m)^2}{\epsilon_m-\epsilon_e}\right\} \\
&+ \left(\frac{2(D-1)}{2D+1}\right)^2\frac{1}{a^6}\left\{3\sum_{m\neq g}\frac{M_g\,(g|M_0|m)^2}{\epsilon_m-\epsilon_g} - \sum_{m\neq e}\frac{M_g\,(e|M_0|m)^2}{\epsilon_m-\epsilon_e}\right. \\
&\qquad \left. - 2M_g\cdot M_e\sum_{m\neq g}\cos^2\theta_{mg}\,\frac{(g|M_0|m)^2}{\epsilon_m-\epsilon_g}\right\} \\
&+ \frac{2(n^2-1)}{2n^2+1}\frac{1}{a^3}\left\{\sum_{m\neq g}(g|M_0|m)^2\left(1-\frac{\epsilon_m-\epsilon_g}{E_n-E_g}\right)\right. \\
&\qquad \left. - \sum_{m\neq e}(e|M_0|m)^2\left(1-\frac{\epsilon_m-\epsilon_e}{E_n-E_g}\right)\right\}
\end{aligned}
$$

The first and the second terms are both called the polarization effect, giving either red shift or blue shift. The third and the fourth terms, giving always blue shift, are called the induction effect and the polarization-induction effect, respectively. The last term, which exists also in non-polar solvents and gives red shift, is called the dispersion effect. The formula above can often be much simplified and is used very conveniently in discussing the light absorption in polar solvents. It has been used to explain Brooker's results and other various effects on the light absorption of merocyanines, successfully.

The treatment without using the perturbation theory is now being developed.

In the formula above, $\Delta\sigma$ is the increase of the wave number of the absorption maximum, D and n are the dielectric constant and the refractive index of solvent, a is the radius of the cavity in which a dye molecule exists, ϵ's and E's are the energy of various states of dye molecule and solvent molecule, respectively, and M's are the matrics elements of dipole moment of dye molecule.

D1. Theory of Collision between simple Molecules and its Applications to some Phenomena in Gases

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Most calculations for the elastic molecular collisions are usually done by employing the rigid sphere model or Lennard-Jones model or other spherically symmetrical potential fields while the calculations of the probabilities of vibrational or rotational transitions have been made for the special orientations of the two colliding molecules.[1]

The object of our present study is to treat the collision processes between non-spherical molecules in the three-dimensional space. For the present, we shall confine ourselves to the cases of collision between two diatomic molecules. The collision between a diatomic molecule and a monatomic one may be treated in exactly the same way, while the triatomic molecules will bring some troublesomeness into the practical calculations.

1

The internal wave function of a free diatomic molecule has the following form (See Fig.1.; Atomic units are used throughout this note.)

$$\frac{1}{\xi}\Phi_n^{\ell}(\xi)\,Y_{\ell m}(\theta,\varphi) \qquad (1)$$

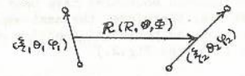


Fig.1

where Φ_n^{ℓ} satisfies the equation of the form

$$\left\{\frac{d^2}{d\xi^2} - \frac{\ell(\ell+1)}{\xi^2} - 2m\,V(\xi) + 2m\,W_{n\ell}\right\}\Phi_n^{\ell}(\xi) = 0, \qquad (2)$$

and $Y_{\ell m}$ are the usual spherical harmonics. The electronic wave function does not appear explicitly in this note. Then we may expand the wave function of the two molecule system in the center-of-gravity system as follows

$$\Psi = \sum \frac{1}{R} f^{j\nu n_1 n_2}_{\ell_1 m_1 \ell_2 m_2}(R)\, Y_{j\nu}(\Theta,\Phi)\,\frac{1}{\xi_1}\Phi_{n_1}^{\ell_1}(\xi_1)\,Y_{\ell_1 m_1}(\theta_1,\varphi_1)\,\frac{1}{\xi_2}\Phi_{n_2}^{\ell_2}(\xi_2)\,Y_{\ell_2 m_2}(\theta_2,\varphi_2). \qquad (3)$$

By substituting this expansion into the Schrödinger equation, we have for the functions f(R) the following set of equations :

$$\frac{1}{2M}\left(\frac{d^2}{dR^2} - \frac{j(j+1)}{R^2} + k_\alpha^2\right) f_\alpha(R) = \sum_{\alpha'}(\alpha|V_{12}|\alpha')\, f_{\alpha'}(R) \qquad (4)$$

Here α stands for a set $(j, \nu, n_1, n_2, \ell_1, m_1, \ell_2, m_2)$ and

$$(\alpha|V_{12}|\alpha') = \iint \sin\Theta\, d\Theta\, d\Phi\, Y^*_{j\nu}(\Theta,\Phi)\, Y_{j'\nu'}(\Theta,\Phi) \int \Phi^{\ell_1}_{n_1}(\xi_1)\,\Phi^{\ell_1'}_{n_1'}(\xi_1)\,d\xi_1 \int \Phi^{\ell_2}_{n_2}(\xi_2)\,\Phi^{\ell_2'}_{n_2'}(\xi_2)\,d\xi_2 \times$$
$$\iint \sin\theta_1\, d\theta_1\, d\varphi_1\, Y^*_{\ell_1 m_1}(\theta_1,\varphi_1)\, Y_{\ell_1' m_1'}(\theta_1,\varphi_1) \iint \sin\theta_2\, d\theta_2\, d\varphi_2\, Y^*_{\ell_2 m_2}(\theta_2,\varphi_2)\, Y_{\ell_2' m_2'}(\theta_2,\varphi_2)\, V_{12}. \qquad (5)$$

V_{12} is the intermolecular force potential.

Alternatively, we may employ the representation in which the total angular momentum quantum number J, ν (these are always good quantum numbers) have definite values. The nuclear spin, if exists, does not couple strongly with the orbital angular momenta and , therefore, we may safely omit this from J and ν. Thus by using

$$\Upsilon^{J\mu}_{j\ell_1\ell_2 L} = \sum_{m_1 m_2} \mathcal{A}^{jL}_{J\mu-m_1\,m_1} \mathcal{A}^{\ell_1\ell_2}_{L\,m_1\,m-m_1}\, Y_{j\,\mu-m}(\Theta\Phi)\, Y_{\ell_1 m_1}(\theta_1\varphi_1)\, Y_{\ell_2\,m-m_1}(\theta_2\varphi_2) \qquad (6)^{*}$$

instead of

$$Y_{j\nu}(\Theta\Phi)\, Y_{\ell_1 m_1}(\theta_1\varphi_1)\, Y_{\ell_2 m_2}(\theta_2\varphi_2) \qquad (7)$$

as the bases in the expansion of the wave function, we have

$$\Psi = \sum_{\beta} \frac{1}{R} F_\beta(R) \frac{1}{\xi_1} \Phi^{\ell_1}_{m_1}(\xi_1) \frac{1}{\xi_2} \Phi^{\ell_2}_{m_2}(\xi_2) \Upsilon^{J\mu}_{j\ell_1\ell_2 L} \qquad (8)$$

$$\frac{1}{2M}\left(\frac{d^2}{dR^2} - \frac{j(j+1)}{R^2} + k_\beta^2\right) F_\beta(R) = \sum_{\beta'} (\beta|V_{12}|\beta') F_{\beta'}(R) \qquad (9)$$

$$\beta \equiv (J, \mu, m_1, m_2, j, \ell_1, \ell_2, L)$$

and $(\beta|V_{12}|\beta') = 0$ for $(J,\mu) \neq (J',\mu')$

The cross sections of any collision processes depend rather sensitively on the intermolecular potential function employed. But the theoretical calculation of the intermolecular force potential is so difficult in practice that few calculations for diatomic molecules have been done previously except for H_2-H_2 force.[3)4)5)] We must use, therefore, the semi-empirical force potential. In any case, the dependence of the potential function on the molecular orientations may be expressed in the form (See Fig.2.)

$$V_{12} = \sum_{\alpha\beta\gamma} v_{\alpha\beta\gamma}(\xi_1, \xi_2, R) P_\alpha(\cos\chi) P_\beta(\cos\chi') P_\gamma(\cos\chi''), \qquad (10)$$

where $P_\alpha(x)$ are the well-known Legendre polynomials. Then by the addition theorem

$$P_\alpha(\cos\chi) = \frac{4\pi}{2\alpha+1} \sum_{\mu=-\alpha}^{\alpha} Y^*_{\alpha\mu}(\Theta\Phi) Y_{\alpha\mu}(\theta_1\varphi_1) \quad \text{etc.} \qquad (11)$$

we can easily calculate the matrix elements of potential function with the aid of the numerical table of the coefficients:[6)]

$$C^L(\ell'm', \ell m) \qquad (12)$$

$$\equiv \left(\frac{2}{2L+1}\right)^{1/2} \iint Y^*_{\ell'm'}(\theta\varphi)\, Y_{L\,m'-m}(\theta\varphi)\, Y_{\ell m}(\theta\varphi)\, d\omega_\theta\, d\theta\, d\varphi.$$

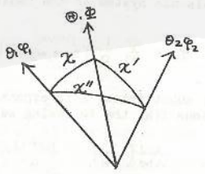


Fig. 2

*) $\mathcal{A}$'s are the well-known coefficients of unitary transformation.[2)]

For the collision between the identical molecules, we must use the properly symmetrized wave function. Thus, instead of

$$\zeta_{N_1}(x_1)\zeta_{N_2}(x_2)\varphi(R) \qquad (13)$$

we must employ

$$\frac{1}{\sqrt{2}}[\zeta_{N_1}(x_1)\zeta_{N_2}(x_2)\varphi(R) \pm \zeta_{N_1}(x_2)\zeta_{N_2}(x_1)\varphi(-R)] \qquad (14)$$
$$= \frac{1}{\sqrt{2}}[\zeta_{N_1}(x_1)\zeta_{N_2}(x_2) \pm \zeta_{N_1}(x_2)\zeta_{N_2}(x_1)] \cdot \frac{1}{2}[\varphi(R) + \varphi(-R)]$$
$$+ \frac{1}{\sqrt{2}}[\zeta_{N_1}(x_1)\zeta_{N_2}(x_2) \mp \zeta_{N_1}(x_2)\zeta_{N_2}(x_1)] \cdot \frac{1}{2}[\varphi(R) - \varphi(-R)]$$

where $\zeta_N(x)$ means the internal wave function of a molecule (abbreviation of the product given by (1)) and N, X stand for (n, ℓ, m) and (ξ, θ, φ) reppectively. The upper of the double sign corresponds to the Bose statistics and the lower to the Fermi statistics. In the following, however, we shall confine ourselves to the Bose statistics only. The treatment for the Fermi statistics can be obtained similarly.

Let

$$\Sigma^{\pm}_{N_1N_2} = \frac{1}{\sqrt{2}}(\zeta_{N_1}(x_1)\zeta_{N_2}(x_2) \pm \zeta_{N_1}(x_2)\zeta_{N_2}(x_1)) \quad , \quad N_1 \neq N_2 \qquad (15)$$
$$\Sigma^{+}_{N_1N_1} = \zeta_{N_1}(x_1)\zeta_{N_1}(x_2) \quad , \quad \Sigma^{-}_{N_1N_1} = 0 \ ,$$

then the wave function of the two molecule system may be written as follows :

$$\Psi = \sum_{N_1N_2} \Sigma^{+}_{N_1N_2} \varphi^{+}_{N_1N_2}(R) + \sum_{N_1N_2} \Sigma^{-}_{N_1N_2} \varphi^{-}_{N_1N_2}(R), \qquad (16)$$

where φ^+ and φ^- mean the functions which are symmetric and antisymmetric for the substitution $R \to -R$ respectively. Inserting this expression into the Schrödinger equation, we have the following set of equations

$$\begin{aligned}(\Delta^2 + k^2_{N_1N_2})\varphi^{+}_{N_1N_2}(R) &= 2M \sum_{N'_1N'_2} (\Sigma^{+}_{N_1N_2}|V^{+}|\Sigma^{+}_{N'_1N'_2})\varphi^{+}_{N'_1N'_2}(R) \\ &\quad + 2M \sum_{N'_1N'_2} (\Sigma^{+}_{N_1N_2}|V^{-}|\Sigma^{-}_{N'_1N'_2})\varphi^{-}_{N'_1N'_2}(R) \\ (\Delta^2 + k^2_{N_1N_2})\varphi^{-}_{N_1N_2}(R) &= 2M \sum_{N'_1N'_2} (\Sigma^{-}_{N_1N_2}|V^{+}|\Sigma^{-}_{N'_1N'_2})\varphi^{-}_{N'_1N'_2}(R) \\ &\quad + 2M \sum_{N'_1N'_2} (\Sigma^{-}_{N_1N_2}|V^{-}|\Sigma^{+}_{N'_1N'_2})\varphi^{+}_{N'_1N'_2}(R)\end{aligned} \qquad (17)$$

where V^+ and V^- are the parts of the potential V_{12} which are symmetric and antisymmetric respectively for the exchange of X_1 and X_2. *

φ^+ and φ^- can further be expanded as follows

$$\varphi^{+}_{N_1N_2}(R) = \sum_{j=\text{even}} \sum_{\nu} (2j+1)^{1/2} \left\{ G^{j\nu}_{N_1N_2}(R)/R \right\} Y_{j\nu}(\Theta\Phi),$$
$$\varphi^{-}_{N_1N_2}(R) = \sum_{j=\text{odd}} \sum_{\nu} (2j+1)^{1/2} \left\{ G^{j\nu}_{N_1N_2}(R)/R \right\} Y_{j\nu}(\Theta\Phi). \qquad (20)$$

First, we shall consider the elastic collision and neglect the non-diagonal elements of potential. For $N_1 = N_2$ we have $\Psi = \Sigma^{+}_{N_1N_1}\varphi^{+}_{N_1N_1}$ and

$$(\Delta^2 + k^2_{N_iN_i})\varphi^{+}_{N_iN_j} = 2M(\Sigma^{+}_{N_iN_i}|V^{+}|\Sigma^{+}_{N_iN_i})\varphi^{+}_{N_iN_j} \ , \qquad (21)$$

thus the orbital angular momentum j is restricted to the even integer. For $N_1 \neq N_2$ the total wave function becomes

$$\Psi = \Sigma^{+}_{N_1N_2}\varphi^{+}_{N_1N_2} + \Sigma^{-}_{N_1N_2}\varphi^{-}_{N_1N_2} \qquad (22A)$$

and the set of equation become

$$(\Delta^2+k_{N_1N_2}^2)\varphi_{N_1N_2}^{+} = 2M(Z_{N_1N_2}^{+}|V^{+}|Z_{N_1N_2}^{+})\varphi_{N_1N_2}^{+} + 2M(Z_{N_1N_2}^{+}|V^{-}|Z_{N_1N_2}^{-})\varphi_{N_1N_2}^{-},$$

$$(\Delta^2+k_{N_1N_2}^2)\varphi_{N_1N_2}^{-} = 2M(Z_{N_1N_2}^{-}|V^{+}|Z_{N_1N_2}^{-})\varphi_{N_1N_2}^{-} + 2M(Z_{N_1N_2}^{-}|V^{-}|Z_{N_1N_2}^{+})\varphi_{N_1N_2}^{+}. \quad (22B)$$

For the homonuclear diatomic molecules these equations are separated as

$$(\Delta^2+k_{N_1N_2}^2)\varphi_{N_1N_2}^{+} = 2M\{(N_1N_2|V^{+}|N_1N_2)+(N_1N_2|V^{+}|N_2N_1)\}\varphi_{N_1N_2}^{+},$$
$$(\Delta^2+k_{N_1N_2}^2)\varphi_{N_1N_2}^{-} = 2M\{(N_1N_2|V^{+}|N_1N_2)-(N_1N_2|V^{+}|N_2N_1)\}\varphi_{N_1N_2}^{-}. \quad (23)$$

It must be noted that the exchange potential $(N_1N_2|V^{+}|N_2N_1)$ appears in this case which does not appear in the unsymmetryzed treatment. Therefore, the two identical molecules belonging to the different internal states must not be treated as dissimilar. On the other hand, para-hydrogen and ortho-hydrogen can be treated as dissimilar because their nuclear spins are different from each other which makes the exchange potential vanish practically. (If the resultant nuclear spin is not zero, we must include this degree of freedom in N_1.)

Next we shall consider the inelastic collision. Here again we shall assume $V^{-}=0$ for simplicity, and compare the two processes

$$(N_1)+(N_1) \rightleftarrows (N_1)+(N_2), \quad (24_B^A)$$
$$(N_3)+(N_1) \rightleftarrows (N_3)+(N_2). \quad (25_B^A)$$

In the unsymmetrized theory, the cross sections of these processes will be proportional to the following square of matrix elements

$$Q_{(24a)} \sim |(N_1N_2|V^{+}|N_1N_1)|^2$$
$$Q_{(25a)} \sim |(N_3N_2|V^{+}|N_3N_1)|^2 \quad (26)$$

and $Q_{(24a)} \simeq Q_{(25a)}$ in the first approximation.**

According to the Bose statistics, on the other hand, we have

$$Q_{(24a)} \sim |(Z_{N_1N_2}^{+}|V^{+}|Z_{N_1N_2}^{+})|^2 = 2|(N_1N_2|V^{+}|N_1N_1)|^2$$
$$Q_{(25a)} \sim |(Z_{N_3N_2}^{\pm}|V^{+}|Z_{N_3N_1}^{\pm})|^2 \simeq |(N_3N_2|V^{+}|N_3N_1)|^2 \quad (28)$$

and in the first approximation $Q_{(24a)} \simeq 2Q_{(25a)}$. In the unsymmetrized treatment of (24A), we must take into account the possibility that either molecule may suffer the transition. Thus the effective cross section of inelastic collision is obtained from the above value by multiplying 2. It is not the case in the Bose statistics, because the only one final state $Z_{N_1N_2}^{+}$ is permissible for this case. As a result, approximate relation $Q_{(24a)} \simeq 2Q_{(25a)}$ is valid for both unsymmetrized theory and the symmetrized treatment. Furthermore, the collision number in gas phase is reduced to half for the identical pair of molecules. Thus the reaction rates of (24A) and (25A) are approximately the same. From the principle of detailed balance, this equality must hold for the inverse processes (24B) and (25B) too. It can be confirmed easily. For the unsymmetrized theory we have

$$Q_{(24b)} \sim |(N_1N_1|V^{+}|N_1N_2)|^2$$
$$Q_{(25b)} \sim |(N_3N_1|V^{+}|N_3N_2)|^2 \quad (29)$$

and in the first approximation $Q_{(24b)} \simeq Q_{(25b)}$.

In the symmetrized treatment, on the other hand, we have

$$Q_{(24b)} \sim \tfrac{1}{2}\cdot|(N_1N_1|V^{+}|Z_{N_1N_2}^{+})|^2 = |(N_1N_1|V^{+}|N_1N_2)|^2$$
$$Q_{(25b)} \sim |(Z_{N_3N_1}^{+}|V^{+}|Z_{N_1N_2}^{+})|^2 \simeq |(N_3N_1|V^{+}|N_3N_2)|^2 \quad (30)$$

where the factor $\frac{1}{2}$ corresponds to the fact that only the partial waves with even orbital angular momentum j can be combined with the final state. Thus we have $Q_{(24b)} \simeq Q_{(25b)}$ as required.***

*)For instance, we shall consider the problem by neglecting the vibrational degrees of of freedom. Then, from the simple consideration, we can get the following relation for the coefficients in the expression (10) of the intermolecular potential :

$$v_{\alpha\beta\gamma}(\xi_1=\xi_2,R) = (-1)^{\alpha+\beta}v_{\beta\alpha\gamma}(\xi_1=\xi_2,R). \quad (18)$$

In this case, therefore, it is obvious that

$$V_{12} = V^{+}+V^{-}, \quad V^{+}=\sum_{\alpha+\beta=\text{even}}, \quad V^{-}=\sum_{\alpha+\beta=\text{odd}}. \quad (19)$$

For the homonuclear diatomic molecules, V^{-} vanishes, even if we take the vibrational degrees of freedom into account.

**) Here and in the following, the equality $\simeq$ corresponds to the approximate form of the potential function :

$$(N_1N_2|V^{+}|N_3N_4) \simeq a\,\delta(N_1,N_3)\,\delta(N_2,N_4) + b\,\delta(N_1,N_3)(N_2|v|N_4) + c\,\delta(N_2,N_4)(N_1|v|N_3). \quad (27)$$

***) On these effects of the statistics, our previous considerations have been mistaken, in which we concluded $Q_{(24b)} \simeq \frac{1}{2}Q_{(25b)}$.

3

We have investigated the H_2-H_2 collisions at low energies.* This is a typical elastic collision between non-spherical molecules because both the rotational and the vibrational transition probabilities are extremely small for this case. On the other hand, owing to the small mass of this molecule, the quantum effects are rather large. Furthermore, the recent measurement on the difference in viscosity for various concentration ratios of para- and ortho-hydrogen by Becker and Stehl[9] aroused our interest on this collision problem.

Historically speaking, Halpern and Gwathmey[10] predicted such variation of viscosity by making use of the rigid sphere model.[11] But the use of the rigid sphere model is inadequate to estimate the small effects such as viscosity variation we are considering. In fact, the predicted variation of viscosity in hydrogen given by Halpern and Gwathmey is the opposite sense from the observed variation and about ten times larger in absolute value. This rather large discrepancy can be avoided by replacing the rigid sphere model with a little more likely potential field, as you will see in the following. Moreover, they considered that the two H_2 molecule, for example two para-hydrogen molecules characterized by different rotational quantum numbers are regarded as distinct. But it is not true, because such pair of molecules obey partly Bose statistics and partly Fermi statistics. (See (22A).)

Now Becker and Stehl analyzed their observed data to get the difference in the cross sections effective to the viscosity, i.e. to obtain

$$\left(\frac{\Delta Q}{Q}\right)_{oo} \equiv \frac{Q_{oo}-Q_{pp}}{Q_{pp}} \quad \text{and} \quad \left(\frac{\Delta Q}{Q}\right)_{op} \equiv \frac{Q_{op}-Q_{pp}}{Q_{pp}} \qquad \begin{matrix}\text{o...ortho}\\ \text{p...para}\end{matrix}$$

separately. Thus we may fix our attention, for a while, to the comparison of para-para

and para-ortho cross sections only. Then omitting the trivial suffixes $n_1(=0)$, $n_2(=0)$, $\ell_2(=0)$, $L(=\ell_1)$ from the equation (9) we have

$$\frac{1}{2M}\left(\frac{d^2}{dR^2} - \frac{j(j+1)}{R^2} + k^2\right) F^{j\ell_1}_{J\mu}(R) = \left(J\mu j\ell_1 \middle| V_{12} \middle| J\mu j\ell_1\right) F^{j\ell_1}_{J\mu}(R) \tag{31}$$

Because of low temperatures, the para-H_2 is practically in the state $\ell=0$, and ortho-H_2 is in the state $\ell=1$. Furthermore, we have assumed that the orbital angular momentum j will be a good quantum number at low energy collisions between light molecules. Remembering that the incident wave has the asymptotic form

$$Y_{\ell m}(\theta,\varphi)\, e^{ikR\cos\Theta} \sim \sum_{j,J} \delta_{J\ell m}^{j\ell}\, \frac{[4\pi(2j+1)]^{1/2}}{kR}\, i^{j}\, e^{i\delta_j}\, \sin\left(kR - \tfrac{1}{2}j\pi\right) Y^{Jm}_{j\ell} \tag{32}$$

we look for the solution of (31) which vanishes at the origin and which is normalized asymptotically as

$$F^{j\ell_1}_{J\mu} \sim \frac{1}{kR}\sin\left(kR - \tfrac{1}{2}j\pi + \delta_{Jj\ell_1}\right). \tag{33}$$

Then the asymptotic form of the total wave function is

$$\Psi_{\ell m} \sim Y_{\ell m}\, e^{ikR\cos\Theta} + \frac{e^{ikR}}{R} G_{\ell m}(\Theta,\Phi,\theta,\varphi) \tag{34}$$

where

$$G_{\ell m} = \frac{1}{ik}\sum_{j=0}^{\infty}\sum_{J} \delta_{J\ell m}^{j\ell}\, [\pi(2j+1)]^{1/2}\left[e^{2i\delta_{Jj\ell}} - 1\right] Y^{Jm}_{j\ell}$$

which gives the total cross section

$$Q^{tot}_{\ell m} = \frac{4\pi}{k^2}\sum_{j=0}^{\infty}\sum_{J}(2j+1)\left(\delta_{J\ell m}^{j\ell}\right)^2 \sin^2\delta_{Jj\ell}. \tag{35}$$

The cross section which is effective to the viscosity can be obtained easily, but this has not so simple form.

As the intermolecular potential we have adopted the following expression

$$V_{12} = [20 + 16(\cos^2\chi + \cos^2\chi')]\, e^{-2R} - [10 + 2(\cos^2\chi + \cos^2\chi')]\frac{1}{R^6} \tag{36}$$

which is rather close to the theoretical predictions[3)4)] and also to the semi-empirical one.[12)] But a recent report by Evett and Margenau states that the interaction between the permanent quadrupoles can not be neglected. If it is true, our assumption on the potential is a poor approximation. In any case, the matrix elements of the potential (36) can be obtained easily and the effective potential for the para-para collision is found to be

$$V_{pp} = \frac{92}{3}\, e^{-2R} - \frac{34}{3}\frac{1}{R^6}, \tag{37}$$

and that for the para-ortho collision is

$$V_{po} = V_{pp} + \left(\frac{32}{15}\, e^{-2R} - \frac{4}{15}\frac{1}{R^6}\right) V_j^J \tag{38}$$

where

$$V_j^J = \begin{cases} j/(2j+3) & \text{for } J = j+1 \\ -1 & j \\ (j+1)/(2j-1) & j-1 \end{cases} \tag{39}$$

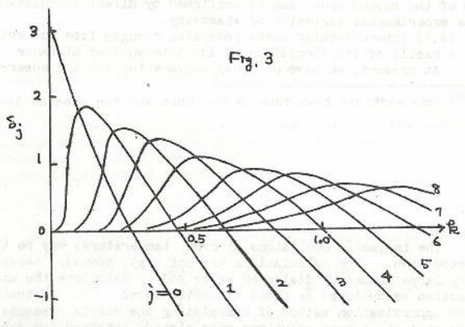
For these potentials we have calculated the phase shifts δ_j by making use of the W.K.B. approximation (for larger phase shifts) and Born approximation (for smaller phase shifts and some phase shifts have been estimated by interpolation from others. (Fig.3 illustrates the phase shifts for V_{pp}.)

In the following, we shall enumerate the various effects which seem to contribute to the observed variation of the viscosity with the para-ortho concentration ratio.

(1) Symmetry Effect: This is the effect of the Bose statistics, and is divided into three partial effects.

(1.a) For para-ortho collisions, the phase shifts of all j contribute to the cross section, while for para-para collisions, only the phase shifts with even j are employed. The resulting cross sections are illustrated in Fig.4. The fluctuation behaviour of para-para collision cross section is the most important departure from that of the rigid sphere model. Clearly such a fluctuation is an effect of the positive part of the phase shifts (see Fig.3) which comes from the van der Waals forcepotential. It must be noted, further, that para-para and para-ortho cross sections become practically equal when averaged over the Maxwellian velocity distribution. Since we have used the approximation method to compute the phase shifts, the remaining small difference after this averaging can't be estimated quantitatively.

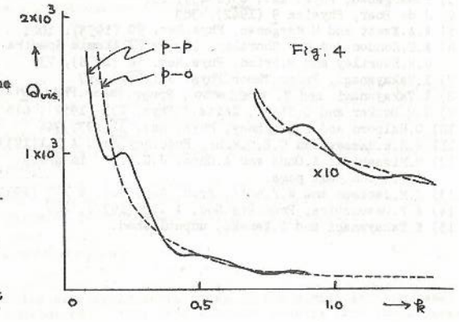
Fig. 3



(1.b) The presence of H_4 molecule must be taken into account at low temperatures. We may consider the hydrogen gas as a mixed gas consisting of H_2 and H_4. The state of H_4 with $j=0$ is stable. The state with $j=1$ is virtual for our potential (37) which, however, is very close to zero energy and is practically stable, being surrounded by a thick potential barrier (due to the centrifugal force). Thus, for para-ortho pair there exist two possible states of H_4 (one of which is degenerate) while for para-para pair, there exists only one state, which makes the concentration of H_4 vary with the para-ortho concentration ratio. Such effect may contribute to the viscosity variation. It must be noted that the concentration of H_4 varies with temperature nearly in proportion to $(kT)^{-3/2}$ which is exactly in the same way as the change of $(\Delta Q/Q)_{op}$, though $(\Delta Q/Q)_{pp}$ changes more slowly.

(1.c) According to the quantum hydrodynamics, we must replace the classical Boltzmann equation for the transport phenomena by the Uehling-Uhlenbeck equation, which gives to the effective cross sections of various processes some correstion factors. These effects (1.b) and (1.c) are pressure-dependent.

Fig. 4



(2) Rotational Effect:

(2.a) In the different rotational states we have different effective potentials, because the interaction potential field is non-spherical. In our present case, the difference is due to the term containing V_j^J in the equation (38). But after averaging over the possible J values for each j, the difference between para-para and para-ortho cross sections becomes very small since the average of the potential V_j^J itself with proper weight vanishes identically. In this way this effect

is of the second order and is confirmed by direct calculation to be too small to explain the experimental variation of viscosity.

(2.b) Intermolecular force potential changes from one rotational state to another, as a result of the elongation of the internuclear distance.

At present, we have no final explanation for the observed evidence.

*) This work has been done by Mr. Ohno and the present lecturer.

The inelastic collisions at room temperatures may be treated by the method of distorted wave. The calculations are not easy, however, because we have to determine a very large number of distorted waves and to calculate the matrix elements of potential function sandwitched by these distorted waves. It is, therefore, desirable to employ some approximation method of calculating the matrix elements. In this place we must note that the S-wave solutions were already obtained for exponential[13] and Morse potential[14] fields. What is hard to treat is the centrifugal force. On the other hand the main contribution to the transition matrix elements comes from a finite region around the classical turning point (say, $R=R_0$) for that collision. Thus we may roughly replace the potential $j(j+1)/2MR^2$ by its suitable average value, e.g. $j(j+1)/2MR_0^2$.

Using this method with some further simplifications, we have calculated the probability of the rotational transitions of para-hydrogen gas for 200°K and 300°K, and the vibrational transition probability of O_2-He collision for room temperature. The results were compared with the experimental data derived from the ultrasonic dispersion in these gases and reasonable agreements were obtained for both cases.[7][8][15]

1) e.g. C.Zener, Phys.Rev. 37(1931)556; Proc.Cambr.Phil.Soc.29(1932)136
R.N.Schwartz, Z.I.Slawsky and K.F.Herzfeld, J.Chem.Phys.20(1952)1591
K.Takayanagi, Progr.Theor.Phys. 8(1952)111
2) E.Wigner, Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren.
3) H.Margenau, Phys. Rev. 63(1943), 131
4) J.de Boer, Physica 9 (1942), 363
5) A.A.Evett and H.Margenau, Phys.Rev. 90 (1953), 1021
6) E.U.Condon and G.H.Shortley, Theory of Atomic Spectra (1935)
G.H.Shortley and B.Fried, Phys.Rev. 54 (1938), 739
7) K.Takayanagi, Progr.Theor.Phys. 8 (1952),497
8) K.Takayanagi and T. Kishimoto , Progr.Theor.Phys. 9(1953),
9) E.W.Becker and O.Stehl, Zeits.f.Phys. 133 (1952), 615
10) O.Halpern and E.Gwathmey, Phys. Rev. 52(1937)944
11) H.S.W.Massey and C.B.O.Mohr, Proc.Roy.Soc. A 141(1933),434 144(1934),188
12) M.Mizushima, K.Ohno and A.Ohno, J.C.P. in press. The abstract of this paper is in the next page.
13) J.M.Jackson and N.F.Mott, Proc. Roy. Soc. A 137 (1932), 703
14) A.F.Devonshire, Proc.Roy.Soc. A 158 (1937), 269
15) K.Takayanagi and S.Kaneko, unpublished.

D2

Pressure induced Absorption

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Pressure induced absorption has been found recently as a new effect in the absorption spectrum of gases and liquids resulting from the molecular interaction.

When a system of molecules α is compressed the absorption coefficient A, corresponding to a definite density n_α and temperature T can be developed as:

$$A(\omega; T, n_\alpha) = a_1^{(\alpha)} n_\alpha + a_2^{(\alpha)} n_\alpha^2 + \cdots \qquad (1)$$

Here a_1 is the absorptioncoefficient of the isolated molecules, including natural linewidth and Doppler broadening. The second term a_2 accounts for several effects:

1) "pressure broadening" i.e. collision broadening, resonance broadening and other effects of the intermolecular interaction in a frequency region, where absorption occurs in the isolated molecules.

2) "pressure induced absorption" i.e. absorption in a frequency region, where a forbidden transition occurs for the isolated molecules. These forbidden transitions may forbidden electronic transitions, inactive rotational transitions or inactive vibrational bands, as for instance the optically inactive vibration bands in H_2, O_2 and N_2 for which pressure induced absorption has been observed by Herzberg (1949) and Crawford, Welsh and Locke (1949).

When a gas of molecules is compressed with a foreign gas β one may write:

$$A(\omega; T, n_\alpha, n_\beta) = a_1^{(\alpha)} n_\alpha + a_1^{(\beta)} n_\beta + a_2^{(\alpha)} n_\alpha^2 + a_2^{(\beta)} n_\beta^2 + 2a_2^{(\alpha\beta)} n_\alpha n_\beta + \cdots \qquad (2)$$

where $a_2^{(\alpha)} n_\alpha^2$ can be neglected in general and where one is particularly interested in the mixing term $a_2^{(\alpha\beta)}$. This accounts for:

1) pressure broadening due to foreign gas in an absorptionregion of molecules α caused by the interaction of the molecules β. This effect has been extensively studied for electronic transitions in the alkali atoms.

2) induced pressure absorption due to foreign gas in a frequency region in which no absorption occurs for the molecules α. This effect has been studied extensively by Crawfoed, Welsh, Macdonald and Locke(1950) observing the inactive vibration band induced by compressed He, A and N_2 and by Welsh, Pashler and Dunn (1951) in the case of methane vibrationband.

In both cases the general expression for the total absorption coefficient $a_2^{(\alpha)}$ resp. $a_2^{(\alpha\beta)}$, integrated over the absorptionline considered is:

$$a_2^{(total)} = \frac{2\pi\bar{\omega}}{kc} \frac{1}{2} \sum_{i,f}' P_i \int g(r) \left| \vec{\mu}_{if}(r) \right|^2 d\vec{r} \qquad (3)$$

Here g(r) is the distribution fucntion of pairs $\alpha\alpha$, resp. $\alpha\beta$ which in first approximation is given by $\exp -\varphi(r)/kT$, $\bar{\omega}$ is the frequency in the centre of gravity of the absorption and the summation is carried out over initial and final states contributing to the same absorptionline, P_i being a weighting factor. The dipole moment $\mu(r)$ for the system of two molecules on a distance r is calculated in three successive steps:

I) The instantaneous dipolemoment.

The instantaneous dipolemoment of the system of two molecules α, β for a given nuclear configuration q, ω, r ($q = q_\alpha, q_\beta$ = vibrational coordinates; $\omega = \omega_\alpha, \omega_\beta$ = orientational coordinates; r = distance of centres of gravity) is given by:

$$\mu(q, \omega; r) = \int |\Psi(\rho; q, \omega, r)|^2 \mu(\rho) \, d\rho \qquad (4)$$

where the averaging is made over the electronic coordinates ρ (for simplicity the case of no electronic transition is considered). This dipole moment results from two effects:

a) The atomic distortioneffect: resulting from the overlap of the wavefunctions, which has been evaluated in detail by Van Kranendonk and Bird (1951) for the system H_2-H_2; D_2- D_2; H_2-He and D_2-He.

b) The dipole or quadrupole distortioneffect, resulting from the mutual polarisations resulting from dipole moments or quadrupole moments in one or both of the molecules α and β. When for instance both molecules have a quadrupole moment (H_2-H_2) one must distinguish still two contributions:

b1) the dipolemoment $\alpha_\alpha \Theta_\beta f(\omega_\beta)/r^4$ induced by the perturbing molecule β in the radiating molecule α, considered by Mizushima (1949)

b2) the dipole moment $\alpha_\beta \Theta_\alpha f(\omega_\alpha)/r^4$ induced by the radiating molecule α in the perturbind molecule β, added by van Kranendonk and Bird (1951)

It will be seen in (II) that because the pair α, β has to be considered as one system during the collision, that also b2) contributes to the bressure induced absorption.

II) Integration over vibrational coordinates:

When $Q_i(q)$ and $Q_f(q)$ are the vibrational wavefunctions of initial and final state of the vibration rotaion band considered, one obtains:

$$\mu_{if}(\omega;\gamma) = \int Q_f^*(q_\alpha q_\beta)\,\mu(q_\alpha, q_\beta, \omega;\gamma)\,Q_i(q_\alpha q_\beta)\,dq_\alpha\,dq_\beta \qquad (5)$$

Before introducing the instantenious dipolemoment one must develop:

$$\mu(q_\alpha q_\beta, \omega;\gamma) = \mu_{q=0} + \left(\frac{\partial\mu}{\partial q_\alpha}\right)_{q=0} q_\alpha + \left(\frac{\partial\mu}{\partial q_\beta}\right)_{q=0} q_\beta + \frac{1}{2}\left(\frac{\partial^2\mu}{\partial q_\alpha^2}\right)_{q=0} q_\alpha^2 + \cdots \qquad (6)$$

It is easily seen that for a vibrational transition $\Delta v_\alpha = \pm 1$ the intensity is determined by $(\partial\mu/\partial q_\alpha)_{q=0}$, for a transition $\Delta v_\alpha = \pm 2$ by $(\partial^2\mu/\partial q_\alpha^2)_{q=0}$, etc. Thus the instantaneous dipolemoment itself is only determining the intensity in pure rotational transitions, but for vibrational transitions the derivatives with respect to q_α are of importance.

III) Interaction over rotational coordinates:

When $Y_j(\omega)$ is sympolically the rotational eigenfunction, corresponding to the rotational quantumnumberrs ($j =$ J, M for a diatomic molecule), one obtains finally for the dipolemoment $\mu(r)$ which must be substituted in (3):

$$\mu_{if}(\gamma) = \int Y_{j_f}^*(\omega)\,\mu_{if}(\omega;\gamma)\,Y_{j_i}(\omega)\,d\omega \qquad (7)$$

Again, before substituting $\mu(\omega;\gamma)$ we develop in spherical harmonics:

$$\vec{\mu}(\omega;\gamma) = \sum_{j_\alpha j_\beta} \vec{D}_{j_\alpha j_\beta}(\gamma)\,Y_{j_\alpha}(\omega_\alpha)\,Y_{j_\beta}(\omega_\beta) \qquad (8)$$

Substitution in (7) then gives:

$$\vec{\mu}_{if}(\gamma) = \sum_{j_\alpha j_\beta} \langle j_{\alpha f}|j_\alpha|j_{\alpha i}\rangle \langle j_{\beta f}|j_\beta|j_{\beta i}\rangle \vec{D}_{j_\alpha j_\beta}(\gamma) \qquad (9)$$

where $\langle j_f|j|j_i\rangle = \int Y_{j_f}^*(\omega)\,Y_j(\omega)\,Y_{j_i}(\omega)\,d\omega$ are numerical coefficients related to Racah coefficients.

When the molecules are homonuclear molecules, all coefficients D with odd values of J are zero. This has the effect that for this case the selection rule for J must be: $\Delta J = J_f - J_i = 0, \pm 2$, etc, as has actually been observed.

Numerical results.

Numerical calculations have been carried out in Amsterdam by van Kranendonk and Bird (1951) for the case of hydrogen and deuterium, where pressure induced absorption has been observed due to high pressure and due to high pressure of a foreign gas helium. The results of the total absorption in the different branches observed in the pressure induced $0 \rightarrow 1$ vibration band are collected in the table:

Integrated absorption coefficients in $10^{-32}cm^{-1}sec^{-1}(mol/cm^3)^{-2}$ for the 0 - 1 vibrationband of H_2 or D_2 at 300°K.

Branch:	H_2-H_2	D_2-D_2	H_2-He	D_2-He
O(3)	0.11	0.07	0.01	X -
O(2)	0.12	0.19	0.01	0.03
Q	3.35	1.49	2.80	1.44
S(0)	0.74	0.50	0.12	0.08
S(1)	2.36	0.35	0.37	0.05
S(2)	0.38	0.59	0.06	0.09
S(3)	0.28	0.17	0.05	0.03
S(4)	0.02	0.14	0.-	0.02
Total theor:	7.36	3.50	3.42	1.47
Total exp.:	10.5		7.44	

Herzberg (1949) Nature 163, 170

Crawford, Welsh and Locke (1949) Phys. Rev. 75, 1607; 76, 580

Crawford, Welsh, Macdonald and Locke (1950) Phys. Rev. 80, 469

Mizushima (1949) Phys. Rev. 76, 1268

Kranendonk, Bird (1951) Physica 17, 953, 968

Welsh, Pashler and Dunn (1951)

Theory of Intermolecular Potential and Second Virial Coefficient of Hydrogen at Low Temperatures

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At low temperatures, the second virial coefficient must be calculated quantum-mechanically and theories are presented by various authors in the case of the central force.

We have tried to extend the quantum-mechanical calculation to H_2 which has the internal degrees of freedom, taking into account the dependence of the intermolecular potential on the relative orientation of the molecules.

The repulsive short range intermolecular potential is assumed to be expressible as a sum of interatomic repulsive potentials $Ae^{(-l/\rho)}$ where l is the interatomic distance and A and ρ are parameters. The attractive long range intermolecular potential is obtained by the second order perturbation calculation using dipole-dipole interaction as the perturbation.

We assume that the rotational quantum numbers (J, M_J) of each molecule are good quantum numbers throughout collision at low temperatures, where M_J is the magnetic quantum number relative to the intermolecular axis. Then we can calculate the matrix elements of the potential, namely the effective potentials for the translational motion, by averaging the potential with rotational wave functions of two colliding molecules. As the intermolecular potential depends on the relative orientation of the two molecules as well as distance between them, the resulting matrix elements depend on the rotational quantum numbers. Thus it is pointed out that the second virial coefficient of usual hydrogen and pure para-hydrogen must be different from each other, even if there were no statistical effect.

At temperatures below 250°K, hydrogen molecules may be regarded as being in the ground vibrational state ($\Theta_v \simeq 6100$°K) and in the ground or first excited rotational state according as they belong to para or ortho hydrogen ($\Theta_{rot}=85.3$°K).

At temperatures higher than 150°K, quantum effects are not so important that we can determine values of the parameters involved in the potentials so as to fit the second virial coefficients calculated by the semi-quantum-mechanical theory[1] to the experimental values in this temperature range ($250°K > T > 150°K$).

In region $T < 25$°K, the quantum effects being very large, we must solve the Schroedinger wave equation for radial wave functions. Using those effective potentials, we obtain phase shifts $\eta_j(k)$. In terms of them the virial coefficients for Bose-Einstein statistics ($B^{(s)}$) and Fermi-Dirac statistics ($B^{(as)}$) are expressed as follows :

$$B^{(s)} = B_{n,id}(j=\text{even}) + B_{disc}(j=\text{even}) - \frac{N}{16}\left(\frac{h^2}{\pi m \kappa T}\right)^{3/2}$$

$$B^{(as)} = B_{n,id}(j=\text{odd}) + B_{disc}(j=\text{odd}) + \frac{N}{16}\left(\frac{h^2}{\pi m \kappa T}\right)^{3/2}$$

$$B_{n,id} = -N\left(\frac{h^2}{\pi m \kappa T}\right)^{3/2}\left\{\frac{\hbar^2}{\pi m \kappa T}\int_0^\infty \exp\left(-\frac{\hbar^2 k^2}{m \kappa T}\right)\sum_j (2j+1)\, k\eta_j(k)\,dk - \sum_{j,n}(2j+1)\right\}$$

$$B_{disc} = -N\left(\frac{h^2}{\pi m \kappa T}\right)^{3/2}\sum_{j,n}(2j+1)\, e^{-E_{j,n}/\kappa T}$$

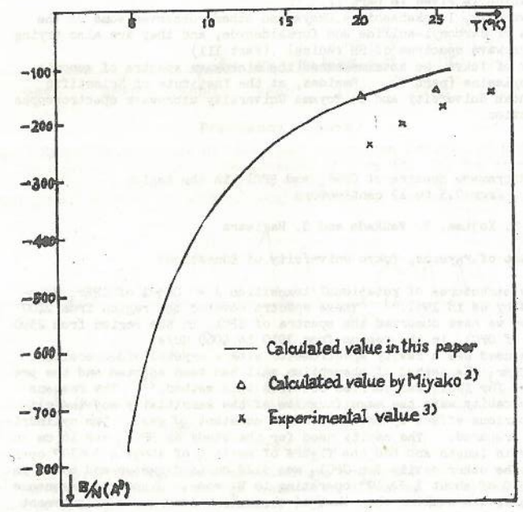
When the ratio of para to ortho molecule is 1:1, the observable coefficient is given by

$$B = \left(\frac{1}{t+1}\right)^2 \frac{5}{9} B_{1,1}^{(s)} + \frac{2t}{(t+1)^2}\frac{1}{2} B_{1,0}^{(s)} + \frac{1}{(t+1)^2} B_{0,0}^{(s)} + \left(\frac{t}{t+1}\right)^2 B_{1,1}^{(as)} + \frac{2t}{(1+t)^2}\frac{1}{2} B_{1,0}^{(as)}$$

where $B_{j,j'}$ is the second virial coefficient corresponding to the collision of J=j and J=j' state molecules.

Since the numerical calculation is very laborious we limited our calculation to the case of t=0, that is, $B=B_{0,0}$. The numerical values of $B_{0,0}$ thus obtained are shown in the following table and figure.

T(°K)	5	10	15	20	20.41	25	25.25
$B_{0,0}/N$ (A^3)	-696	-355	-223	-155		-115	
B/N (A^3) (Miyako[2])				-149		-141	
B_{exp}/N (A^3) (pure para)[3]					-240.8		-176.5



These values are somewhat larger than the experimental value for pure para hydrogen. This may be due to the fact that we could not fix uniquely the value of parameters of intermolecular potential.

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1) A. Buckingham and J. Corner, Proc. Roy. Soc. A 189 (1947), 118.
2) R. Miyako, Proc. Physico-Math. Soc. of Japan, 24, 852 (1942).
3) K. Schaefer, Zeits. f. Phys. Chem. B 36, (1937), 85.

E2.

Studies of Microwave Molecular Spectra in Japan

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The experimental studies of free molecules by the microwave method are not so much performed in Japan as in other countries because of difficulties in obtaining microwave generators of short wavelength.

At the Tokyo University of Education, S.Kojima and others are investigating the microwave spectra of molecules at the frequency of several kilomegacyles. The result on bromoform was already reported. They are now investigating phosphoryl chrolide and thio-phosphoryl chrolide. The preliminary results are given in part I with the theoretical spectra of these molecules in the ground vibrational state calculated by T.Itoh. Concerning to this, the rotational spectrum of XYZ_2-type molecule including isotopic species of Z was theoretically treated by T.Itoh and M.Mizushima, which is given in part II.

At Kyoto University, I.Takahashi, A.Okaya and others observed some of the millimeter spectra of carbonyl-sulfide and formaldehyde, and they are also trying to observe the microwave spectrum of SH radical .(Part III)

At University of Tokyo, we have measured the microwave spectra of ammonia (part IV) and methylamine (part V). Besides, at the Institute of Scientific Measurement in Tohoku University and at Toyama University microwave spectroscopes are under construction.

I. Microwave Spectra of $OPCl_3$ and $SPCl_3$ in the Region from 7.5 to 12 centimeters

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The hyperfine structures of rotational transition $J = 0 \rightarrow 1$ of $CHBr_3$ molecules were studied by us in 1951.[1] These spectra covered the region from 2400 to 2660 Mc/s. Now we have observed the spectra of $SPCl_3$ in the region from 2590 to 2790 Mc/s. and of $OPCl_3$ in the region from 3910 to 4050 Mc/s.

The apparatus used was a cavity spectrometer with a crystal videoreceiver. At the study for $CHBr_3$ the method of absorption cell had been adopted and the preliminary experiment for $SPCl_3$ was carried out with this method.[2] The reasons for the use of the cavity were the magnification of the sensitivity and the elimination of the spurious effect by the dielectric constant of gas. Two cylindrical cavities were prepared. The cavity used for the study on $SPCl_3$ was 16 cm in diameter and 60 cm in length and had the figure of merit Q of about 4.5×10^4 operating in H_9 mode. The other cavity for $OPCl_3$ was 5.22 cm in diameter and 65 cm in length and had the Q of about 1.2×10^4 operating in H_1 mode. Since the resonance width of the cavities was smaller than that of absorption lines. A measurement of the depression of the Q by the absorption yielded only one point on the spectrum.

By measuring 150 points for $SPCl_3$ the spectrum shown in Fig. 1(a) was obtained.[3] The hyperfine structure due to nuclear quadrupole moment calculated by T.Itoh[4] is reproduced in Fig. 1(b). The wide spreading of the observed spectrum seems to come from vibrational states.

The spectrum of $OPCl_3$ was obtained by measurements of 74 points[3]. Fig.2 shows the observed and calculated spectra. In this case too the spreading of the former is wider than the latter which does not contain excited vibrational states.

Because of the complication of the spectra their analysis is difficult. To distinguish the lines due to different vibrational states we have attempted

the study of temperature effect. Simple calculation shows that the change from 300°K to 250°K yields 20% decrease of the intensity ratio of the first vibrational state to the ground state. A preliminary experiment on $SPCl_3$, which was carried out in the frequency region between 2690 Mc/s and 2705 Mc/s by changing the temperature from -4°C to 42°C, suggensted that the temperature effect was exist.[5] The survey covering whole range of the spectrum will be attempted before long.

We have extended the range of microwave spectroscopy to longer wavelength by the studies on $CHBr_3$, $SPCl_3$ and $OPCl_3$. In all three cases the absorption coefficient was about 10^{-3} cm^{-1}.

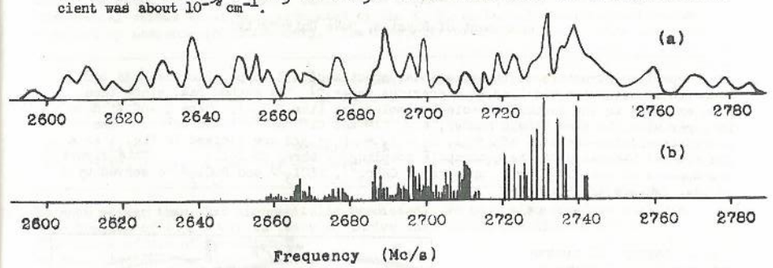

Fig. 1 Hyperfine structure of rotational transition $J = 0 \rightarrow 1$ of $SPCl_3$.
(a) The observed spectrum at the pressure of 2 mm Hg. (b) The calculated spectrum with the following constants: $\overline{SP}$ = 1.95 A, $\overline{PCl}$ = 2.02 A, ∠ ClPCl = 104° and $(eQq)_{Cl^{35}} = -90$ Mc/s and without consideration for excited vibrational state.

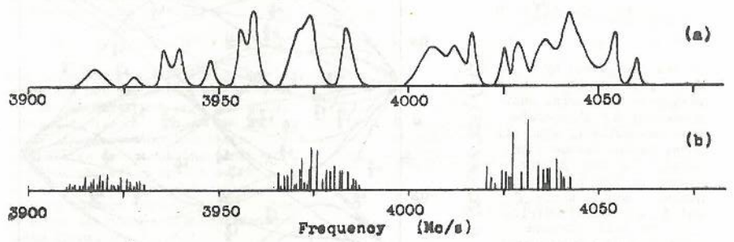

Fig. 2. Hyperfine structure of rotational transition $J = 0 \rightarrow 1$ of $OPCl_3$.
(a) The observed spectrum at the pressure of 3.2 mm Hg. (b) The calculated spectrum with the following constants : $\overline{OP}$ = 1.45 Å, $\overline{PCl}$ = 1.99 A, ∠ ClPCl = 103.6° and $(eQq)_{Cl^{35}} = -90$ Mc/s and without consideration for excited vibrational state.

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1) S.Kojima, K.Tsukada, S.Hagiwara, M.Mizushima and T.Itoh, J. Chem. Phys. 20 (1952), 804
2) Reported by Kojima and Tsukada at the Sendai Meeting May 9, 1952
3) Reported by Kojima, Tsukada and Hagiwara at the Kyoto Meeting October 31,1952
4) Reported by Itoh at the Kyoto Meeting October 31, 1952
5) Reported by Kojima, Tsukada and Hagiwara at the Osaka Meeting April 30, 1953.

II. On the Hyperfine Structure of the Rotational Spectra of Molecules with Three Quadrupolar Nuclei

Takashi Itoh

(Department of Physics, University of Tokyo)

and Masataka Mizushima

(Department of Physics, Duke University)

Hyperfine structure of the rotational spectra of XYZ_3-type molecules has been computed by Mizushima and Itoh in a previous paper.[1] The method has, since then, been extended to the isotopic species of molecules like XYZ_2Z', where Z and Z' mean isotopes with the same atomic number, e.g. Cl^{35} and Cl^{37} or Br^{79} and Br^{81}. The energy levels for the case of $J=1$, $I_1 = I_2 = I_3 = 3/2$ are plotted in Fig. 1 as a function of the ratio of the quadrupole coupling of three nuclei. This figure was applied to the $J=0 \rightarrow 1$ spectra of $CHBr_3$[2], $PSCl_3$[3] and $POCl_3$[3] observed by Kojima, Tsukada and Hagiwara.

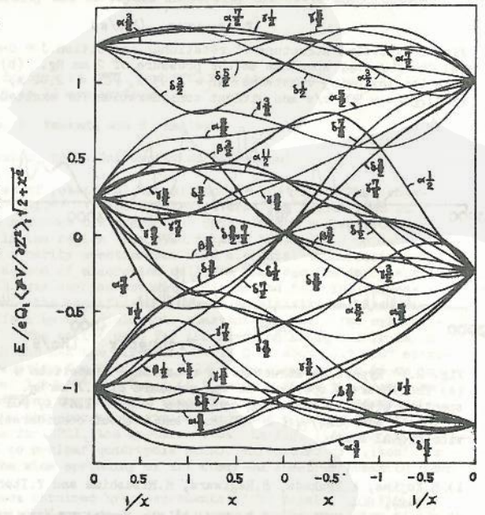


Fig. 1 Energy of quadrupole coupling of three nuclei of spin 3/2 when $J=1$. Parameter

$$x = eQ_3\langle\partial^2V/\partial Z^2_3\rangle / eQ_1\langle\partial^2V/\partial Z^2_1\rangle = eQ_3\langle\partial^2V/\partial Z^2_3\rangle / eQ_2\langle\partial^2V/\partial Z^2_2\rangle$$

States designated by α, β and γ, δ are those which pass into symmetric, antisymmetric and degenerate ones respectively when all three nuclei become identical. α and γ are symmetric with respect to nuclei 1 and 2, while β and δ are antisymmetric.

The half integers written in the figure are the values of F.

References :

1) M.Mizushima and T.Itoh, J.Chem.Phys. 19 (1951),739
2) S.Kojima, K.Tsukada, S.Hagiwara, M.Mizushima and T.Itoh, J. Chem. Phys. 20 (1952)804
3) See the preceeding report in this text.

III. The Recent Studies of Microwave Spectroscopy at Kyoto University

I. Takahashi, A. Okaya and T. Ogawa

(Department of Physics, Kyoto University)

(1) New lines of formaldehyde We have observed two new lines of formaldehyde which are shown in the following table. The observed frequencies agree with the theoretical values which are calculated by the K. H. C. method employing constants obtained by Lawrence and Strandberg. The intensity of $19_{3,17} - 19_{3,16}$ line seems to

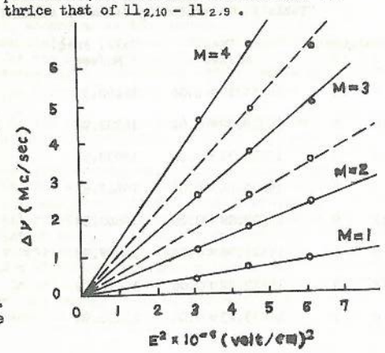
Assignment $J_{K_{-1},K_{+1}}$	Intensity (Theor.)cm^{-1}	Measured Freq. Mc/sec	Calculated Freq. Mc/sec	Correction Used Mc/sec
$11_{2,10} - 11_{2,9}$	8×10^{-5}	48612.7± 0.1	48615.4	−120.1
$19_{3,17} - 19_{3,16}$	4×10^{-5}	45063.1± 0.1	45064.8	−438.5

be much weeker than that theoretically predicted.. We have also observed that the line breadth of $4_{1,4} - 4_{1,3}$ is twice or thrice that of $11_{2,10} - 11_{2,9}$.

(2) Stark effect of formaldehyde
We have observed the Stark pattern of $4_{1,4} - 4_{1,3}$ in the 6 mm region. The pattern is shown in the following figure. The solid curves show the lines which agree with the theory of Golden and Wilson, and are represented by the empirical formula,

$$\Delta\nu = (5.58+8.50\ M^2)\times10^{-8}\ E^2$$

The dotted curves show the lines which are not expected theoretically but can be separated when the Stark voltage is larger than 1×10^3 volt/cm. These lines are weak and their intensities are about one tenth of those of the lines on the solid curves. We are now making experiment to observe a Stark pattern of $0_{0,0} - 1_{0,1}$ line in order to explain the appearance of these lines.



(3) Instrument for mm wave spectoscopy For 6 to 4 mm wave spectroscopy, we have used the 200 kc/sec Stark modulation system containing superheterodyne receiver, d.c. amplifier, 50 c/sec low pass filter, and long persistence C.R.O. The mm wave power is produced by the new type demountable silicon frequency multiplier from 2K33A klystron. This frequency multiplier has merits of broad band frequency characteristics, good conversion efficiency, and simple operation. The new type Stark cell is of very low loss and we expect it is applicable to the lower mm wave region.

(4) Lamda-type doubling of SH radical In order to detect lamda-type doubling of $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states of SH radical with 1 cm and 6 mm waves refered to the optical data of D. A. Ramsay, we are preparing a Zeeman modulation spectroscope which is similar to that used by C. H. Townes to OH radical.

IV. New Lines of the Inversion Spectrum of Ammonia

T. Nishikawa and K. Shimoda

(Department of Physics, University of Tokyo)

Eight lines of the inversion spectrum of ammonia in the frequency range between 15 and 17 kMc/sec were found in course of investigating metrylamine by the source modulation microwave spectrograph. The second harmonics from a crystal multiplier driven by a klystron, 2K25, were used. The measured frequencies of the lines are given in Table I. The calculated frequencies using the empirical formula of Costain[1] and their deviations from the obserbed frequencies are also listed. The correction of K-type splitting[3] on the frequency of 8,3 line is taken as +116.42 Mc/sec. According to his revised formula, the errors are reduced to about -1.2 Mc/sec[2].

The frequencies and intensities of lines, (8,3), (10,6), (11,7), (12,8) and (9,4), show good agreements with the values reported as the lines of deutero-ammonias by H.Lyons and others.[4] It was ascertained that those should be attributed to the undeuterated ammonia.

Table I. Inversion Spectrum of Ammonia

Assignment J	K	Obs. Freq. Mc/sec	Calc. Freq. Mc/sec	Error Mc/sec	Obs. Rel. Intensity	Calc. Intensity *
8	3	16455.13±0.04	16460.35	- 5.22	S	79×10^{-7}cm^{-1}
10	6	16319.38±0.04	16322.92	- 3.54	S	66
11	7	15933.32±0.06	15938.51	- 4.19	M	18
8	2	15639.84±0.06	15642.88	- 3.04	MS	15
12	8	15632.88±0.08	15640.14	- 7.26	W	8.3
9	4	15523.96±0.05	15527.93	- 3.97	MW	7.4
13	9	15412.52±0.06	15422.09	- 9.57	MS	27
8	1	15233.23±0.04	15236.94	- 3.71	MW	3.3

* These values were calculated assuming the line widths are independent on J and K.

Reference

1) C. C. Costain , Phys. Rev. 82 (1951), 108
2) private communication.
3) H. H. Nielsen and D. M. Dennison, Phys. Rev. 72 (1947), 1101
4) H. Lyons, L. J. Rueger, R. G. Nuckolls, and M. Kessler, Phys. Rev. 81 (1951), 630

V. Microwave Spectrum of Methylamine

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(Department of Physics, University of Tokyo)

Investigation of molecules with internal rotation by the microwave spectra is of quite interest. Methylalcohol CH_3OH, the simplest molecule with internal rotation has been almost completely studied by many workers.[1] We are now investigating the microwave spetrum of methylamine CH_3NH_2, in the frequency range between 15 and 30 kMc/sec. Although the analysis and determination of molecular constants have not yet been completed, the preliminary results are to be given.

As much as 130 lines of the methylamine spectrum and their Stark effects have been measured. The measured frequencies and intensities of the lines are given in Table 1, where the relative intensities are given by S, M, and W. It is estimated that $\alpha > 1\sim2\times10^{-6}$ cm^{-1} for S, $1\sim2\times10^{-6}$ cm$^{-1} > \alpha > 1\sim2\times10^{-7}$ cm^{-1} for M, and $\alpha < 1\sim2\times10^{-7}$ cm^{-1} for W near 24 kMc/sec. though α's are smaller at the lower frequency.

The Stark effect of each line is shown in the table, classified into five kinds, though the Stark components of most lines are not perfectly resolved. The lines showing first order Stark effect are denoted by 1(i) or 1(o), according as the inner or outer Stark components are stronger. The lines showing second order Stark effect are denoted by 2(+) or 2(-), according as the components shift to higher or lower frequency side with Stark field. The remaining lines denoted by (1→2) show some peculiar Stark effect: at the lower field (of less than 100 V/cm) the Stark pattern is similar to those of the first order Stark effect, while at higher field all Stark components shift to higher frequency side showing the second order Stark effect.

The frequencies of lines belonging to the two groups 1(o) and (1→2) form pairs of series in good order, which are marked respectively as (p_1), (p_2) and (q_1), (q_2) in Table 1.

The analysis and assignment of these lines are rather difficult, since the methylamine is an asymmetric top molecule, the amine group of which is rotatable with respect to methyl group, and futher it may invert itself about nitrogen. We must consider therefore (1) the overall rotation energy, (2) K-type doubling or asymmetric doubling, (3) internal rotation energy, (4) inversion doubling, (5) nuclear quadrupole effect, and (6) vibration-rotation interactions.

The theory for internal rotation of a slightly asymmetric molecule has been developed by Dennison and others[2] in order to analyse the spectrum of methylalcohol. According to the theory, the energy level of molecule with internal rotation is approximately expressed to be

$$E(J,K,\tau,n) = \hbar^2[(J+J^2-K^2)/2A + K^2/2C]$$
$$+\hbar\nu_t(n+1/2) - \beta_n\cos\gamma_{K\tau} - \beta_n'\cos 2\gamma_{K\tau} - \beta_n''\cos 3\gamma_{K\tau} - \cdots\cdots$$
$$\gamma_{K\tau} = \frac{2\pi}{3}\left(\frac{C_1}{C}K+\tau-1\right)$$

where A and C are the moment of inertia of the molecule about the axis perpendicular and parallel to the methyl axis respectively, and C_1 is the moment of inertia of the amine group about the methyl axis. In this treatment, amine and methyl groups are assumed to be symmetric rotors. J and K are the usual rotational quantum number, n is the quantum number for torsional vibration, and τ(= 1,2, 3) is the quantum number related to the three-fold symmetry of potential barrier. ν_t is the frequency of the torsional vibration. $\beta_n, \beta_n', \beta_n''\cdots$ are constants depending on the height of hindering potential and n. Because $\beta_n', \beta_n''\cdots$ are much smaller than β_n, we may express the energy of internal rotation equal to $-\beta_n\cos\gamma_{K\tau}$ in the first approximation.

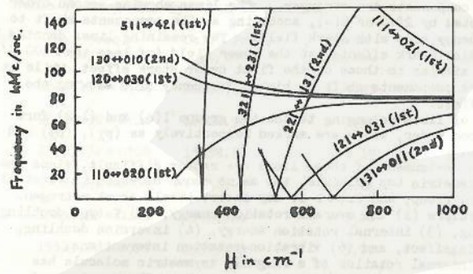
The selection rules are $\Delta J = 0, \pm 1$, $\Delta K = 0, \pm 1$, $\Delta(K+\tau) = 0$, and $\Delta n = 0$ for microwave spectrum. The transition corresponding to $\Delta K = 0$ would be very weak, because the dipole moment of the molecule lies nearly perpendicular to the molecular axis. Accordingly, the observed lines are probably due to the $\Delta K = \pm 1$ transitions. Among them the spectrum of $\Delta J = 0$ is usually called internal rotation spectrum, and that of $\Delta J = \pm 1$ is called pure rotation spectrum.

The frequency of internal rotation spectrum is given by

$$h\nu(J\,K-1\;\tau+1\;n \to J\,K\,\tau\,n) = \frac{h^2}{2C}(2K-1) - \beta_n\,(\cos\gamma_{K\tau} - \cos\gamma_{K-1\,\tau+1})$$

Although the transitions of $J = K, K+1, K+2, \cdots$ have the same frequency in this expression, they will be separated into a series of lines according to J-values because of the slight asymmetry. Since β_n depends remarkably on the potential height H which is not yet known decisively, the frequency was calculated as a function of H. The result is shown in Figure 1.

Fig. 1. Frequencies of K, τ, $n \leftrightarrow K-1, \tau+1$, n transitions for $n = 0$ and $n = 1$. The order of Stark effect is indicated in parentheses.



The ground state spectrum ($n = 0$) is outside the range of our measurement for the probable value of H ($= 500 \sim 1000\ cm^{-1}$).[3] As mentioned above, we have observed two pairs of series of lines; the one (p_1 and p_2) shows the first order Stark effect and the other (q_1 and q_2) shows peculiar Stark effect though intrinsically the second order. These series of lines are assigned to be probably $n = 1$.

The first order series, p_1 and p_2, are tentatively assigned to be the spectrum of $K, \tau = 1,2 \leftrightarrow 0,3$, while the other pair of series, q_1 and q_2, may be the spectrum either of $K, \tau = 1,3 \leftrightarrow 0,1$ or $K, \tau = 2,2 \leftrightarrow 1,3$. The decision of this alternative is made by the consideration of inversion doubling. The separation of the series, p_1 and p_2 or q_1 and q_2, must be due to the inversion doubling like that of ammonia. According to the theory of inversion doubling, the intensity ratio of each pair of series should be 1 : 3, corresponding to the singlet and triplet states of proton spins in the amine group. We have found that the series of lines in the lower frequency region (p_1 and q_1) are roughly three times stronger than those in the higher frequency region (p_2 and q_2). It can be shown from this results, that the second order series are due to the transitions, $K, \tau = 1,3 \leftrightarrow 0,1$. This interpretation requires that the height of potential barrier for internal rotation should be about $650\ cm^{-1}$.

As to the pure rotatical transitions, $J \to J \pm 1$, $K \to K \mp 1$, Dr. Lide assigned three lines and determined the rotational constants as a rigid rotor.[4] However, the other rotational lines are inconsistent with his result. We fined no lines predicted from those constants in the observed frequency range. This fact is

explained, if we consider the effect of inversion doubling and internal rotation, the magnitude of which is estimated to be several kilomegacycles. With these corrections, some of the predicted rotational lines will be shifted out of the observed range, and some other lines will come into the range. Consistent evaluation of the effect of internal motion upon overall molecular rotation has not been made because of some difficulties in the theoretical analysis, but it is clear that the rotational constants which were calculated assuming a rigid model should be considerably modified.

In conclusion, remaining problems are briefly stated. First, as mentioned above, the effect of inversion doubling and internal rotation tripling on the pure rotation spectrum has not yet been analysed, because there remain several possibilities for assignment. Second, many lines found in the lower frequency region have not been interpreted at present. Third, the interaction of inversion and internal rotation seems to be rather complicated though the magnitude of inversion doubling has been explained by a preliminary consideration. Fourth, the peculiar Stark effect denoted by (1⇔2)(series q_1, q_2) are not yet explained. Finally, it is hardly possible, therefore, to obtain definite values of molecular constants of methylamine untill the pure rotational spectrum is completely analysed.

Table I. Microwave Spectrum of Methylamine

Obs. Freq. Mc/sec	Int.	Stark-effect	Obs. Freq. Mc/sec	Int.	Stark-effect
15146.16	S	2(+)	19013.55	MS	2(+)
15252.52	W	2(+)	p_1 19110.66	S	1(o)
15357.69	S	2(+)	19724.62	S	2(+)
p_1 15397.72	MS	1(o)	19776.40	W	1?
q_2 15842.14	S	1⇔2	19776.66	WW	1?
16088.98	s	2(+)	19776.84	W	1?
16089.84	S	2(+)	q_1 19919.46	MS	1⇔2
16410.63	S	2(+)	p_2 19933.57	W	1(o)
16661.73	S	2(+)	q_2 20076.00	S	1⇔2
p_1 16670.02	MS	1(o)	p_1 20243.54	MS	1(o)
16681.80	MW	2?	20325.82	W	2?
16742.98	S	2(+)	20547.17	MS	1(i)
p_2? 16947.65	W	1(o?)	20831.28	MW	1(i)
17042.46	MS	2(+)	p_2? 21019.17	W	1(o?)
17108.99	MS	2(+)	21051.62	W	1(i?)
17200.97	MS	2(+)	p_1 21297.12	MS	1(o)
17237.77	W	1?	21712.65	MW	1(i)
17238.04	W	1?	21765.23	M	2(+)
17263.86	WW	2(+)?	21842.31	MW	2(+)
q_1 17302.03	M	1⇔2			
17345.10	MW	2(+)	21930.00	MW	1(i?)
17345.70	W	2(+)	21931.48	MW	1(i?)
17360.58	W	2(+)	p_2 22112.26	WW	1(o)
17361.10	WW	2(+)	p_1 22258.35	MS	1(o)
17475.66	MW	2(+)	q_2 22527.93	MS	1⇔2
17476.28	MW	2(+)	q_2 22528.21	MS	1⇔2
17585.33	WW	2(+)	22581.49	M	1(i)
17660.45	WW	?	22588.42	W	1(o?)
q_2 17849.46	S	1⇔2	22722.62	S	1(i)
p_2? 17871.76	WW	1(o?)	q_1 22759.22	MS	1⇔2
17887.20	M	2(+)	q_1 22759.63	M	1⇔2
p_1 17913.74	MS	1(o	22765.62	WW	1?
18023.18	W	1?	22980.95	M	2(+)
18562.40	W	1?	22981.60	M	2(+)
18680.50	MW	2(+)	p_1 23119.06	MS	1(o)

Table I. Continued.

	Obs. Freq. Mc/sec	Int.	Stark-effect	
p_2	23219.21	MW	1(o)	
*	23300.79	W	2(+)	
*	23311.31	W	2(-)	
	23315.55	MW	1(i)	
	23340.67	MS	2(+)	$5_{14} \rightarrow 4_{22}$
	23341.31	M	2(+)	$5_{14} \rightarrow 4_{22}$
	23409.16	M	1(i)	
	23424.70	WW	1(i)	
	23429.42	M	1(i)	
	23432.84	WW	2?	
	23449.39	M	2(-)	$5_{23} \rightarrow 6_{15}$
	23449.65	W	2(-)	$5_{23} \rightarrow 6_{15}$
	23450.17	M	2(-)	$5_{23} \rightarrow 6_{15}$
	23683.17	MW	1(i)	
	23861.40	MS	1(o?)	
p_1	23873.61	MS	1(o)	
	24019.01	M	2(+)	
	24078.75	M	1(i)	
p_2	24320.57	MW	1(o)	
	24382.16	WW	2(+)	
p_1	24520.75	M	1(o)	
	24889.42	MS	2(+)	
	24889.80	M	2(+)	
	24993.76	WW	1(i)?	
p_1	25063.65	MS	1(o)	
q_2	25206.62	MS	1→2	
p_2	25401.99	W	1(o)	
p_1	25507.61	M	1(o)	
q_1	25810.49	M	1→2	
q_1	25810.96	MW	1→2	
p_1	25861.23	M	1(o)	
p_1	26134.72	M	1(o)	
p_1	26339.57	M	1(o)	
p_2	26448.15	W	1(o)	
p_1	26487.00	M	1(o)	
	26493.54	M	2(+)	
	26493.82	MW	2(+)	
p_1	26588.65	MW	1(o)	
p_1	26654.86	M	1(o)	
p_1	26695.43	M	1(o)	
p_1	26717.89	MW	1(o)	
p_1	26728.77	W	1(o)	
	26733.54	WW	1(o?)	
	27323.13	W	2(+)	
p_2	27445.47	MW	1(o)	
	27504.75	W	1(o?)	
	27758.40	W	1(i?)	
q_2	28107.75	MS	1→2	
	28142.85	MS	2(+)	
#	28183.46	W	2(+)	
#	28186.02	W	2	
p_2	28380.93	M	1(o)	
	28515.45	M	1(i)	
	28533.92	WW	1?	
q_1	29055.20	M	1→2	
	29138.85	W	1(i)	
	29147.37	W	1(i)	
	29191.47	MW	2(+)	
p_2	29244.20	W	1(o)	

It is estimated that the frequencies are accurate within ±0.10 Mc/sec for weaker lines and within ±0.04 Mc/sec or better for stronger lines.
*, # image pairs.

1) R. H. Hughes, W. E. Good, and D. K. Coles, Phys. Rev. 84 (1951), 418.
2) J. S. Koehler and D. M. Dennison, Phys. Rev. 57 (1940), 1006.
D. G. Burkhard and D. M. Dennison, Phys. Rev. 84 (1951), 408.
3) E. N. Lassettre and L. B. Dean, Jr., J. Chem. Phys. 17 (1949), 317.
J. G. Aston and P. M. Doty, J. Chem. Phys. 8 (1940) 743.
J. G. Aston, C. W. Siller, and G. H. Messerly, J. Am. Chem. Soc. 59 (1937), 1743.
4) D. R. Lide, Jr., J. Chem. Phys. 20 (1952), 1812.

E3. The Studies on Pure Quadrupole Spectra in Japan

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(Tokyo University of Education)

1. Introduction

The pure nuclear electric quadrupole absorption in solid was discovered by Dehmelt and Krüger in 1950[1]. Their method has been used in Japan since 1952. In this country there are two line of research, one of which is the research for the determination of quadrupole moments and the other is of quadrupole couplings. The former has been done at the Institute of Science and Technology of the University of Tokyo, and the latter mainly at the Department of Physics of Tokyo University of Education.

2. Nuclear quadrupole moment of iodine

At the Institute of Sience and Technology, where K. Murakawa has been studying the nuclear quadrupole moment by the method of the hyperfine structure of atomic spectra, T. Kamei studied the pure quadrupole spectra in crystalline bromine and iodine[2]. By the measurement of two resonance frequencies due to the two bromine isotopes he determined the quadrupole moment ratio of Br^{79} to Br^{81} as 1.1975 ± 0.0010. On iodine he measured two lines due to I^{127} at temperatures ranging from 85°C to the liquid air temperature. Assuming covalent bonding of iodine molecules and using the formula by Townes[3] he obtained the quadrupole moment of the iodine nucleus as -0.69×10^{-24} cm^2.

3. Quadrupole couplings of bromine

At Tokyo University of Education we had studied the microwave spectrum of bromoform ($CHBr_3$) and determined through its analysis the quadrupole couplings of Br^{79} and Br^{81} to be 577 Mc/s and 482 Mc/s respectively[4]. Although Dehmelt and Krüger[5] reported in their paper on methyl bromide the observation of the pure quadrupole absorption in solid bromoform, they did not give its frequency. Then we have attempted the method of pure quadrupole absorption. The apparatus used was a simple superregenerative oscillator unit with a transmission line tuned circuit. The frequency of the absorption lines was measured by a heterodyne wave meter, which contained a crystal oscillator and an interpolation oscillator.

Measurements on solid bromoform have been made at temperatures ranging from about 250 °K to the liquid air temperature. The observed spectrum corresponding to each bromine isotope had a triplett structure. The result is plotted against to the temperature in Fig. 1(a). The quadrupole couplings at the liquid air temperature of bromine isotopes Br^{79} and Br^{81} in solid bromoform were about 600 Mc/s and 501 Mc/s respectively. Generally it is known that in alkyl halides the quadrupole couplings in gaseous state are slightly stronger than that in solid state. If it is so about bromoform, our previous values seem to be rather small. The analysis of the microwave spectrum, however, may be not much affected by this correction.

With this apparatus we have studied number of bromine compounds: ethyl bromide, normal-propyl bromide, normal-butyl bromide, bromobenzene, stanic bromide and phosphorous tribromide. On these substances the resonance frequencies of Br^{79} and Br^{81} were measured. The ratio of the frequency was 1.1970 ± 0.0001, which accord with Kamei's value on Br_2 and with Dehmelt Krüger's value on CH_3Br. Assuming that the field

gradients were axial symmetry the quadrupole couplings were calculated by doubling the resonance frequencies. The results were summarized in Table III. The spectra of PBr_3 and $SnBr_4$ were a doublet and quartet respectively. On $SnBr_4$ the temperature dependency was studied, which is shown in Fig. 1(b). The absorption frequencies of these substances will be published soon[6].

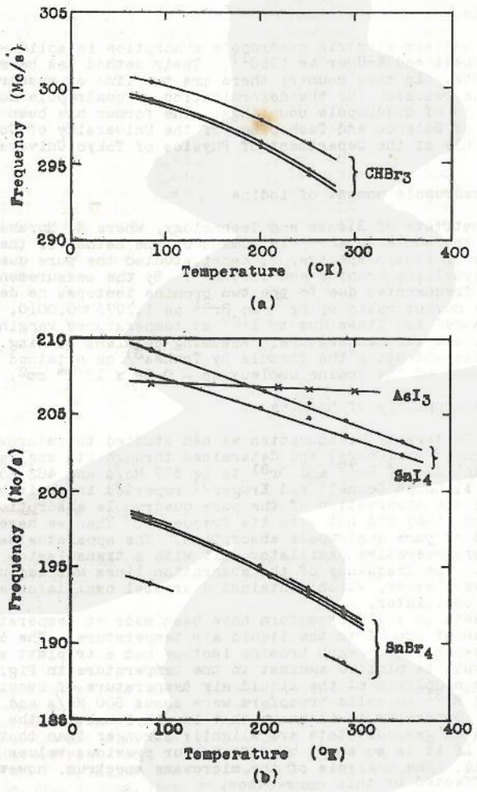

Fig. 1. Pure quadrupole resonance frequencies as a function of temperature.
(a) $CHBr_3^{79}$
(b) $SnBr_4^{79}$ and the lower frequencies of AsI_3 and SnI_4.

4. Quadrupole couplings of alkyl halides

The quadrupole couplings of the three alkyl halides given above and the known coupling of methyl bromide[5] showed that they were not represented by a smooth function of the number of carbons in alkyl. But it was found that there was a correlation between the couplings and the melting points. This relation is shown in Table I.

Table I. Quadrupole couplings of Br^{79}.

Molecule	eQq (Mc/s)	Melting point[7] (°C)	Reference
CH_3Br	528.9	- 93	5)
C_2H_5Br	497.0	- 119.0	6)
n-C_3H_7Br	503.0	- 110.0	6)
n-C_4H_9Br	499.9	- 112.7	6)

We had obtained the coupling factor assuming the axial symmetry of field gradient. In the case of the bromine isotopes which have the spin of 3/2 we can not easyly determine the deviation from the symmetry. The iodine isotope having the spin of 5/2 has two kinds of transition. With these two absorption frequencies ν_1 and ν_2 we can calculate the coupling eQq and the asymmetry factor η by the formulas:

$$\nu_1 = \frac{3}{20} eQq\left(1 + \frac{59}{54}\eta^2\right) \text{ and } \nu_2 = \frac{3}{10} eQq\left(1 - \frac{11}{54}\eta^2\right).$$

We have carried out the study for alkyl iodides. The results are shown in Table II. The coupling in CH_3I observed by Dehmelt[9] was 1753 Mc/s, which is slightly different from ours.

Table II.[8] Quadrupole coupling of I^{127}.

Molecule	ν_1 (Mc/s)	ν_2 (Mc/s)	η (%)	eQq (Mc/s)	Melting point (°C)[7]
CH_3I	264.973 ± 0.01	529.515 ± 0.01	2.5	1765.3	- 66.45
C_2H_5I	247.115 ± 0.01	494.058 ± 0.01	1.6	1647.0	- 111.1
n-C_3H_7I	250.810 ± 0.02	499.810 ± 0.01	5.2	1666.9	- 101.3
n-C_4H_9I	249.062 ± 0.02	497.539 ± 0.03	3.0	1658.8	- 103.0

These results show the same relation that the compounds having the higher melting point have the larger coupling. Since melting is interpreted as an intermolecular phenomenon, the changing part of the coupling factor seems to relate to the intermolecular binding.

5. Summary of the results on quadrupole couplings in solid

In addition to the studies mentioned above there are number of experiments in Japan. K. Torizuka at Tokyo University of Liberal Arts measured the resonance frequencies of Cl^{35} and Cl^{37} in potassium chlorate and in para-dichlorobenzene. K. Shimomura at Minami Branch of Hiroshima University observed absorptions of Br^{79} and Br^{81} in stanic bromide, dibromoethane and potassium bromate, and studied the intensity distribution in the multiplet of the absorption line of I^{127} in stannic iodide. T. Kushida and his colaborators at Department of Physics of

Hiroshima University measured the absorptions of bromine isotopes in silber bromate.

We measured the absorption lines of lower frequency of I^{127} in arsenic iodide, stannic iodide and monoiode acetic acid. On arsenic iodide and stannic iodide the resonance frequencies were measured in the region from room temperature to the liquid air temperature. The results are plotted in Fig. 1(b). The measurement on the lines of higher frequency will be completed soon.

The quadrupole coupling factors obtained in Japan are summarized in the Table III. Table IV gives the quadrupole couplings, of Na, which was not obtained by pure quadrupole spectra, but by fine structures of nuclear magnetic resonances.

Table III. Nuclear quadrupole couplings.

Nucleus	Molecule	eQq (Mc/s)	Temperature	Multiplicity of resonance	Reference
Cl^{35}	$KClO_3$	56.16	27.5 °C	1	10)
Br^{79}	$CHBr_3$	600.	liquid air	3	6)
	C_2H_5Br	497.0	liquid air	1	6)
	$n\text{-}C_3H_7Br$	503.0	liquid air	1	6)
	$n\text{-}C_4H_9Br$	499.9	liquid air	1	6)
	C_6H_5Br	528.5	liquid air	1	6)
	$CH_2Br\text{-}CH_2Br$	522	liquid air	2	11)
	$AgBrO_3$	340	room temp.	1	12)
	$KBrO_3$	345.9	25 °C	1	11)
	PBr_3	439.6	liquid air	2	6)
	$SnBr_4$	382	16.? °C	4	6)
I^{127}	CH_3I	1765	liquid air	1	8)
	C_2H_5I	1647	liquid air	1	8)
	$n\text{-}C_3H_7I$	1667	liquid air	1	8)
	$n\text{-}C_4H_9I$	1659	liquid air	1	8)
	CH_2ICOOH	1926 *	liquid air	2	13)
	AsI_3	1380 *	liquid air	1	13)

The eQq of Br^{81} is obtained from the eQq of Br^{79} by dividing by 1.197.
* provided that $\eta = 0$.

Table IV. Nuclear quadrupole couplings from nuclear magnetic resonances.

Nucleus	Crystal	eQq (Mc/s)	η	Reference
Na^{23}	$Na_2S_2O_3\ 5H_2O$	2.255	0.334	14)
		0.830	0.407	14)
	$NaClO_3$	0.800	0	14)
	$NaBrO_3$	0.832	0	14)

6. On the pure quadrupole absorption in gaseous state

In general the pure quadrupole spectrum of a free molecule has a large number of lines due to the splitting of energy levels by the rotation. But when a linear molecule contains a only one nucleus having quadrupole moment and spin of 3/2, many lines of the spectrum superpose each other. In this case there are three kinds of transition:

$$F = J + \frac{3}{2} \rightarrow J + \frac{1}{2} \qquad \nu_1 = \frac{1}{4} eQq,$$
$$F = J + \frac{1}{2} \rightarrow J - \frac{1}{2} \qquad \nu_2 = \frac{1}{4} eQq \frac{3(2J+1)}{(2J-1)(2J+3)},$$
$$F = J - \frac{1}{2} \rightarrow J - \frac{3}{2} \qquad \nu_3 = \frac{1}{4} eQq.$$

The lines of the first kind and of the second kind do not depend on rotational states and coincide into one. For such molecules the observation of pure quadrupole absorption in gaseous state may be possible. We are planning the study for hydrogenbromide, in which the deviation from above formulas due to the second order effect of quadrupole couplings seems to be small.

Except this case the absorption apectra are complex. T. Itoh at the Department of Physics of the University of Tokyo studied spectra of symmetric top molecules theoretically. He took into account the transition due to the electric dipolemoment of the molecule in place of the nuclear magnetic moment which was important in the cases of crystals or linear molecules. And he calculated the spectra of methyl bromide and of bromoform which are reproduced in Fig. 2 and Fig. 3. The width of lines was estimated to be about 3 Mc/s in both cases. The absorption coefficients were the order of 10^{-8} cm^{-1} for methyl bromide at 1 mm Hg and of 10^{-11} cm^{-1} for bromoform at 10 mm Hg. The absorbing intensities are so small that measuring instruments are required a very high sensitivity.

The study of the pure quadrupole spectra of free molecules is now speculative, but its observation will be possible in future.

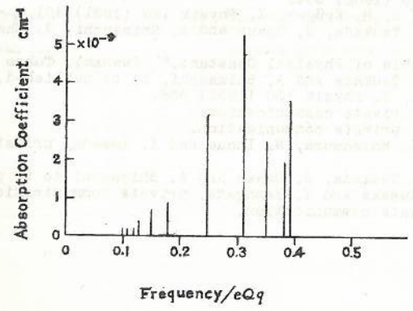

Fig. 2. Theoretical spectrum of CH_3Br^{79} at p = 1 mm Hg calculated by Itoh, beirg assumed eQq as 577 Mc/s. Only the lines with $J = K \leqq 6$, which were predominantly strong, were taken into account.

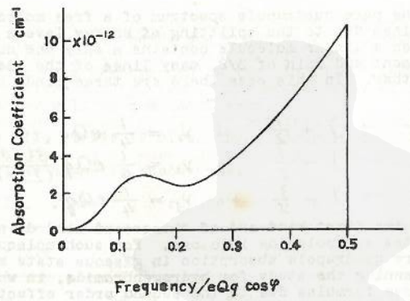

Fig. 3. Theoretical spectrum of $CHBr_3^{79}$ at p = 10 mm Hg calculated by Itoh, being assumed that eQq = 577 Mc/s, <BrCBr = φ = 111° and J = ∞ because of the large values of probable J's.

References

1) H. G. Dehmelt u. H. Krüger, Naturwiss. 37 (1950) 111.
2) T. Kamei, J. Phys. Soc. Japan 7 (1952) 649; Rep. Inst. Sci. Tech. 6 (1952) 237 in Japanese.
3) C. H. Townes, Phys. Rev. 71 (1948) 909.
4) S. Kojima, K. Tsukada, S. Hagiwara, M. Mizushima and T. Ito, J. Chem. Phys. 20 (1952) 804.
5) H. G. Dehmelt u. H. Krüger, Z. Physik 129 (1951) 401.
6) S. Kojima, K. Tsukada, S. Ogawa and A. Shimauchi, J. Chem. Phys. in press.
7) K. Shiba, "Table of Physical Constant." Iwanami, Tokyo (1944).
8) S. Kojima, K. Tsukada and A. Shimauchi, to be published.
9) H. G. Dehmelt, Z. Physik 130 (1951) 356.
10) K. Torizuka, private communication.
11) K. Shimomura, private communication.
12) T. Kuchida, K. Shimomura, N. Inoue and Y. Imaeda, private communication.
13) S. Kojima, K. Tsukada, S. Ogawa and A. Shimauchi to be published.
14) J. Itoh, R. Kusaka and Y. Yamagata, private communication.
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