

The Quadrupole Coupling of Three Nuclei in a Rotating Molecule

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done by T. Nishiyama,⁴ who obtains, however, by this method a result equivalent to that which I have derived.

It is very difficult to reconstruct the argument of Riddell and Uhlenbeck between (10) and (11), but an independent calculation shows that their result (11) is incorrect. In fact, one obtains for the right-hand side an expression which may be written simply

$$\left(q \frac{\partial}{\partial q} + q' \frac{\partial}{\partial q'} \right) \langle q | \exp -\beta \mathcal{H} | q' \rangle, \quad (c)$$

on the understanding that $\partial/\partial q$ and $\partial/\partial q'$ do not operate on $W(q/L)$. Since $W(q/L)$ must in any case be zero except outside the fluid, this last stipulation does not have any quantitative effect, the integration being limited to the region occupied by the fluid.

The statement (iii) above is almost self-evident. The condition necessary for the permutation of the operators is that the expectation values of certain physical quantities should be negligible at the wall; and Riddell and Uhlenbeck have not investigated the circumstances under which this condition is satisfied. I find that the condition is not satisfied in quantum liquids, and I believe that many of the properties of He II can be understood from this point of view.

¹ Riddell and Uhlenbeck, *J. Chem. Phys.* **18**, 1066 (1950).

² J. de Boer, *Physica* **15**, 843 (1949).

³ H. S. Green, *Physica* **15**, 882 (1949).

⁴ A short note on the virial theorem. I am much indebted to Dr. Nishiyama for sending me a copy of his manuscript.

Investigations on the Hydrated Molybdenum Blue

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May 28, 1950

IN connection with the different conclusions reported¹ on the constitution of hydrated molybdenum blue, the composition of this compound, prepared from hydrochloric solutions of Mo^V and Mo^{VI} , has been investigated.

Varying the ratios of $\text{Mo}^{VI}:\text{Mo}^V$ in the solutions from 9.0 to 0.56, the empirical unitary formula of the produced molybdenum blue lies between $\text{Mo}_{2.89} \cdot x \text{H}_2\text{O}$ and $\text{Mo}_{2.93} \cdot x \text{H}_2\text{O}$ and the ratios of $\text{Mo}^{VI}:\text{Mo}^V$ in the blues varies from 3.4 to 6. The amount of water present in the compounds ranges from 17.96 to 19.38 percent. The slight paramagnetism exhibited by the compounds (about one-tenth to one-twentieth that for one unpaired electron) suggests that pentavalent molybdenum, in the blue, is mainly bound with covalents $\text{Mo}^V\text{-Mo}^V$ linkages.

The hydrated blue, treated at 195°C in an atmosphere of nitrogen, loses nearly all the water of hydration. At 350°C decomposition takes place with separation of MoO_3 and formation of a more reduced blue oxide. X-ray analysis showed that both hydrated and dehydrated (at 195°C) molybdenum blues are essentially amorphous. The few diffuse halos on continuous background in the powder photographs are coincident with the x-rays lines produced by MoO_3 . Electric resistance determinations on molybdenum blue showed that the blue treated at 195°C behaves as a typical semiconductor. The values of conductivity range from $10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$ at 20°C to $10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$ at 180°C. The temperature coefficient is strongly positive and the classical relation $\sigma = A e^{-B/T}$ is satisfied. The results indicate that amorphous molybdenum blue, behaving as a reduction semiconductor, is a non-stoichiometric compound with a stoichiometric defect of oxygen.

Treatment of the blue at 350°C causes the conductivity to reach values of the order of $1 \text{ ohm}^{-1}\text{cm}^{-1}$ and the temperature coefficient, between 350°C and 20°C, becomes almost nil, which con-

firms that thermal treatment at 350°C causes decomposition and yields a different blue oxide. This oxide, indeed, separated with aqueous ammonia, exhibits a similar conductivity, while the conductivity of MoO_3 , the variation of which with temperature has not yet been reported, varies from $10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$ at 20°C to $10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$ at 350°C.

The investigation continues chiefly in regard to the study of the compounds which arise from thermal treatment of hydrated molybdenum blue.

¹ J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longman and Company, London), Volume XI; R. Abegg and Fr. Auerbach, *Handbuch der Anorganischen Chemie* (Verlag S. Hirzel, Leipzig), Volume IV; O. Glemser and E. Lutz, *Naturwiss.* **34**, 215 (1947).

Erratum: Parabolic Oxidation Rates of Metals

[*J. Chem. Phys.* **18**, 231 (1950)]

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IN footnote 2 of this letter it is stated that the theoretical equation of Mott and Gurney for the parabolic rate constant K contains an incorrect factor of 2. Actually their equation is given correctly in *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 257. The author regrets this mistake.

The Quadrupole Coupling of Three Nuclei in a Rotating Molecule

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May 25, 1950

RECENTLY the microwave spectra of a number of molecules (AsCl_3 ,¹ PCl_3 ,¹ CHBr_3 ,² PBr_3 ,² CHCl_3 ,³) with three quadrupolar nuclei have been measured. The calculation of the energy levels of such a molecule is most simply done by the tensor methods of G. Racah.⁴ His procedure in fact yields directly the matrix elements for any quadrupole coupling problem.

Let the spins be I_1, I_2, I_3 , the quadrupole moments Q_1, Q_2, Q_3 and $(\partial^2 V / \partial z^2)$ (i) be the derivative of the potential taken at the position of the i th nucleus with respect to a z -axis fixed in space. Let $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$, $\mathbf{I} = \mathbf{I} + \mathbf{I}_3$, $\mathbf{F} = \mathbf{I} + \mathbf{J}$. The matrix elements of the molecular quadrupole Hamiltonian are

$$\begin{aligned} \langle IJF | H_Q | I'J'F' \rangle &= \frac{5}{4} (-1)^{I_1+I_2+I_3-I-I'+J'-F} \\ &\times \frac{eQ_1(J | \partial^2 V / \partial z^2 (1) | J') [(2I+1)(2I'+1)(2I+1)(2I'+1)]^{\frac{1}{2}}}{(I_1 I_1 - I_1 I_1 | I_1 I_1 20) (JJ' - JJ | JJ' 20)} \\ &\times W(I_1 I_1 I'; I_2) W(I I' I'; I_3) W(I J I' J'; F_2) \\ &+ \frac{5}{4} (-1)^{I_1+I_2+I_3-2I+J'-F} eQ_2(J | \partial^2 V / \partial z^2 (2) | J') \\ &\times \frac{(I_2 I_2 - I_2 I_2 | I_2 I_2 20) (JJ' - JJ | JJ' 20)}{(I_1 I_1 - I_1 I_1 | I_1 I_1 20) (JJ' - JJ | JJ' 20)} \\ &\times W(I_2 I_2 I'; I_1) W(I I' I'; I_3) W(I J I' J'; F_2) \\ &\times [(2I+1)(2I'+1)(2I+1)(2I'+1)]^{\frac{1}{2}} \\ &+ \frac{5}{4} (-1)^{I_1+I_2+I_3-I-I'+J'-F} eQ_3(J | \partial^2 V / \partial z^2 (3) | J') \\ &\times \frac{[(2I+1)(2I'+1)]^{\frac{1}{2}} \delta_{I_1, I'} W(I_3 I_3 I_3'; 12)}{(I_3 I_3 - I_3 I_3 | I_3 I_3 20) (JJ' - JJ | JJ' 20)} \\ &\times W(I J I' J'; F_2). \end{aligned}$$

$W(j_1 j_2 j_3'; j_1 j_2 j_3)$, introduced by Racah, is essentially the matrix element of the scalar product of two irreducible tensors of rank k

between the states $(j_1 j_2 j m |$ and $(j_1' j_2' j m |$. In the special cases that the three nuclei are identical, have identical coupling constants, and have spins of 1 or $\frac{3}{2}$, the matrix elements have been calculated as a function of J .⁵ For each energy level $J(J \geq 2)$, six cubic and two quartic equations must be solved.

* Now at Columbia University, New York, New York.

¹ P. Kisliuk and C. H. Townes, *Phys. Rev.* **78**, 347 (1950); *J. Chem. Phys.* **18**, 1109 (1950).

² Q. Williams and W. Gordy, *Phys. Rev.* **79**, 195 (1950).

³ Unterberger, Trambarulo, and Smith, *J. Chem. Phys.* **18**, 565 (1950).

⁴ G. Racah, *Phys. Rev.* **62**, 438 (1942).

⁵ R. Bersohn, thesis, Harvard University, 1949.

Electron Deficient Compounds. V. The Structure of Dimethylberyllium*

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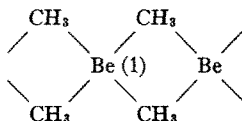
May 29, 1950

EMPIRICAL¹ and theoretical² justification has been given for the rule that metals tend to use all low energy orbitals for bond formation, even when orbitals exceed valence electrons numerically. This accounts for known electron deficient compounds, and allows prediction of their occurrence.

On the basis of the above rule dimethylberyllium, a compound subliming at 200°C, should involve four tetrahedral, electron-deficient bonds to beryllium. The structure fulfills these predictions.

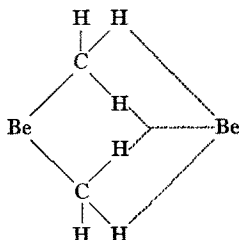
Dimethylberyllium is body-centered, orthorhombic, $a_0 = 6.14$, $b_0 = 11.53$, $c_0 = 4.18$ Å, $\rho = 0.9$, $z = 4$. Reflections $(h0l)$ and $(0kl)$ occur with even indices only, so the space group is $Ibam$ or Iba . In either case the eight carbon positions are $(000, \frac{1}{2}, \frac{1}{2}) \pm xy0$, $\pm xy\frac{1}{2}$, with $x = 0.182 \pm 0.003$, $y = 0.101 \pm 0.003$. The beryllium positions are $(000, \frac{1}{2}, \frac{1}{2}) + 00z$, $00z + \frac{1}{2}$, with $z = \frac{1}{4}$ for $Ibam$. Reflections $(00l)$ limit z to 0.25 ± 0.026 for Iba . The structure determination, when refined, will be published elsewhere.

The structure, isomorphous with SiS_2 , consists of chains,



The configuration about Be is approximately tetrahedral with $Be-C = 1.92 \pm 0.03$ Å, versus 1.84 calculated by Pauling's radii and rule,³ assuming half an electron pair per bond. The $C-Be-C$ angle, (1), is 114° . The $Be-Be$ distance is 2.09 ± 0.01 Å, which, by Pauling's rule, indicates a bond number of 0.3. The larger than tetrahedral $C-Be-C$ bond angle, (1), lends support to the idea that $Be-Be$ bonding is important. The angle may also be explained by the need for a sharp $Be-C-Be$ angle. The distance is long enough to suggest that the $Be-Be$ bond does not share electrons equally with the $Be-C$ bonds.

Symmetry of even the lower space group rules out methyl bridges like those suggested by Pitzer and Gutowsky for the trimethylaluminum dimer,⁴ and the distances rule out analogous bridges,



By analogy this structure suggests symmetrical bridges in trimethylaluminum, as has been proposed.^{5,6} There is nothing in the distances to suggest material contribution of $C-H$ bonds to the electrons of the bridge. The bonding probably consists essentially of one tetrahedral orbital from carbon symmetrically overlapping tetrahedral orbitals from each of two beryllium atoms to form one molecular orbital for the $Be-C-Be$ half-bond pair. The $Be-C-Be$ angle, only 66° , permits good utilization of the carbon tetrahedral orbital in this arrangement, first suggested by Mulliken.⁶ An analogous type of geometry of the migrating group in molecular rearrangements would account for the observed retention of configuration.

The structure does not appear to be predominantly ionic. Moreover, negative methyl ions should require larger $C-C$ distances between chains than the 4.1 Å observed.

Electron deficient compounds, historically limited to third group elements, now include platinum and beryllium compounds. Extension to other groups of the periodic table is to be expected from the rule above.

* Paper No. 96 from the Institute for Atomic Research, Iowa State College, Ames, Iowa. This work was performed in the Ames Laboratory, AEC.

¹ R. E. Rundle, *J. Am. Chem. Soc.* **69**, 1327 (1947).

² R. E. Rundle, *J. Chem. Phys.* **17**, 671 (1949).

³ L. Pauling, *J. Am. Chem. Soc.* **69**, 542 (1947).

⁴ K. Pitzer and Gutowsky, *J. Am. Chem. Soc.* **68**, 2204 (1946).

⁵ R. S. Mulliken, *Chem. Rev.* **41**, 207 (1947).

A Theoretical Calculation of Valence-Bond Parameters

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May 29, 1950

THE valence bond method enables us to express the energy of the π -electrons in terms of two parameters: the Coulomb integral Q and the (single) exchange integral α . E.g., for benzene, we have

$$Q = \int a(1)b(2)c(3)d(4)e(5)f(6)Ha(1)b(2)c(3)d(4)e(5)f(6)d\tau$$

and

$$\alpha = \int a(1)b(2)c(3)d(4)e(5)f(6)Ha(2)b(1)c(3)d(4)e(5)f(6)d\tau.$$

Here a, b, c , etc., are the p_z -wave functions of the carbon atoms and the π -electrons are labeled by 1, 2, 3, etc.¹

In this treatment the non-orthogonality integrals $s_{12} = \int a(1)b(1)d\tau$, etc., the single-exchange integrals between non-neighboring atoms and all double-, triple-, etc., exchange integrals are neglected. So it is possible to express the energy of a certain structure of a molecule as $Q + m\alpha$. For instance the Kékulé-structure of benzene has the energy $Q + 1.5\alpha$; the stationary ground state $Q + 2.61\alpha$.

If we take now the energy difference between two states, e.g., to calculate a resonance energy (R.E.) or an ultraviolet transition, Q cancels out and we are left with an expression in α . By putting this equal to the experimental R.E., α can be calculated. It is possible however to evaluate theoretically $\alpha(\alpha')$ and also other exchange integrals neglected hitherto. Hence it is no longer justifiable to neglect the non-orthogonality integrals and so we have to transform α into $\alpha' \equiv \alpha - S_{12}^2 Q$, for only after this transformation Q cancels out in the expression for the R.E.'s and the excitation energies. Of course the other exchange integrals have to be transformed in an analogous way. In general, an exchange integral becomes $\lambda' = \lambda - lQ$, where l is equal to the integral for λ with the Hamiltonian H replaced by unity; thus l is the product of a number of non-orthogonality integrals.