A OneDimensional Treatment of the Hydrogen Molecule Ion

Mac Walsh and F. A. Matsen

Each complete MO so constructed holds on the average zero, one, or two electrons, the number being uniquely determined by the structures used. (A pair of electrons in a bond can be considered as one electron on each nucleus or two electrons on one nucleus and none on the other. However, if any of the structures used show a nucleus with no electrons, or one or two unpaired electrons, then the MO constructed on that nucleus must have the same electron population in all structures.)

The coefficients a, b, $c \cdots$ above can be found by solving the secular equation

$$\begin{vmatrix} H_{II} - W & H_{I\ II} - \Delta_{I\ II} W \cdots \\ H_{I\ II} - \Delta_{I\ II} W & \cdots \cdots \\ \cdot \\ \cdot \\ \cdot \end{vmatrix} = 0, \qquad (2)$$

where since the total electronic energy is to be a minimum, H_{II} is the sum of the electronic energies in structure I, each calculated in terms of Coulombic integral q and exchange integral β by the usual simplified MO method. $H_{I\ II}$ is the sum of the electronic energies calculated, for example, for an electron in the MO centered on nucleus A:

$$H'_{I\ II} = \int \psi_I(A) H' \psi_{II}(A) d\gamma \qquad (3)$$

where H' is a single electron Hamiltonian. $\Delta_{I\ II}$ is the average value of the overlap integral $\Delta'_{I\ II}$

$$\Delta'_{I\ II} = \int \psi_I(A) \psi_{II}(A) d\gamma \qquad (4)$$

for each MO weighted according to its population. The lowest root of (2) then gives the values of a, b, $c \cdots$ which make the total energy of the system a minimum.

This method in general gives excellent agreement with ground state energies calculated by either the usual MO method or the valence bond method and is frequently simpler to use. It has the advantage for chemists of emphasizing conventional bond structures while retaining the simplicity of MO calculations.

As an example, calculate the energy of the six π-electrons of benzene considering only the two Kekulé structures. (For simplicity but not by necessity the usual assumptions as to orthogonality and exchange integrals between non-adjacent atoms will be made.) The secular equation calculated by the rules given above is

$$\begin{vmatrix} 6q + 6\beta - W & 3q + 6\beta - \dfrac{W}{2} \\ 3q + 6\beta - \dfrac{W}{2} & 6q + 6\beta - W \end{vmatrix} = 0 \qquad (5)$$

which has the lowest root $W = 6q + 8\beta$. The six complete molecular orbitals centered on each carbon nucleus are all equivalent and of the form $\psi(B) = 1/(6)^{\frac{1}{2}}(2\psi_B + \psi_A + \psi_C)$, etc. Each has an average population of one electron with an energy of $q + 4/3\beta$. It is of interest to note that the inclusion of the Dewar structures of benzene does not improve the energy; in fact, they make no contribution in this method of calculation.

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October 8, 1949

THE Pauling treatment[1] of the H_2^+ leads to the energy expression

$$E = W_H + e^2/R_{ab} + (J+K)/(1+\Delta),$$

where

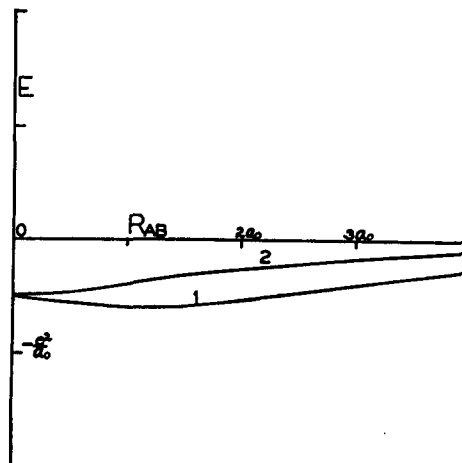$$J = \int \frac{U_{1a} U_{1a} d\tau}{r_b},$$

$$K = \int \frac{U_{1a} U_{1b} d\tau}{r_b},$$

$$\Delta = \int U_{1a} U_{1b} d\tau.$$

This treatment yields a binding energy for H_2^+ of $0.384e^2/a_0$ compared with the experimental $0.603e^2/a_0$.

One of the reasons for the low result is the lack of polarization in the atomic wave functions. It was of interest, therefore, to ascertain the effect of 100 percent polarization, i.e., the restriction of the motion of the electron along the axis of the molecule. The exchange integral $K/1+\Delta$ can be evaluated for this model although the Coulomb integral $J/1+\Delta$ cannot.

The one-dimensional hydrogen atom Schroedinger equation[2] is

$$d^2\psi/dx^2 + (8\pi^2 M)/h^2(W + e^2/|x|)\psi = 0$$

with solution $\psi = (2/a_0^{\frac{1}{2}})|x| \exp - |x|/a_0$ corresponding to the ground state energy, $W_H = 0.5e^2/a_0$. The expression for $K/(1+\Delta)$ in units of e^2/a_0 becomes

$$\frac{-(R^2 + R + 1)e^{-R}}{1 + (R^3/3 + R + 1)e^{-R}},$$

where $R = (R_{ab})/a_0$. As is expected, the value of $K/1+\Delta$ is larger for the one-dimensional (100 percent polarized) model than for the three-dimensional model (see Fig. 1). Combining the former with the three-dimensional $J/1+\Delta$ the binding energy is 37 percent greater than the exact value.

[1] L. Pauling, Chem. Rev. 5, 173 (1928); L. Pauling and E. B. Wilson, Introduction to Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1935), p. 327.
[2] V. R. Vrkljan, Zeits. f. Physik. 52, 735 (1927).

The Transport Properties for Non-Polar Gases

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October 17, 1949

OUR attention has just been called to the work of T. Kihara and M. Kotani on the determination of intermolecular forces from transport phenomena in gases.[1]

In this article Kihara and Kotani performed essentially the same integrations as we did[2] to obtain the Chapman and Coeling collision integrals for non-polar gases using the Lennard-Jones potential, with an inverse twelfth power energy of repulsion and an inverse sixth power energy of attraction.

The $F_n{}^m$ tabulated by Kihara and Kotani are very simply related to the $W^{(m)}(n)$ which we presented in our publication: $W^{(m)}(n) = (2\epsilon/kT)^{1/6}F_n{}^m$. Table I exhibits typical numerical agreement in the values of the collision integrals.

TABLE I.

	$kT/\epsilon=1$		$kT/\epsilon=20$	
	Kihara and Kotani	Hirschfelder, Bird, and Spotz	Kihara and Kotani	Hirschfelder, Bird, and Spotz
$W^{(1)}(1)$	0.7199	0.7197	0.3320	0.3320
$W^{(1)}(2)$	1.806	1.806	0.9442	0.9439
$W^{(1)}(3)$	6.455	6.456	3.631	3.629
$W^{(2)}(2)$	1.590	1.587	0.7437	0.7432
$W^{(2)}(3)$	5.550	5.550	2.866	2.864
$W^{(2)}(4)$	25.15	25.16	13.92	13.90

This excellent agreement obtained by the two independent groups greatly increases our confidence in the accuracy of our respective tables. We are sorry that we were previously unaware of this Japanese publication.

A few values of these integrals were calculated by J. deBoer and J. Van Kranendonk,[3] and excellent agreement was obtained with their results. A few other numerical calculations were made by Rowlinson.[4]

[1] T. Kihara and M. Kotani, Proc. Phys.-Math. Soc. (Japan) 24, 76 (1942); 25, 602 (1943).
[2] Hirschfelder, Bird, and Spotz, J. Chem. Phys. 16, 968 (1948).
[3] J. deBoer and J. Van Kranendonk, Physica 14, 442 (1948).
[4] J. S. Rowlinson, J. Chem. Phys. 17, 101 (1949).

Hydrocarbon Flame Spectra*

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October 3, 1949

THE combustion of hydrocarbons has been studied intensively for many years because of its theoretical and practical interest. The spectra of hydrocarbon flames were first investigated in detail under low dispersion by Vaidya.[1] He described the appearance of a system of bands called the hydrocarbon (or ethylene) flame bands which are degraded to the red and lie between 2500 and 4100A. These bands were arranged in a vibrational scheme and it was suggested that the emitter of this system was the HCO radical. Since that time many investigations with explosion and various types of stationary hydrocarbon flames have been conducted with the result that the hydrocarbon flame bands have been reported in practically all cases of hydrocarbons burning with air, oxygen or atomic oxygen.[2]

Since most of these flame spectra were investigated with rather low dispersion instruments we have been studying the stationary flames of methane and ethylene under a variety of conditions. A 2-meter Baird grating spectrograph was employed with dispersion 4A/mm and 8A/mm in the regions 3000–4000A and 7000–9000A, respectively.

In a recent note[3] we reported the appearance of the $^1\Pi_g{-}^1\Pi_u$ Deslandres-D'Azambuja band system of the C_2 molecule in the spectra of the low pressure stationary flames of ethylene and methane burning with oxygen at stoichiometric proportions. Further studies of these flames reveal, in the region 3000–4000A, bands of the $^3\Sigma_u{-}^3\Sigma_g{-}$ Schumann-Runge system of the O_2 molecule in addition to the C_2 bands mentioned above, as well as various OH and CH bands, e.g., the (0,1) OH band at 3428A and the (1,0) CH band at 3628A. The O_2 bands are stronger the higher the relative concentration of oxygen. These results are similar to those reported by one of us[4] in the $CO+O_2$ explosion flame.

At this point in our investigations we suggest the possibility that the overlapping of the various bands of the diatomic species OH, CH, C_2 and O_2 may produce, in the region 3000–4000A, what has the appearance of a system of bands heretofore ascribed to the HCO radical. Whether or not the above mentioned diatomic species account for all the band structure in this spectral region requires more detailed study.

We have also observed in emission from hydrocarbon flames the heads of the (0,0) and (1,1) bands of the $^1\Sigma_g{+}{-}^3\Sigma_g{-}$ atmospheric absorption system of O_2 which lie at 7594 and 7685A respectively. In addition we find the (2,0) band at 8751A of the recently discovered $^1\Pi_u{-}^1\Sigma_g$ Phillips' system[5] of the C_2 molecule. Since the Phillips' bands involve the lower states of the $^1\Pi_g{}^1{-}\Pi_u$ Deslandres-D'Azambuja and the $^1\Sigma_u{+}{-}^1\Sigma_g{+}$ Mulliken systems, one would expect both the Deslandres-D'Azambuja and Phillips' bands to be found together in the flame spectrum. The Mulliken bands of C_2 as well as the Fourth Positive bands of CO appear in flames of ethylene and oxygen. These bands have been observed by Gaydon[2] in the oxyacetylene flame. Thus, all the known band systems of the C_2 molecule have been observed in hydrocarbon flames except the $^3\Pi_g{-}^3\Pi_u$ Fox-Herzberg bands and we are now searching for the latter system which may account for some of the structure in the region 3000–4000A.

We hope in the near future to report the detailed results of these investigations as well as further studies of the hydrocarbon flame spectrum between 2500–3000A.

We wish to thank Dr. G. Herzberg and Dr. J. G. Phillips for their interest and many profitable discussions.

[1] W. M. Vaidya, Proc. Roy. Soc. A147, 513 (1934).
[2] A. G. Gaydon, Spectroscopy and Combustion Theory (Chapman and Hall Ltd., London, 1948).
[3] G. A. Hornbeck and R. C. Herman, J. Chem. Phys. (to be published).
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[5] J. G. Phillips, Ap. J. 107, 389 (1948).

Chemical Oxidation States of Cl and N Formed by the $S^{34}(p, n)Cl^{34}$ and $O^{16}(p, \alpha)N^{13}$ Reactions in Crystals

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October 20, 1949

ALTHOUGH many studies have been made of the fate of atoms after radiative neutron capture (Szilard-Chalmers reaction), little has been done in determining the chemical fate of transmuted atoms arising from bombardment with high energy ions, especially in inorganic crystals. Libby[1] has discussed the expected fate of hot transmuted atoms in crystal lattices, and a few investigations of such processes have been made.[2]

We are extending this work of determining chemical states after bombardment of inorganic crystals with high energy ions, and wish to report our work on the chemical state of Cl and N produced by the $S^{34}(p, n)Cl^{34}$ and $O^{16}(p, \alpha)N^{13}$ reactions.

Chlorine was chosen because of the many oxidation states possibly present after bombardment: -1 (Cl^-), 0 (Cl_2), $+1$ (ClO^-), $+3$ ($ClO_2{}^-$), $+4$ (ClO_2), $+5$ ($ClO_3{}^-$), and $+7$ ($ClO_4{}^-$). Production of the higher oxidation states would presumably be favored by bombardment of crystals rich in oxygen,[3] so sulfates and peroxydisulfates were chosen as targets. Powdered anhydrous C.P. Na_2SO_4 and $K_2S_2O_8$ samples were wrapped in thin aluminum foils and bombarded with 14-Mev protons in the circulating beam of the U.C.L.A. 37-in. frequency-modulated cyclotron[4] for 30-min. periods (current ~ 1 μa). The targets showed activities with half-