The values of $\Delta\bar{\lambda}$ are approximately the same as for the hindered phenols. This is to be expected in view of the steric hindrance the t-butyl groups on the ortho positions will offer to the approach of ethanol molecules and to the fact that in the intramolecular hydrogen bond the dipole moments of the hydroxyls will partially cancel each other, thus reducing the attraction of such a molecule for the alcohol molecules.

It is interesting to note that the center of the fundamental band for each of these compounds is about 280 mμ. This is further to the red than the centers of the corresponding band for the simpler phenols. Part of this displacement may be thought to be due to the hydrogen bonding or close proximity effects of the two phenol rings on each other. The positioning of one phenol group in close proximity to another should be expected to produce a red shift just as ethyl alcohol solvent does for a simpler phenol. Therefore, the spectra of a bis-phenol in isoöctane solution would be expected to show the center of its fundamental band at longer wave lengths than a simple phenol.

Summary

A study has been made of the changes in ultraviolet absorption spectra for twenty-one phenols that occur when the solvent is changed from a paraffin to an alcohol. Three different effects are observed: a shift of the spectral center of gravity to longer wave lengths, a smoothing of the band structure, and an asymmetrical broadening of the fundamental absorption band. It is found that that the spectral change depends upon the degree of steric hindrance offered to the approach of the alcohol molecules to the hydroxyl group of the phenol. In alcohol solutions the spectra of the phenols and other compounds do not change with increasing temperature, indicating that the processes primary to the spectral changes do not depend on stable hydrogen bonded complexes. Data are given for the unhindered, partially hindered and hindered phenols..

Tentative explanations are provided for some of the temperature effects, the smoothing of the band structure, and the asymmetrical broadening of the bands. These are based on considerations of the intermolecular interactions. No significant spectral changes were observed for benzene or toluene whereas a shift to the red was observed for aromatic hydrocarbons of higher conjugation. This is discussed in terms of the stabilization of the excited polar states through interactions with the alcohol molecules. Data and discussion are provided for four bis-phenols.

Correlated Molecular Orbitals[1]

BY ARTHUR A. FROST, JERRY BRAUNSTEIN AND WARREN SCHWEMER

The molecular orbital method of Hund, Mulliken, Lennard-Jones and others for the approximate quantum mechanical treatment of the electronic structure of molecules has the advantage over the valence bond method of Heitler and London, Pauling, Slater and others[1a–5] in being simpler in concept and simpler for the calculation of numerical results. The molecular orbital method has the disadvantage, however, in that it overemphasizes ionic structures, permitting electrons to pile up without restriction on any given atom of the molecule. This is due to the fact that the potential energy of repulsion of the various electrons is brought in only indirectly through its average effect, the interelectronic distances not appearing in the wave function. That these interelectronic distances should appear explicitly is shown by their required presence for the accurate calculations of Hylleraas[6] on the helium atom and of James and Coolidge[7] on the hydrogen molecule. The "correlated" motions of electrons in solids has been considered by Wigner and Seitz,[8,9] and it is this previous use of this word that gives the title to the method considered here.

When antisymmetrized molecular orbitals[10] are used no more than two electrons are in the

(1) This paper was presented at the meeting of the American Chemical Society, New York, N. Y., September 15–19, 1947.

(1a) J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, **7**, 167 (1935).

(2) E. Hückel, *Z. Elektrochem.*, **43**, 752, 827 (1937).

(3) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944.

(4) S. Glasstone, "Theoretical Chemistry," D. Van Nostrand Co., New York, N. Y., 1944.

(5) L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935.

(6) E. A. Hylleraas, *Z. Physik.*, **54**, 347 (1929); **65**, 209 (1930).

(7) H. M. James and A. S. Coolidge, *J. Chem. Phys.*, **1**, 825 (1933); **3**, 129 (1935).

(8) E. Wigner, *Phys. Rev.*, **46**, 1002 (1934); *Trans. Faraday Soc.*, **34**, 678 (1938).

(9) F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 231, 234, 246 ff., 342.

(10) M. Goeppert-Mayer and A. Sklar, *J. Chem. Phys.*, **6**, 645 (1938); A. L. Sklar, *Rev. Modern Phys.*, **14**, 323 (1942).

same atomic orbital simultaneously. Nevertheless, even here it is recognized that there is too much piling-up of electrons.

The present method is an attempt to bring into consideration the electron correlations due to their mutual repulsions and at the same time preserve the simplicity of the molecular orbital concept.

General Statement of the Method

It is postulated that a good approximate electronic wave function for a molecule (or an atom or system of atoms or ions) with n electrons can be written as

$$\psi = \prod_{i=1}^{n} \psi_i(i) \prod_{k<l} f(r_{kl})$$

where $\psi_i(i)$ is a molecular orbital wave function depending on the coördinates of only electron i and represents a possible state for a single electron moving in the field of the nuclei. The functions $f(r_{kl})$ are introduced to give rise to explicit correlations between electron motions. They are assumed to all be functions of the same form except for the particular interelectronic distance, r_{kl}, involved, and must increase in magnitude with increasing r_{kl} so that it becomes more probable for any two electrons to be some distance apart than close together. Since the product of the $\psi_i(i)$'s is analogous to the function used in ordinary molecular orbital theory, the present ψ can be considered as an ordinary molecular orbital type of wave function multiplied by a function which results in correlations between the electron motions. A function ψ of this form will be referred to as a *correlated molecular orbital* wave function.

The wave function should properly include the spin coördinates and be antisymmetrized. However, the simpler technique, of satisfying the Pauli principle by placing no more than two electrons in each molecular orbital, will be used here. For convenience the ψ_i's will be considered as linear combinations of atomic orbitals.

Given such a wave function as ψ, above, with explicit expressions for the ψ_i's and $f(r_{kl})$ the energy can in principle be calculated in the usual way as the mean value of the Hamiltonian operator. Because of difficulties of integration semiempirical methods of calculation will be useful.

The present method is designed to be valid over the complete range of internuclear distance so that it can be applied to energy calculations for activated complexes as well as for normal molecules. Consideration of a two-electron diatomic molecule such as hydrogen in its limiting forms of the separated atoms and the "united" atom gives valuable information as to the proper form for the function $f(r_{kl})$.

Separated Atoms

Consider the hydrogen molecule in its normal state. The wave function, using linear combination of atomic orbitals, can here be written as

$$\psi = (A_1 + B_1)(A_2 + B_2)f(r_{12})$$

where A_1 and B_1 are considered to be normalized, polarized 1s atomic orbitals of electron 1 on nuclei a and b, respectively. The subscript 2 refers to electron 2.

In the case of the separated atoms where the internuclear distance, R_{ab}, becomes indefinitely large the function $f(r_{12})$ must be of such a nature that ψ approaches the form which represents the

$$\psi \longrightarrow A_1B_2 + B_1A_2$$

electrons on opposite nuclei with no chance of two being present on one. It is recognized[1] that ordinary molecular orbital theory does not give this proper result but instead gives on multiplication (taking $f(r_{12})$ as unity for this special case)

$$\psi = A_1A_2 + A_1B_2 + B_1A_2 + B_1B_2$$

the first and last terms being ionic terms, which should not appear in this case of separated atoms.

The correlated molecular orbital wave function when multiplied out yields

$$\psi = A_1A_2f + A_1B_2f + B_1A_2f + B_1B_2f$$

If the coördinates of the electrons are such that both are on the same atom, as in the first and fourth terms, the effective value of the f will be that for small values of r_{12} where A_1A_2 or B_1B_2 are large. On the other hand, for the second and third terms where the electrons are on different atoms which are far apart the effective value of f will be that for large r_{12}. For ψ to reduce to the desired second and third terms only, $i.\ e.$, for these terms to be infinitely larger than the first and the fourth, all that is required then is for f to increase indefinitely as r_{12} increases. f could be proportional to any power of r_{12} or be a polynomial in r_{12} such as

$$f = c_0 + c_1r_{12} + \cdots + c_nr_{12}^n$$

From this present consideration a constant term is unnecessary but as shown below is required for the "united" atom to be represented properly. The simplest function then would be of the form

$$f = 1 + pr_{12}$$

where p is a constant coefficient, the constant term being arbitrarily taken as unity or absorbed in a normalization constant. The wave function would have to be partially normalized with a factor such as $1/(1 + pR_{ab})$ varying with internuclear distance in such a way as to keep ψ finite. Then

$$\psi = \frac{(A_1A_2 + A_1B_2 + B_1A_2 + B_1B_2)(1 + pr_{12})}{1 + pR_{ab}}$$

and

$$\lim_{R_{ab} \to \infty} \psi = \frac{(A_1B_2 + B_1A_2)r_{12}}{R_{ab}}$$
$$\longrightarrow A_1B_2 + B_1A_2$$

since $r_{12}/R_{ab} \to 1$ for the values of the two electron coördinates where A_1B_2 or B_1A_2 are appreciably different from zero.

The "United" Atom

As the internuclear distance, R_{ab}, approaches zero a hydrogen molecule approaches electroni-

cally the state of a helium atom. The correlated molecular orbital, if properly chosen, should yield a suitable value for the energy of this united atom.

The ordinary molecular orbital treatment at its best is here equivalent to the Hartree[11] calculation. This yields for the total electronic energy of the helium atom a value of -5.75 Rydberg units as compared with the correct value of -5.807. The difference of 0.06 Rydberg unit or 0.81 volt-electron may be called the correlation energy. Correlation energies in general are found to be of the order of 0.45 volt-electron for each electron in the atom.[9]

The correlated molecular orbital for this case (or perhaps more appropriately, the correlated atomic orbital) would be represented by

$$\psi = A_1 A_2 f(r_{12})$$

where the two electrons are in the same 1s atomic orbital, represented by A. Hylleraas has calculated the energies of helium corresponding to several different forms for the wave function, the most successful wave functions including explicitly the interelectronic distance, r_{12}. Among these functions are two which are of the product type indicated above.

$$\psi = e^{-z(r_1 + r_2)} e^{cr_{12}}$$

with $z = 1.86$ and $c = 0.26$ and

$$\psi = e^{-z(r_1 + r_2)}(1 + pr_{12})$$

with $z = 1.849$ and $p = 0.364$. The latter function has the simple form for the function f considered at the end of the previous section. The energy, which is minimized by the values of the parameters which are given, is slightly better for this latter function, the result being -5.7824 Rydberg units. This is in error by about 60% less than the error of the Hartree calculation. A more appropriate comparison, however, would be with the function

$$\psi = e^{-z(r_1 + r_2)}$$

which is the same as the function above but with the $f(r_{12})$ function omitted. This is minimized with $z = 1.6875$ and gives the energy -5.695 with an error of 0.112 Rydberg unit. In comparison with this it is thus seen that the introduction of the correlation function, f, reduces the error by 78%. If this same percentage improvement would apply to the best Hartree type of function when multiplied by a correlation function, the energy error would be reduced to only about 0.01 Rydberg unit or 0.13 volt-electron. Such a low error would be highly satisfactory for an approximation of this type.

Application to the Hydrogen Molecule at its Normal Separation

The dissociation energy of the normal hydrogen molecule calculated according to ordinary molecular orbitals is 3.47 e. v. using 1s atomic orbitals with variable effective nuclear charge,[12] and 3.60

(11) D. R. Hartree, *Cambridge Phil. Soc.*, **24**, 89, 111 (1928).

(12) C. A. Coulson, *Trans. Faraday Soc.*, **33**, 1479 (1937).

e. v. for Coulson's best molecular orbital as obtained by the variation method.[13] Comparing with the experimental value of 4.72 e. v. (all values refer to the minimum in the potential energy curve) the corresponding correlation energy is 1.12 e. v. as calculated from Coulson's best molecular orbital. That such a correlation energy can be derived on the basis of correlated molecular orbitals is shown by the following approximate calculation.

The total electronic energy of the molecule can be written

$$E = T_1 + V_1 + T_2 + V_2 + V_{12}$$

where T_1 and T_2 are mean kinetic energies of electrons 1 and 2, V_1 and V_2 are mean potential energies of each electron with respect to the nuclei, and V_{12} is the mean repulsive potential energy between the two electrons. Each of these energies can be represented by an integral involving the chosen form of wave function and the appropriate operator. To evaluate the correlation energy theoretically each of these separate energies would have to be calculated both with and without the correlation factor in the wave function and the differences taken. The major contribution is expected to be in the V_{12} term since it is the only one where the interelectronic distance, r_{12}, appears explicitly in the operator. V_{12} has been evaluated for 1s atomic orbitals with variable effective atomic number z and variable parameter p in the correlation factor as follows

$$V_{12} = \frac{\int \psi^2 \frac{1}{r_{12}} d\tau}{\int \psi^2 d\tau} =$$

$$\frac{\int (e^{-zr_{a1}} + e^{-zr_{b1}})^2 (e^{-zr_{a2}} + e^{-zr_{b2}})^2 \frac{(1 + pr_{12})^2}{r_{12}} d\tau}{\int (e^{-zr_{a1}} + e^{-zr_{b1}})^2 (e^{-zr_{a2}} + e^{-zr_{b2}})^2 (1 + pr_{12})^2 d\tau}$$

r_{a1}, etc., are distances in atomic units (Bohr radii) between nucleus a and electron 1, etc., and V_{12} is the energy in atomic units (twice the Rydberg unit), the operator being merely $1/r_{12}$.

Upon expanding numerator and denominator the separate integrals fall into one of the three classes:

Coulomb integrals

$$\int e^{-z(2r_{a1} + 2r_{b2})} r_{12}{}^n d\tau$$

Mixed Coulomb-Exchange Integrals

$$\int e^{-z(2r_{a1} + r_{a2} + r_{b2})} r_{12}{}^n d\tau$$

Exchange Integrals

$$\int e^{-z(r_{a1} + r_{b1} + r_{a2} + r_{b2})} r_{12}{}^n d\tau$$

where n takes on the values -1, 0, $+1$, $+2$. The first two classes of integrals were evaluated easily using elliptical coördinates. The exchange integrals were evaluated using the technique of James and Coolidge.[7] Numerical results were obtained with the aid of tables given by Rosen[14] and by Bartlett.[15]

(13) C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **34**, 204–212 (1938).

(14) N. Rosen, *Phys. Rev.*, **38**, 2099 (1931).

(15) J. H. Bartlett, Jr,. *ibid.*, **37**, 507 (1931).

Table I summarizes some of the pertinent results of this calculation. All values are for the hydrogen equilibrium separation of 1.40 atomic units. Two values are shown for z corresponding to the hydrogen molecule-ion calculation ($z = 1.38$) and to the simpler molecular orbital calculation of hydrogen ($z = 1.20$). Two values are also shown for p corresponding to the simpler molecular orbital calculation ($p = 0$) and for correlated molecular orbitals using the same p as found best by Hylleraas for helium ($p = 0.364$).

TABLE I

REPULSIVE POTENTIAL ENERGY, V_{12}, IN ATOMIC UNITS

	$z = 1.38$	$z = 1.20$
$p = 0$	0.733	0.658
$p = 0.364$	0.597	0.525

The contribution of V_{12} to the correlation energy would be given by the decrease in V_{12} as p is increased from zero to the best value for the correlated molecular orbital. As p is increased, however, the appropriate z would be expected to change from the value of 1.20, already known for the simple molecular orbital approximation, to a value such as 1.38 as found in the hydrogen molecule-ion calculation since the inclusion of a correlation factor in the wave function spreads out the probability distribution in somewhat the same way as does a decrease in z. Therefore from the information tabulated the contribution of V_{12} to the correlation energy would be calculated as 0.658 minus 0.597 or 0.061 atomic unit, or 1.66 e. v.

Changes in T_1, T_2, V_1 and V_2 in going from or-dinary molecular orbitals to correlated molecular orbitals may also contribute to the correlation energy. The calculation of the various integrals in this case is unusually tedious and difficult and has not been carried out. However, study of the Hylleraas calculation of helium reveals that the principal effect is an increase in T_1 and T_2 with a slight decrease (increase negatively) of V_1 and V_2. The net result is an increase positively in these energy terms equal to about one-third of the decrease in V_{12}. If such a relationship holds also for hydrogen the total correlation energy should be roughly two-thirds of 1.66 e. v. or 1.1 e. v. That this is so close to the experimental value of 1.12 e. v. is probably a coincidence. Nevertheless it illustrates that correlated molecular orbitals give the right order of magnitude for the correlation energy and that more detailed calculations on such a basis should be successful.

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Summary

The ordinary expression of the electronic wave function of a molecule as a product of one-electron molecular orbital wave functions is modified by including factors for each pair of electrons such as $(1 + pr_{ij})$ where p is a constant and r_{ij} is the distance between electrons i and j. It is shown that this form has improved accuracy for the extreme cases of the separated and united atoms and also for normal internuclear distances in molecules.

Equilibrium and Velocity of the Sodium–Hydrogen Exchange on Carbonaceous Exchangers in Contact with Chloride Solutions

BY WALTER JUDA* AND MORRIS CARRON†

Introduction

The base exchange equilibrium on inorganic exchangers (clays, zeolites, etc.) has been the subject of many investigations. Some authors attempted unsuccessfully to apply simple mass action equations to the experimental data, and were therefore led to believe that the exchange equilibria could be more correctly represented by adsorption isotherms.[1] Other investigators, however, affirmed that mass action could account for the equilibria provided that the appropriate activities of the

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(1) G. Wiegner, J. Soc. Chem. Ind., 50, 65T (1931); H. Jenny, J. Phys. Chem., 36, 2217 (1932). (These papers include bibliographies of previous work on base exchange with inorganic exchangers.) H. Jenny, ibid., 40, 501 (1936); C. E. Marshal and R. S. Gupta, J. Soc. Chem. Ind., 52, 434T (1933).

ions were used.[2] With the comparatively recent development of the carbonaceous exchangers the question of the exchange equilibrium was extended to materials of very different chemical constitution, namely, to sulfonated coals or synthetic resinous products containing, in the so-called hydrogen form, sulfonic acid groups, carboxylic acid groups or phenolic groups, or combinations of these groups, available for cation exchange. As in the case of the inorganic materials, the published data and interpretations leave it unsettled whether an appropriate mass action law or an adsorption isotherm can account more satisfactorily for the equilibria on the organic ex-

(2) (a) A. P. Vanselow, Soil Sci., 33, 95 (1932). (b) J. Kielland, Tids. Kjemi, 15, 74 (1935); J. Soc. Chem. Ind., 54, 233T (1935). (c) J. Møller, Kolloid-Beihefte, 46, 1 (1937). (d) L. E. Davis, Soil Sci., 59, 379 (1945).