Electronic States of para-Benzoquinone. I. Calculation of the Energy Levels by a Semi-empirical Molecular Orbital Method Neglecting Configuration Interaction

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Introduction

The electronic structure and the spectrum of *p*-benzoquinone have been studied by many workers. Evans et al.[1] as well as Basu[2] have discussed the oxidation-reduction potential of this molecule with reference to π-electron structure. Absorption spectrum in vapor phase was studied by Light[3] and Seshan[4] and solution-spectrum data are also available[5]. Fixl and Schauenstein, whose paper we can see in only a brief abstract form[6], studied the absorption spectrum of the *p*-benzoquinone crystal using the polarized light and showed that in the region of 23,000-cm^{-1} (ca. 4,500 Å) absorption band this molecule absorbs the light polarized along the long axis more intensely than the light polarized along the short axis. Recently, Sidman[7] has also investigated the *p*-benzoquinone crystal in wider wavelength region than Fixl and Schauenstein and arrived at the conclusion concerning the direction of polarization opposed to that of Fixl and Schauenstein. From the solvent effect of the absorption spectrum, McConnell[8] as well as Nagakura and Kuboyama[9] concluded that the absorption near 4,500 Å was due to an n-π transition while the absorption around 3,000 Å was due to a π-π transition. Nagakura and Kuboyama[9] have also calculated the electonic structure of this molecule using the naive empirical molecular orbital (MO) method based on the one-electron approximation.

On the other hand the semi-empirical MO method proposed by Pariser and Parr[10] has been applied by various authors[11-13] to the elucidation of the π-electronic structures and spectra of conjugated hydrocarbons and heteromolecules and has proved to be very useful. Kon[13] has calculated the electronic states of *p*-benzoquinone combining this method with the self-consistent field method of Roothaan[14]. In these previous works only the π-electrons have been taken explicitly into the electronic interaction term in the Hamiltonian and the so-called non-bonding electrons (n-electrons) localized at the heteroatoms, in the case of the heteromolecules, have been considered implicitly in the core. Therefore, no information about the excited states of the heteromolecules due to the excitation of n-electrons have been obtained. Thus, in spite of the usefulness of Pariser and Parr's method in explaining the π-electronic structure of conjugated molecules, there has been no attempt to apply this method to the problems of the excitation of n-electrons.

In the present series of papers, both the theoretical and the experimental studies in the electronic states of *p*-benzoquinone will be reported. As the first part of this series, the calculation of energy levels of this molecule by the semi-empirical MO method due to Pariser and Parr will be

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[1] M. G. Evans, *Trans. Faraday Soc.*, **42**, 113 (1946); M. G. Evans, J. Gergely and J. de Heer, *ibid.*, **45**, 312 (1949).

[2] S. Basu, ibid., **52**, 6 (1956).

[3] L. Light, *Z. physik. Chem.*, **122**, 414 (1926).

[4] P. K. Seshan, *Proc. Indian Acad. Sci.*, **3A**, 172 (1936). For earlier works see reference cited there.

[5] Collected in Landolt-Börnstein, "Zahlenwerte und Funktionen" Springer, Berlin, (1951), Vol. I, Part 3, Molekeln II. See especially Fig. 263 on p. 307.

[6] J. O. Fixl and E. Schauenstein, *Monatsh.*, **81**, 598 (1950); C A., **45**, 4136f (1951).

[7] J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 2363 (1956).

[8] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[9] S. Nagakura and A. Kuboyama, *J. Chem. Soc. Japan* (Pure Chem. Sect.), **74**, 499 (1953), and *J. Am. Chem. Soc.*, **76**, 1003 (1954).

[10] (a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).
(b) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

[11] R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

[12] C. M. Moser, *J. Chem. Soc.*, **1954**, 3455.

[13] H. Kon, This Bulletin, **28**, 275 (1955).

[14] C. C. J. Roothaan, *Rev. Modern Phys.*, **23**, 69 (1951).

given taking account of the n-electrons explicitly as well as π-electrons into the electronic interaction term in the Hamiltonian.

Outline of the Theory[14a)]

In our approximation the Hamiltonian operator will be expressed in the form

$$H = H_{\text{core}} + (1/2) \sum_{i \neq j} (e^2/r_{ij}), \tag{1}$$

where e^2/r_{ij} is the electrostatic repulsion between electrons i and j, and

$$H_{\text{core}} = \sum_{i} H_{\text{core}}(i), \tag{2}$$

where

$$H_{\text{core}}(i) = T(i) + U_{\text{core}}(i), \tag{3}$$

in which $T(i)$ is the kinetic energy operator for electron i and $U_{\text{core}}(i)$ is the potential energy operator for this electron in the field of the core. It should be noted that the n-electrons are considered explicitly apart from the core; i. e., i and j denote any one of π- or n-electrons.

The MO ϕ_i will be taken to be the orthonormal linear combination of atomic orbitals χ_p on the several nuclei:

$$\phi_i = \sum_{p} C_{ip} \chi_p. \tag{4}$$

As we are considering n-electrons as well as π-electrons it will be convenient to distinguish between π-atomic orbital (AO) and the so-called non-bonding orbital (n-orbital). The former is one of $2p$-AO's and has its node in the molecular plane and is represented by χ_p without superscript. In the case of the p-benzoquinone molecule each n-orbital is the $2p$-orbital of the oxygen atom, the node of which is in a plane perpendicular to the molecular plane and containing the C–O axis. These n-orbitals will be represented by χ_p^n with a superscript n. Subscript p denotes the atom to which the AO χ_p refers. Neglecting formally the differential overlap, the configurational energies and the interaction matrix elements among different configurations are expressible in terms of the core integrals over AO's and the coulomb interaction integrals over AO's of the following form:

$$(pp \mid qq) = \iint \chi_p^*(1) \chi_p(1) (e^2/r_{12}) \chi_q^*(2) \chi_q(2)\, dv_1 dv_2, \tag{5}$$

and

$$(pp \mid q^n q^n) = \iint \chi_p^*(1) \chi_p(1) (e^2/r_{12}) \chi_q^{n*}(2) \chi_q^n(2)\, dv_1 dv_2. \tag{6}$$

The evaluation of the integral of the type (5) has been discussed by Pariser and Parr[10)]. We shall describe the method for evaluation of the latter type of integrals. If the distance between p and q is fairly great, $(pp \mid q^n q^n)$ will be evaluated fairly correctly using the Slater AO's as χ's. If p and q are close to each other,

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[14a)] Note added in proof — In the case of p-benzoquinone for which the application of the theory is intended in the present paper, descriptions concerning the integral of the type $(pp \mid q^n q^n)$ in the present and the following sections are correct only when both p and q lie on the y-axis (Fig. 1). When p refers to a carbon atom which is not on the y-axis and q refers to an oxygen atom $(pp \mid q^n q^n)$ may be expressed as

$$(pp \mid q^n q^n) = \cos^2\theta (pp \mid q^{\bar{\pi}} q^{\bar{\pi}}) + \sin^2\theta (pp \mid q^{\sigma} q^{\sigma}), \tag{P1}$$

where p is the $2p\pi$ AO of atom p and q^n is the $2p$ AO of atom q nodal plane of which is perpendicular to the molecular plane and containing the y-axis. $q^{\bar{\pi}}$ and q^{σ} represent $2p$ AO's of atom q whose nodal planes are perpendicular to the molecular plane and containing and perpendicular to the pq-direction, respectively. θ is an angle between pq-direction and the y-axis. It may be clear that it is for $(pp \mid q^{\bar{\pi}} q^{\bar{\pi}})$ in Eq. (P1) that the extrapolation formula presented in this paper (see especially Eq. (17)) applies. For $(pp \mid q^{\sigma} q^{\sigma})$ it can be shown that following extrapolation formula applies from a similar reasoning as that used by Pariser and Parr (ref. 10b) for $(pp \mid qq)$:

$$(pp \mid q^{\sigma} q^{\sigma}) - (1/2)\{(pp \mid p^{\sigma} p^{\sigma}) + (qq \mid q^{\sigma} q^{\sigma})\} = a'' r^2 + b'' r. \tag{P2}$$

One-center integrals $(pp \mid p^{\sigma} p^{\sigma})$ and $(qq \mid q^{\tau} q^{\sigma})$ are identical with $(pp \mid p^{\bar{\pi}} p^{\bar{\pi}})$ and $(qq \mid q^{\bar{\pi}} q^{\bar{\pi}})$, respectively. If a'' and b'' are determined from values of one-center integrals derived from atomic spectral data and the theoretical values of $(pp \mid q^{\sigma} q^{\sigma})$ at 2.80 and 4.14 Å Eq. (P2) becomes

$$(pp \mid q^{\tau} q^{\sigma}) \text{ (in ev)} = 11.23 - 2.81589r + 0.227815r^2, \tag{P3}$$

where r is in Å. We use Eq. (P3) in obtaining $(pp \mid q' q')$ when $r_{pq} < 2.80$ Å and when $r_{pq} > 2.80$ Å we use theoretical value for $(pp \mid q^{\sigma} q^{\sigma})$. Thus, using the molecular dimension shown in Fig. 2, it follows that

$$(C'_1 C'_1 \mid O^n{}_1 O^n{}_1) = 5.691 \text{ ev},$$

$$(C'_2 C'_2 \mid O^n{}_1 O^n{}_1) = 3.958 \text{ ev}.$$

These values should be used instead of those included in Table III. Fortunately, the changes in the value of these integrals over AO's are small. Moreover, it can be shown that such a change does not affect the energies of those configurations which are produced by "pure $\pi - \pi$ transitions" from the ground configuration when the energy of the ground configuration is taken as the reference. Even in the other cases changes of the configurational energies amount only to a few thousandths which are within the computational errors. Therefore, corrections of Fig. 3 may be unnecessary.

[15)] The following abbreviations are used:

$$(4!)^{-\frac{1}{2}} \operatorname{Det}\{(\chi_p\alpha)^1(\chi_q\beta)^2(\chi_p^n\alpha)^3(\chi_q^n\beta)^4\}$$

$$= (1/4!)^{\frac{1}{2}} \begin{vmatrix} (\chi_p\alpha)^1(\chi_q\beta)^1(\chi_p^n\alpha)^1(\chi_q^n\beta)^1 \\ (\chi_p\alpha)^2(\chi_q\beta)^2(\chi_p^n\alpha)^2(\chi_q^n\beta)^2 \\ (\chi_p\alpha)^3(\chi_q\beta)^3(\chi_p^n\alpha)^3(\chi_q^n\beta)^3 \\ (\chi_p\alpha)^4(\chi_q\beta)^4(\chi_p^n\alpha)^4(\chi_q^n\beta)^4 \end{vmatrix}, \text{ etc.,}$$

where α and β are the usual spin functions and should not be confused with the similar symbols for the core integrals. Superscript i (i=1,2,3,4) indicates that the variable in the spin orbital function to which i refers is the coordinate of the i-th electron.

$(pp \mid q^n q^n)$ must be extrapolated using atomic data just as for $(pp \mid qq)$.

Let us consider a four-electron double π-bond between atoms p and q. The covalent structure with two good bonds is expressed as a superposition of the following wave functions[15]:

$$\left.\begin{aligned}
\Phi_1 &= (4\,!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\alpha)^1(\chi_q\beta)^2(\chi_p^n\alpha)^3(\chi_q^n\beta)^4\}\\
\Phi_2 &= (4\,!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\alpha)^1(\chi_q\beta)^2(\chi_p^n\beta)^3(\chi_q^n\alpha)^4\}\\
\Phi_3 &= (4\,!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\beta)^1(\chi_q\alpha)^2(\chi_p^n\alpha)^3(\chi_q^n\beta)^4\}\\
\Phi_4 &= (4\,!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\beta)^1(\chi_q\alpha)^2(\chi_p^n\beta)^3(\chi_q^n\alpha)^4\}
\end{aligned}\right\}. \tag{7}$$

While the singly ionic structure with unit positive charge on atom q and with a single covalent bond is described in terms of the following functions:

$$\left.\begin{aligned}
\Phi_5 &= (4\,!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\alpha)^1(\chi_q\beta)^2(\chi_p^n\alpha)^3(\chi_p^n\beta)^4\}\\
\Phi_6 &= (4\,!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\beta)^1(\chi_q\alpha)^2(\chi_p^n\alpha)^3(\chi_p^n\beta)^4\}\\
\Phi_7 &= (4\,!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\alpha)^1(\chi_p\beta)^2(\chi_p^n\alpha)^3(\chi_q^n\beta)^4\}\\
\Phi_8 &= (4\,!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\alpha)^1(\chi_p\beta)^2(\chi_p^n\beta)^3(\chi_q^n\alpha)^4\}
\end{aligned}\right\}, \tag{8}$$

the reversed singly ionic structure with unit positive charge on atom p and not on q is described by the following functions:

$$\left.\begin{aligned}
\Phi_9 &= (4\,!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\alpha)^1(\chi_q\beta)^2(\chi_q^n\alpha)^3(\chi_q^n\beta)^4\}\\
\Phi_{10} &= (4!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\beta)^1(\chi_q\alpha)^2(\chi_q^n\alpha)^3(\chi_q^n\beta)^4\}\\
\Phi_{11} &= (4!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_q\alpha)^1(\chi_q\beta)^2(\chi_p^n\alpha)^3(\chi_q^n\beta)^4\}\\
\Phi_{12} &= (4!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_q\alpha)^1(\chi_q\beta)^2(\chi_p^n\beta)^3(\chi_q^n\alpha)^4\}
\end{aligned}\right\}. \tag{9}$$

On the other hand

$$\left.\begin{aligned}
&\Phi_{13} = (4!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_p\alpha)^1(\chi_p\beta)^2(\chi_p^n\alpha)^3(\chi_p^n\beta)^4\}\\
&\text{and}\\
&\Phi_{14} = (4!)^{-\frac{1}{2}}\mathrm{Det}\{(\chi_q\alpha)^1(\chi_q\beta)^2(\chi_q^n\alpha)^3(\chi_q^n\beta)^4\}
\end{aligned}\right\}, \tag{10}$$

represent doubly ionic structures $p^{--}q^{++}$ and $p^{++}q^{--}$, respectively.

In Eqs. (7)—(10) χ_p, χ_q, χ_p^n and χ_q^n are "π-orbitals" of atoms p and q, the nodal planes of χ_p and χ_q being perpendicular to those of χ_p^n and χ_q^n. Since in this system

$$H = \sum_{i=1}^{4} H_{\mathrm{core}}(i) + (1/2)\sum_{i \neq j=1}^{4}(e^2/r_{ij}),$$

$$\int \chi_p^*(1)\,H_{\mathrm{core}}(1)\,\chi_p(1)\,\mathrm{d}v_1 = \int \chi_p^{n*}(1)\,H_{\mathrm{core}}(1)\,\chi_p^n(1)\,\mathrm{d}v_1 \equiv \alpha_p,$$

and

$$\int \chi_q^*(1)\,H_{\mathrm{core}}(1)\,\chi_q(1)\,\mathrm{d}v_1 = \int \chi_q^{n*}(1)\,H_{\mathrm{core}}(1)\,\chi_q^n(1)\,\mathrm{d}v_1 \equiv \alpha_q,$$

the matrix elements for the determination of the energy are

$$\left.\begin{aligned}
&H_{1,1} = H_{2,2} = H_{3,3} = H_{4,4} = 2\alpha_p + 2\alpha_q\\
&\quad + 2(pp \mid qq) + 2(pp \mid q^n q^n)\\
&\quad + (pp \mid p^n p^n) + (qq \mid q^n q^n)\\
&\quad - (1/2)\,(pp^n \mid pp^n) - (1/2)\,(qq^n \mid qq^n)\\
&\quad - (pq^n \mid pq^n)\\
&H_{5,5} = H_{6,6} = H_{7,7} = H_{8,8} = 3\alpha_p + \alpha_q\\
&\quad + (pp \mid qq) + (pp \mid pp) + 2(pp \mid p^n p^n)\\
&\quad + 2(pp \mid q^n q^n) - (pp^n \mid pp^n)\\
&\quad - (pq^n \mid pq^n)\\
&H_{9,9} = H_{10,10} = H_{11,11} = H_{12,12} = \alpha_p + 3\alpha_q\\
&\quad + (pp \mid qq) + (qq \mid qq) + 2(pp \mid q^n q^n)\\
&\quad + 2(qq \mid q^n q^n) - (pq^n \mid pq^n)\\
&\quad - (qq^n \mid qq^n)\\
&H_{13,13} = 4\alpha_p + 2(pp \mid pp) + 4(pp \mid p^n p^n)\\
&\quad - 2(pp^n \mid pp^n)\\
&H_{14,14} = 4\alpha_q + 2(qq \mid qq) + 4(qq \mid q^n q^n)\\
&\quad - 2(qq^n \mid qq^n)
\end{aligned}\right\}, \tag{11}$$

where $H_{i,i} = \int \Phi_i^* H \Phi_i \mathrm{d}v$.

From these equations one obtains

$$(1/2)\,(H_{5,5} + H_{9,9}) - H_{1,1} = (1/2)\{(pp \mid pp) + (qq \mid qq)\} - (pp \mid qq). \tag{12}$$

The left-hand side of this equation should become zero when $r_{pq} \to 0$. Therefore, the right-hand side of (12) may be represented as follows:

$$(pp \mid qq) - (1/2)\{(pp \mid pp) + (qq \mid qq)\} = ar^2 + br. \tag{13}$$

This equation is identical with that obtained by Pariser and Parr[10] and may be used for the determination of $(pp \mid qq)$ at moderate internuclear distances using the values of one-center integrals obtained from atomic data and $(pp \mid qq)$-values at large internuclear distances calculated theoretically.

Moreover, one obtains from (11)

$$\begin{aligned}(H_{13,13}+H_{14,14})-2H_{1,1}=&\{2(pp\mid pp)\\&+2(qq\mid qq)-4(pp\mid qq)\}+\{2(pp\mid p^np^n)\\&+2(qq\mid q^nq^n)-4(pp\mid q^nq^n)\}\\&+\{2(pq^n\mid pq^n)-(pp^n\mid pp^n)-(qq^n\mid qq^n)\}.\end{aligned}\tag{14}$$

Let us consider the case where $r_{pq}=0$. In this case, it holds that[15a]

$$(pq^n\mid pq^n)=(pp^n\mid qq^n).\tag{14'}$$

Therefore the right-hand side of (14) becomes

$$\begin{aligned}&-(3/2)\{2(pp\mid qq)-(pp\mid pp)-(qq\mid qq)\}\\&-(5/2)\{2(pp\mid q^nq^n)-(pp\mid p^np^n)\\&\qquad-(qq\mid q^nq^n)\},\end{aligned}\tag{15}$$

where the following relation which holds among integrals over Slater AO's was used:

$$2(pp^n\mid qq^n)=(pp\mid qq)-(pp\mid q^nq^n).\tag{16}$$

Since from (12) the first term of (15) becomes zero when $r_{pq}=0$, the second term of (15) should also be zero in this case, because the left-hand side of (14) becomes zero. Therefore, the approximate analytical expression of the following form may apply for the expression in the second bracket of (15):

$$\begin{aligned}(pp\mid q^nq^n)-(1/2)\{&(pp\mid p^np^n)\\&+(qq\mid q^nq^n)\}=a'r^2+b'r.\end{aligned}\tag{17}$$

Equation (17) may be used to determine $(pp\mid q^nq^n)$ in just the same way as (13) was used for $(pp\mid qq)$.

Evaluation of the Coulomb Integrals Over AO's

In order to calculate the integrals which are needed in the calculation of the energy levels of *p*-benzoquinone from Eqs. (13) and (17), one-center integrals of the type $(pp\mid pp)$ and $(pp\mid p^np^n)$ must be evaluated, where p denotes the carbon or the oxygen atoms. The values of these integrals for the oxygen atom were taken from Fumi and Parr's paper[16], where these were obtained from the analysis of the atomic spectral data.

One-center integrals over carbon atomic orbitals were determined from an analysis of the valence states of C, C^+ and C^-. The energies of these valence states were obtained by Skinner and Pritchard[17] from the Mulliken-type treatment of the atomic spectral data. The location of these valence states in energy is given in Table I, taking the ground state of the neutral carbon atom as reference.

TABLE I

ENERGIES OF SOME OF THE SPECTROSCOPIC AND VALENCE STATES OF C, C^+ AND C^- (eV.)

State	Energy[a]
$C^+(syz,\ V_3)$	19.68
$C^+(s^2p,\ {}^2P)$	11.26
$C(sxyz,\ V_4)$	8.14
$C^-(sx^2yz,\ V_3)$	7.68
$C(s^2p^2,\ {}^3P)$	0.00
$C^-(s^2p^3,\ {}^4S)$	−1.7

a) The figures in this column were obtained from energies of valence states, ionization potentials and electron affinities listed in reference 17 in text taking the ground state of the neutral carbon atom as zero.

Let us consider the following equation relating the theoretical and the experimental energy change for the dissociation process:

$$\begin{aligned}&2C(sxyz,\ V_4)\rightarrow C^+(syz,\ V_3)+C^-(sx^2yz,\ V_3)\\&\varDelta E=(pp\mid pp)=11.08\ \text{eV.},\end{aligned}\tag{18}$$

where the "experimental side" was taken from Table I. On the other hand, the following equation holds:

$$(pp^n\mid pp^n)=3G_2,$$

where G_2 is the Slater-Condon parameter,

[15a] Using Slater AO's it can be shown that this equality holds accurately only when Z_p and Z_q (the effective nuclear charges) are equal to each other. More generally we obtain when $r_{pq}=0$

$$\begin{aligned}\frac{(pq^n\mid pq^n)-(pp^n\mid qq^n)}{(pq^n\mid pq^n)}=1-&\left\{\frac{4}{9}+\frac{1}{4}\left(\frac{Z_p}{Z_q}+\frac{Z_q}{Z_p}\right)\right.\\&\left.+\frac{1}{36}\left(\frac{Z_p^2}{Z_q^2}+\frac{Z_q^2}{Z_p^2}\right)\right\},\end{aligned}\tag{N 1}$$

if we use Slater AO's and we assume that the effective nuclear charge for χ_p is equal to that for χ_p^n and the same applies to χ_q and χ_q^n. If $Z_p=Z_q$ the right-hand side of (N 1) becomes zero, therefore $(pq^n\mid pq^n)$ is exactly equal to $(pp^n\mid qq^n)$ as stated above. It is true that in the heteropolar case $(Z_p\neq Z_q)$ the right-hand side of (N 1) is not equal to zero, but it is nearly equal to zero. For example, if we take the carbon and fluorine atoms as p and q, respectively, the right-hand side of (N 1) becomes -0.0827, using $Z_C=3.25$ and $Z_F=5.20$. This is an extremely heteropolar case and the right-hand side of (N 1) is usually much smaller. Moreover, in the right-hand side of (14) $(pp^n\mid pp^n)$ is much smaller than either $(pp\mid pp)$ or $(pp\mid p^np^n)$, $(qq^n\mid qq^n)$ is much smaller than either $(qq\mid qq)$ or $(qq\mid q^nq^n)$ and $(pq^n\mid pq^n)\simeq(pp^n\mid qq^n)$ is much smaller than either $(pp\mid qq)$ or $(pp\mid q^nq^n)$. Therefore the use of (14′) does not bring any serious errors in the arguments for the validity of (17).

[16] F. G. Fumi and R. G. Parr, *J. Chem. Phys.*, **21**, 1864 (1953).

[17] H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

TABLE II

MOLECULAR ORBITALS AND ORBITAL ENERGIES OF *p*-BENZOQUINONE

(Orbital energies are in units of $\beta_{\text{CC benzene}}$)

$\phi_1(B_{1u})=0.47584(\chi_{O_1}+\chi_{O_2})+0.38010(\chi_{C_1}+\chi_{C_2})+0.25406(\chi_{C_1'}+\chi_{C_2'}+\chi_{C_1''}+\chi_{C_2''})$	$\varepsilon_1=6.259$
$\phi_2(B_{3g})=0.60166(\chi_{O_1}-\chi_{O_2})+0.34963(\chi_{C_1}-\chi_{C_2})+0.08877(\chi_{C_1'}-\chi_{C_2'}+\chi_{C_1''}-\chi_{C_2''})$	$\varepsilon_2=6.041$
$\phi_3(B_{1u})=0.47112(\chi_{O_1}+\chi_{O_2})-0.10035(\chi_{C_1}+\chi_{C_2})-0.36604(\chi_{C_1'}+\chi_{C_2'}+\chi_{C_1''}+\chi_{C_2''})$	$\varepsilon_3=5.247$
$\phi_4(B_{2g})=\quad 0.50000(\chi_{C_1'}+\chi_{C_2'}-\chi_{C_1''}-\chi_{C_2''})$	$\varepsilon_4=5.02$
$\phi_5(B_{3g})=0.35339(\chi_{O_1}-\chi_{O_2})-0.46481(\chi_{C_1}-\chi_{C_2})-0.28202(\chi_{C_1'}-\chi_{C_2'}+\chi_{C_1''}-\chi_{C_2''})$	$\varepsilon_5=4.145$
$\phi_6(B_{1u})=0.22730(\chi_{O_1}+\chi_{O_2})-0.58775(\chi_{C_1}+\chi_{C_2})+0.22680(\chi_{C_1'}+\chi_{C_2'}+\chi_{C_1''}+\chi_{C_2''})$	$\varepsilon_6=2.874$
$\phi_7(A_u)=\quad 0.50000(\chi_{C_1'}-\chi_{C_2'}-\chi_{C_1''}+\chi_{C_2''})$	$\varepsilon_7=2.78$
$\phi_8(B_{3g})=0.11470(\chi_{O_1}-\chi_{O_2})-0.40212(\chi_{C_1}-\chi_{C_2})+0.40320(\chi_{C_1'}-\chi_{C_2'}+\chi_{C_1''}-\chi_{C_2''})$	$\varepsilon_8=1.954$
$\phi_{n1}(B_{3u})=(1/\sqrt{2})(\chi_{O_1}{}^n+\chi_{O_2}{}^n)$	$\varepsilon_{n1}=5.46^{a}$
$\phi_{n2}(B_{1g})=(1/\sqrt{2})(\chi_{O_1}{}^n-\chi_{O_2}{}^n)$	$\varepsilon_{n2}=5.46^{a}$

a) The electronegativities of the carbon and the oxygen atoms are 2.5 and 3.5, respectively (L. Pauling, "The Nature of the Chemical Bond", Corronell University Press, Ithaca, New York (1940), p. 64). From this the coulomb integral at the oxygen atom is found to be 5.46 $\beta_{\text{CC benzene}}$ (see ref. 22 in text), which is taken as the value of the orbital energy of ϕ_{n1} and ϕ_{n2} since the resonance integrals between two oxygen atoms is expected to be small.

the value of which is determined to be 1,665 cm^{-1} by Skinner and Pritchard[17] from the least square treatment of the energy levels of the carbon atom. Thus, one obtains

$$(pp^n \mid pp^n)=0.619\ \text{eV}. \tag{19}$$

From (18) and (19) and using (16) one obtains

$$(pp \mid p^n p^n)=9.84\ \text{eV}.$$

All the coulomb integrals over AO's were calculated for $r_{pq}>2.80$ Å from Roothaan's formula[18,19] using the effective nuclear charge of 3.25 and 4.55 for the carbon and oxygen atoms, respectively. For $r_{pq}<2.80$ Å, they were obtained from Eqs. (13) and (17) in which the coefficients a, b, a' and b' were obtained from the one-center integral values obtained above and theoretically-calculated $(pp \mid qq)$- and $(pp \mid q^n q^n)$- values at $r_{pq}=2.80$ and 4.14 Å. Thus the following formulas were obtained:

$$\begin{aligned}
(\mathrm{CC} \mid \mathrm{OO}) &= 12.80-3.8837\,r+0.39142\,r^2\\
(\mathrm{CC} \mid \mathrm{O}^n\mathrm{O}^n) &= 11.23-2.9506\,r+0.25760\,r^2 \quad ,\\
(\mathrm{CC} \mid \mathrm{C'C'})^{20)} &= 11.08-2.9226\,r\\
&\quad +0.26203\,r^2
\end{aligned} \tag{20}$$

where r is the internuclear distance in Å and the values of the integrals may be obtained in eV.

Application to Para-benzoquinone

In order to apply the present method to a particular molecule, MO's must be expressed linearly in terms of AO's. As we are neglecting the configuration interaction, the choice of the MO's may be important. From the results of previous works on hydrocarbons the recommended MO to be used is that which is self-consistent for the ground state or that which is derived from the naive Hückel-type treatment[11,12]. For simplicity we use the latter type of MO. Of course, in contrast with the case of hydrocarbons, in the case of heteromolecules such as *p*-benzoquinone these MO's will be dependent on the assumed values of α's and β's[21]. The calculation of the orbital coefficient was made using the assumptions described elsewhere[22]. The MO's thus obtained are shown in Table II where the designation of the atoms given in Fig. 1 are used. The designation of the coordinate axes is also given in the figure. Then, the symmetry notations are the same as those given by Herzberg[23]. In Table II the orbital energies are also listed in units of $\beta_{\text{CC benzene}}$[21].

Coulomb integrals over AO's were determined as described above and are shown in Table III, the values of the internuclear distances used being shown in Fig. 2.

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[18] C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

[19] See Appendix I.

[20] C′ denotes the carbon atom different from that which is represented by C.

[21] α's and β's mentioned here are the coulomb and the resonance integrals used in the naive MO method and should not be confused with the core integrals in Pariser and Parr's scheme.

[22] T. Anno and A. Sadô, This Bulletin, **28**, 350 (1955).

[23] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Co., New York (1945), p. 108.

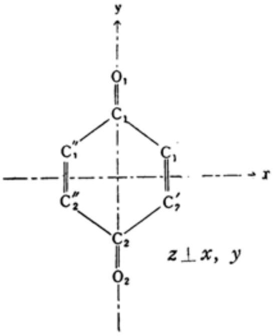

Fig. 1. Designation of the atoms and the coordinate axes in *p*-benzoquinone.

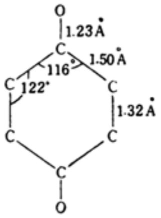

Fig. 2. Internuclear distances and bond angles in *p*-benzoquinone[a].

[a] S. M. Swingle, *J. Am. Chem. Soc.*, **76**, 1409 (1954).

TABLE III

THE VALUES OF THE VALENCE-STATE IONIZATION POTENTIAL[a] AND THE COULOMB INTERACTION INTEGRALS OVER AO'S[b] (eV).

$W^{C}_{2p\pi}$	11.54	$(CC \mid O^nO^n)$[c]	
$W^{O}_{2p\pi}$	17.21	$r_{CO}=1.23$ Å	7.991
W^{O}_{2pn}	14.75	2.391	5.648
$(CC \mid C'C')$		3.5785	3.949
$r_{CC'}=0$ Å	11.08	$(OO \mid O'O')$	
1.32	7.679	$r_{OO'}=0$ Å	14.52
1.50	7.286	5.370	2.667
2.468	5.463	$(OO \mid O'^nO'^n)$	
2.544	5.341	$r_{OO'}=0$ Å	12.62
2.866	4.846	5.370	2.666
$(CC \mid OO)$			
$r_{CO}=1.23$ Å	8.615		
2.391	5.752		
3.5785	3.951		
4.140	3.430		

a) Taken from reference 17 in text.

b) For $r<2.80$ Å the values are obtained from Eq. (20). For $r>2.80$ Å calculated values using Slater AO's with $Z_C=3.25$ and $Z_O=4.55$ are given. One-center integrals are obtained from the analysis of atomic spectral data.

c) Note added in proof—See footnote 14a.

The values of the core integrals α's were calculated from the following equation:

$$\begin{aligned}\alpha_{C_1}=&\int\chi^*_{C_1}(1)H_{\text{core}}(1)\chi_{C_1}(1)\,dv_1\\ =&-W^{C_1}_{2p\pi}-2(C_1C_1 \mid O_1{}^nO_1{}^n)\\ &-2(C_1C_1 \mid O_2{}^nO_2{}^n)-(C_1C_1 \mid O_1O_1)\\ &-(C_1C_1 \mid O_2O_2)-2(C_1C_1 \mid C_1'C_1')\\ &-2(C_1C_1 \mid C_2'C_2')-(C_1C_1 \mid C_2C_2)\\ &-(O_1 : C_1C_1)-(O_2 : C_1C_1)\\ &-2(C_1' : C_1C_1)-2(C_2' : C_1C_1)\\ &-(C_2 : C_1C_1),\end{aligned}$$

$$\begin{aligned}\alpha_{C_1'}=&\int\chi^*_{C_1'}(1)H_{\text{core}}(1)\chi_{C_1'}(1)\,dv_1\\ =&-W^{C_1'}_{2p\pi}-2(C_1'C_1' \mid O_1{}^nO_1{}^n)\\ &-2(C_1'C_1' \mid O_2{}^nO_2{}^n)-(C_1'C_1' \mid O_1O_1)\\ &-(C_1'C_1' \mid O_2O_2)-(C_1'C_1' \mid C_1C_1)\\ &-(C_1'C_1' \mid C_2'C_2')-(C_1'C_1' \mid C_2C_2)\\ &-(C_1'C_1' \mid C_1''C_1'')-(C_1'C_1' \mid C_2''C_2'')\\ &-(O_1 : C_1'C_1')-(O_2 : C_1'C_1')\\ &-(C_1 : C_1'C_1')-(C_2' : C_1'C_1')\\ &-(C_2 : C_1'C_1')-(C_1'' : C_1'C_1')\\ &-(C_2'' : C_1'C_1'),\end{aligned}$$

$$\begin{aligned}\alpha_{O_1}=&\int\chi^*_{O_1}(1)H_{\text{core}}(1)\chi_{O_1}(1)\,dv_1\\ =&-W^{O_1}_{2p\pi}-2(O_1O_1 \mid O_1{}^nO_1{}^n)\\ &-2(O_1O_1 \mid O_2{}^nO_2{}^n)-(O_1O_1 \mid O_2O_2)\\ &-(O_1O_1 \mid C_1C_1)-(O_1O_1 \mid C_2C_2)\\ &-2(O_1O_1 \mid C_1'C_1')-2(O_1O_1 \mid C_2'C_2')\\ &-(O_2 : O_1O_1)-(C_1 : O_1O_1)\\ &-(C_2 : O_1O_1)-2(C_1' : O_1O_1)\\ &-2(C_2' : O_1O_1),\end{aligned}$$

$$\begin{aligned}\alpha^n_{O_1}=&\int\chi^{n*}_{O_1}(1)H_{\text{core}}(1)\chi^n_{O_1}(1)\,dv_1\\ =&-W^{O_1}_{2pn}-(O_1{}^nO_1{}^n \mid O_1{}^nO_1{}^n)\\ &-2(O_1{}^nO_1{}^n \mid O_2{}^nO_2{}^n)-(O_1{}^nO_1{}^n \mid O_1O_1)\\ &-(O_1{}^nO_1{}^n \mid O_2O_2)-(O_1{}^nO_1{}^n \mid C_1C_1)\\ &-(O_1{}^nO_1{}^n \mid C_2C_2)-2(O_1{}^nO_1{}^n \mid C_1'C_1')\\ &-2(O_1{}^nO_1{}^n \mid C_2'C_2')-(O_2 : O_1{}^nO_1{}^n)\\ &-(C_1 : O_1{}^nO_1{}^n)-(C_2 : O_1{}^nO_1{}^n)\\ &-2(C_1' : O_1{}^nO_1{}^n)-2(C_2' : O_1{}^nO_1{}^n),\end{aligned}$$

where $W^q_{2p\pi}$ and W^q_{2pn} are the valence state ionization potentials of a π-electron and n-electron at atom q, respectively. These values of ionization potentials were obtained from Skinner and Pritchard's paper[17] and are also listed in Table III. $(q : pp)$ is the coulomb penetration integral and is defined by

$$(q:pp) = -\int \mathrm{U}_q(1)\chi_p^*(1)\chi_p(1)\,\mathrm{d}v_1,$$

where $\mathrm{U}_q(1)$ is the potential due to neutral atom q. Penetration integrals were neglected throughout except when p and q refer to the nearest neighbors with each other. When p and q are the nearest neighbors, the values of this type of integrals were calculated theoretically[24].

β_{pq} was neglected except in the case where p refers to the nearest neighbor with q. When p and q refer to the nearest neighbors with each other, β_{pq} may be determined semi-empirically. Kon[13] gave a functional form for β_{CC} and β_{CO} with respect to the internuclear distance defined in such a way as to fit the calculated energy levels with experiment. Although the theoretical representation of β[25] is slightly different depending on whether the n-electrons are considered explicitly or not, in our calculation β's were calculated from this formula, because it can be shown that β is approximately the same in both cases using Mulliken's approximation[26] for integrals.

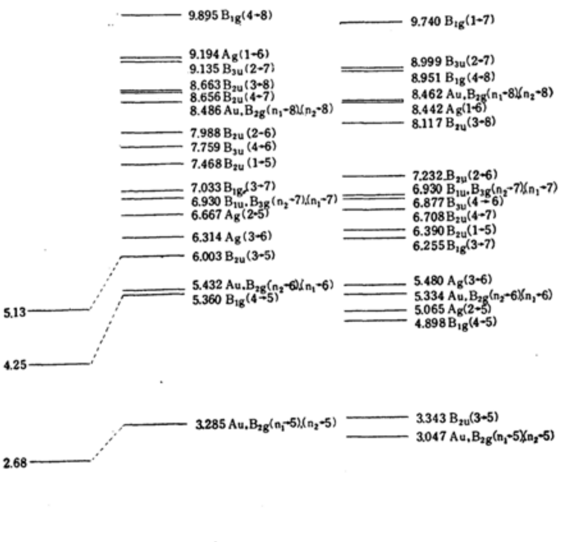

Fig. 3. Calculated and observed energy levels of p-benzoquinone.

The figure on the right of each level is the energy interval (in eV.) above the ground state and is followed by species notation of the state. On the right of the species notation the difference of the electron configuration from the ground state is indicated; e. g., ($n_1\to$ 5) indicates that the participating configuration is produced from the ground configuration with the excitation of an electron from ϕ_{n_1} (see Table II) to ϕ_5.

Using the coulomb and core integrals over AO's the integrals over MO's are obtained from the MO's in LCAO form enbodied in Table II as described above. Energies of various electronic states may be obtained in the usual manner. The state energies thus obtained are shown in Fig. 3 diagramatically, the energy of the ground configuration being taken as reference. Only the singly-excited states which lie within 10 eV. above the ground state are given and the effect of the configuration interaction was neglected. Two singlets which result from doubly-excited configurations lie within this energy region, i. e., at 8.506 eV. (A_u, B_{2g}) and 7.495 eV. (B_{1u}, B_{3g}) above the ground state. It is to be noted that any one of A_u states is found to be degenerate with one of B_{2g} states. The same applies to B_{1u} and B_{3g} states. These degeneracies are accidental, so they are not exact but only approximate degeneracy. However, it can be shown that they persist even after the effect of the configuration interaction is taken into account.

Discussion

The hexane solution of p-benzoquinone has three absorption regions in visible or the near ultraviolet; these are $\lambda_{\max}=2400$ Å (5.13 eV., $\log \varepsilon_{\max}=4.2$), $\lambda_{\max}=2900$ Å (4.25 eV., $\log \varepsilon_{\max}=2.5$) and $\lambda_{\max}=4600$ Å (2.68 eV., $\log \varepsilon_{\max}=1.2$[5]). The longest-wavelenth absorption band was assigned to an $n-\pi$ transition by McConnell[8] and Nagakura and Kuboyama[9] from the solvent effect on this band. From the MO point of view and from the comparison of the spectral data of various molecules containing CO group, McMurry[27] has also suggested this assignment. The shortest-wavelength one of the above mentioned absorptions has the extinction coefficient of 20,000, which shows that this absorption may be due to an allowed electronic transition. The remaining one is assigned to a $\pi-\pi$ transition from the solvent effect[8,9]. The extinction coefficient might suggest that this absorption would be due to an allowed electronic transition. The alternative

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[24] See Appendix II.

[25] See footnote 11 in reference 10a and references cited there.

[26] R. S. Mulliken, "Report on Molecular Orbital Theory", 1947-8 and 1948-9 ONR Reports of the Physics Department Spectroscopic Laboratory of the University of Chicago, Eqs. (63) and (154b).

[27] H. L. McMurry, *J. Chem. Phys.*, **9**, 241 (1941).

assignment for this absorption is that it may be due to a forbidden transition and the fairly large extinction coefficient of it might be due to the proximity of this absorption to an allowed electronic transition. We prefer the latter assignment with some reservations.

From the above argument the observed bands at 2.68 eV. and 5.13 eV. may be assigned to the ${}^1A_g \rightarrow {}^1A_u$, ${}^1B_{2g}$ (nearly degenerate) and ${}^1A_g \rightarrow {}^1B_{2u}$ transitions, respectively. It is to be noted that the theory indicates that two electronic transitions are involved in 2.68-eV. absorption. The remaining absorption band at 4.25 eV. may be correlated with the calculated values of 5.432 eV. or 5.360 eV., both of which are predicted to correspond to forbidden transitions. As mentioned previously the solvent effect shows that this absorption may be due to a $\pi-\pi$ transition, so we correlate this absorption with the calculated value of 5.360 eV. rather than 5.432 eV.

One thing should be mentioned concerning the absorption spectrum of the *p*-benzoquinone crystal. If the assignment proposed above is correct the electronic transition corresponding to the band at 5.13 eV. is produced with the transition moment lying in the long-axis (axis connecting two oxygen atoms) of the *p*-benzoquinone molecule and it is interpreted that electronic transitions corresponding to 2.68- and 4.25-eV. bands are made allowed through the vibrational-electronic interaction with 5.13-eV. transition. This is consistent with the result of Fixl and Schauenstein⁶⁾ on the *p*-benzoquinone crystal, since they concluded that 2.68-eV. absorption is polarized along the long axis. However, recently Sidman⁷⁾ has also investigated the *p*-benzoquinone crystal in a wider wavelength region than Fixl and Schauenstein and arrived at the opposite conclusion. Although, Sidman could not investigate the region around 5.13 eV., he inferred that this absorption is polarized along the short axis of the molecule and the excited state of this absorption has the symmetry of B_{3u} (in our notation) from the polarization experiment at 2.68- and 4.25-eV. absorption regions. Then, our assignment concerning the symmetry of the first allowed electronic transition of the *p*-benzoquinone molecule is apparently inconsistent with Sidman's result.

As for the absorptions appearing in the visible region Sidman⁷⁾ reported that at least three electronic transitions exist in this region, all of which are $n-\pi$ transitions. He assigned two of these transitions to singlet-singlet absorptions. These assignments are in agreement with the present theory in the fact that there exists a pair of nearly degenerate electronic states, transitions to which from the ground state lie in the visible region. The third absorption region found by Sidman⁷⁾ was very weak and lay in the longer wavelength region than the above-mentioned two absorptions, although the separation from these two absorptions was small. Sidman⁷⁾ assigned it to a singlet-triplet $n-\pi$ transition. This is also consistent with the present calculation.

In conclusion, although there are some inconsistencies between the theory and the experiments, the results of the present calculation are encouraging. The reason for the inconsistencies is not clear at present, since the configuration interaction is neglected on the theoretical side and the vibrational analysis and the polarization experiments have not been completed on the experimental side. The oriented gas model as applied to the pure *p*-benzoquinone crystal may lead us to false conclusions²⁸⁾.

Summary

A semi-empirical MO method proposed by Pariser and Parr was extended, taking account of the non-bonding electrons at the heteroatoms explicitly as well as π-electrons. The electronic states of *p*-benzoquinone were calculated neglecting configuration interactions.

The authors express their sincere thanks to Professor S. Imanishi for his encouragement throughout this work and for his helpful suggestions. Discussions with the members of authors' laboratory are also acknowledged.

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Appendix I: Calculation of Coulomb Integrals over AO's

In the course of calculations reported in this paper we have calculated several coulomb integrals over Slater AO's using Roothaan's formula¹⁸⁾. In Roothaan's method coulomb integrals over AO's are expressed in terms of "basic integrals".

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28) D. S. McClure, *J. Chem. Phys.*, **22**, 1668 (1954); **24**, 1 (1956).

TABLE IV

THE VALUES OF BASIC COULOMB INTEGRALS (ATOMIC UNIT[a])

(IV A) *a*: Carbon with effective nuclear charge of 3.25.
b: Oxygen with effective nuclear charge of 4.55.

r(Å)	$[3S_a \mid 3S_b]$	$[3S_a \mid 3D\Sigma_b]$	$[3D\Sigma_a \mid 3S_b]$	$[3D\Sigma_a \mid 3D\Sigma_b]$	$[3D\Delta_a \mid 3D\Delta_b]$
1.1615	4.2535^{-1}[b]	7.8303^{-3}	1.7041^{-2}	6.6494^{-4}	7.5582^{-4}
1.230	4.0761^{-1}	7.5598^{-3}	1.6203^{-2}	7.2766^{-4}	6.3216^{-4}
2.391	2.2127^{-1}	2.0572^{-3}	4.0449^{-3}	2.0847^{-4}	3.8425^{-5}
2.800	1.8902^{-1}	1.3002^{-3}	2.5501^{-3}	1.0276^{-4}	1.7620^{-5}
3.5785	1.4791^{-1}	6.2514^{-4}	1.2253^{-3}	3.1025^{-5}	5.1797^{-6}
4.140	1.2785^{-1}	4.0377^{-4}	7.9141^{-4}	1.4994^{-5}	2.4994^{-6}

(IV B) *a, b*: Carbon with effective nuclear charge of 3.25.

r(Å)	$[3S_a \mid 3S_b]$	$[3S_a \mid 3D\Sigma_b]$	$[3D\Sigma_a \mid 3D\Sigma_b]$	$[3D\Delta_a \mid 3D\Delta_b]$
1.320	3.7291^{-1}	1.0619^{-2}	5.7500^{-4}	7.5658^{-4}
1.500	3.3848^{-1}	9.5678^{-3}	7.0566^{-4}	5.0462^{-4}
2.468	2.1418^{-1}	3.5880^{-3}	3.1092^{-4}	6.3199^{-5}
2.544	2.0786^{-1}	3.3044^{-3}	2.7790^{-4}	5.4652^{-5}
2.800[c]	1.8898^{-1}	2.5246^{-3}	1.8879^{-4}	3.4379^{-5}
2.866	1.8463^{-1}	2.3594^{-3}	1.7060^{-4}	3.0576^{-5}
2.910	1.8185^{-1}	2.2574^{-3}	1.5956^{-4}	2.8365^{-5}
4.140	1.2785^{-1}	7.9133^{-4}	2.9354^{-5}	4.8986^{-6}

(IV C) *a, b*: Oxygen with effective nuclear charge of 4.55.

r(Å)	$[3S_a \mid 3S_b]$	$[3S_a \mid 3D\Sigma_b]$	$[3D\Sigma_a \mid 3D\Sigma_b]$	$[3D\Delta_a \mid 3D\Delta_b]$
5.370	9.8566^{-2}	1.8502^{-4}	2.0838^{-6}	3.4730^{-7}

a) Atomic unit: energy in $e^2/a_H = 27.204$ eV.
b) 4.2535^{-1} is the abbreviation of 4.2535×10^{-1}.
c) Interpolated.

We shall give here the values of these basic integrals rather than the integrals over AO's. These basic integrals give quickly the values of coulomb integrals over 2*s* or 2*p* AO's of respective atoms using Roothaan's formula. The results are shown in Table IV, the notations being the same as those used by Roothaan.

Appendix II: Calculation of Coulomb Penetration Integrals

The potential of electron 1 due to a neutral carbon atom Uc(1) is represented by

$$U_C(1) = U_C^{4+}(1) + \int |2s_C(2)|^2 (e^2/r_{12}) dv_2$$
$$+ \int |2p\sigma_C(3)|^2 (e^2/r_{13}) dv_3$$
$$+ \int |2p\pi_C(4)|^2 (e^2/r_{14}) dv_4$$
$$+ \int |2p\bar{\pi}_C(5)|^2 (e^2/r_{15}) dv_5, \qquad \text{(A 1)}$$

where $U_C^{4+}(1)$ is the potential due to carbon nucleus plus two 1*s* electrons and is approximated by

$$U_C^{4+}(1) = -(4e^2/r_{C1}),$$

in which r_{C1} is the distance between the carbon nucleus and the electron 1. $2s_C$, $2p\sigma_C$, $2p\pi_C$ and $2p\bar{\pi}_C$ are the carbon AO's $2p\pi$ and $2p\bar{\pi}$ are π-orbitals whose nodal planes are perpendicular to each other.

On the other hand, the potential of electron 1 due to neutral oxygen atom $U_O(1)$ is represented by

$$U_O(1) = U_O^{6+}(1) + 2\int |2s_O(2)|^2 (e^2/r_{12}) dv_2$$
$$+ \int |2p\sigma_O(3)|^2 (e^2/r_{13}) dv_3$$
$$+ \int |2p\pi_O(4)|^2 (e^2/r_{14}) dv_4$$
$$+ 2\int |2p\bar{\pi}_O(5)|^2 (e^2/r_{15}) dv_5, \qquad \text{(A2)}$$

where $U_O^{6+}(1)$ is the potential due to oxygen nucleus plus 1*s* electrons and is approximated by

$$U_O^{6+}(1) = -(6e^2/r_{O1}),$$

the notations being analogous to those in (A 1).

Therefore, coulomb pentration integrals are expressed as

$$\left.\begin{aligned}
&\int \mathrm{U_C}(1)\chi_q^*(1)\chi_q(1)\,\mathrm{d}v_1 \equiv -(\mathrm{C}:qq)\\
&=-4(\mathrm{C}\mid qq)+(2s_\mathrm{C}2s_\mathrm{C}\mid qq)\\
&\quad+(2p\sigma_\mathrm{C}2p\sigma_\mathrm{C}\mid qq)+(2p\pi_\mathrm{C}2p\pi_\mathrm{C}\mid qq)\\
&\quad+(2p\bar{\pi}_\mathrm{C}2p\bar{\pi}_\mathrm{C}\mid qq)\\
&\int \mathrm{U_O}(1)\chi_q^*(1)\chi_q(1)\,\mathrm{d}v_1 \equiv -(\mathrm{O}:qq)\\
&=-6(\mathrm{O}\mid qq)+2(2s_\mathrm{O}2s_\mathrm{O}\mid qq)\\
&\quad+2(2p\sigma_\mathrm{O}2p\sigma_\mathrm{O}\mid qq)+(2p\pi_\mathrm{O}2p\pi_\mathrm{O}\mid qq)\\
&\quad+2(2p\bar{\pi}_\mathrm{O}2p\bar{\pi}_\mathrm{O}\mid qq)
\end{aligned}\right\}, \qquad \text{(A3)}$$

where χ_q is one of $2p$-orbitals and

$$(\mathrm{C}\mid qq)\equiv\int(e^2/r_{\mathrm{C}1})\lambda_q^*(1)\chi_q(1)\,\mathrm{d}v_1,$$

$$(\mathrm{O}\mid qq)\equiv\int(e^2/r_{\mathrm{O}1})\chi_q^*(1)\chi_q(1)\,\mathrm{d}v_1,$$

which may be obtained from literatures[29]. The remaining terms in the right-hand side of Eq. (A3) are coulomb integrals over $2s$- or $2p$-AO's which may be obtained from the basic integrals as described in Appendix I. It is to be noted that in calculating the penetration integrals we have used theoretical values of these coulomb integrals in contrast with the case of the calculation of the electron interaction energy. This is because we have not obtained the values of coulomb integrals referring $2s$- or $2p\sigma$-AO's by the extrapolation using atomic spectral data.

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[29] H. J. Kopineck, *Z. Naturforsch.*, **5A**, 420 (1950).