

energy displacement is small, since in both cases $\alpha'_{\beta'}$ is relatively small. Neither is there any implication here regarding the magnitude of τ_{vib}^{-1} for a nonclassical process such as $|b, 3\rangle \rightarrow |b, 2\rangle$. The cooling rate $\tau_{\text{vib}}^{-1}(b)$ might be very small in weakly coupled systems, particularly with a gross mismatch in vibrational energy levels in the environment, independently of anything we have said. And apparently it is, for N_2 impurities in solid argon, for example. It seems highly unlikely, however, that reverse tunneling from the ground singlet to the lowest triplet state of a molecule like anthracene in condensed matter should extend the triplet lifetime.

It should be stated once again that no effects of anharmonicity have been included here. Undoubtedly they are of importance in many or most actual cases. We do not believe that their inclusion would change the physical conclusions drawn here, even though the

numerical values of the Franck-Condon factors could change by large factors.

V. CONCLUSIONS

To summarize our conclusions, we have shown that, with specific exceptions, spontaneous radiative and radiationless transition probabilities in an electronically excited state are greater in a vibrationally excited state than in the lowest vibrational state, and that slow vibrational relaxation will shorten the lifetime of an excited electronic state.

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We are indebted to I. J. Kim (University of Rochester) for assistance with numerical computations, and to P. Avakian, J. Hernandez, R. S. Knox, and C. P. Slichter for useful discussions.

Valence States of Carbon in π -Electron Systems. I. Alternant-Hydrocarbon Ground States*

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When the molecular wavefunction is described in part by molecular-orbital theory, new terms (Coulomb self-repulsion integrals) enter the valence-state energy over and above the classic valence-bond valence state of Van Vleck. Atomic orbitals for π -electron theory are obtained by minimizing the energy of carbon in a valence state appropriate for alternant-hydrocarbon ground states. The $2p\pi$ orbital so obtained with a non-integral- n "double" basis, with a simple valence-bond σ wavefunction and a simple molecular-orbital π wavefunction, gives a one-center Coulomb repulsion integral $\langle 2p\pi 2p\pi | 1/r_{12} | 2p\pi 2p\pi \rangle = 12.38$ eV, compared to the semiempirical value of ~ 11 eV.

I. INTRODUCTION

Although the carbon $2p\pi$ atomic orbital (AO) is the basic building block of π -electron theory,¹ so-called nonempirical molecular calculations²⁻⁶ interpreting the AO's literally have given poor results in comparison

with the highly successful semiempirical approach.^{1,7-9} The contrast between the nonempirical and semiempirical theories is often dramatized¹⁰ by the respective values of the one-center Coulomb repulsion integral γ :

$$\gamma = \langle 2p\pi 2p\pi | 1/r_{12} | 2p\pi 2p\pi \rangle. \quad (1)$$

Since γ_{theor} is usually assigned the value of 16.93 eV¹¹ (or sometimes 15.71 eV¹²) while γ_{exptl} is about 11

* Research sponsored in part by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation and by a National Science Foundation Grant.

¹ R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1963).

² M. Goeppert-Mayer and A. K. Sklar, *J. Chem. Phys.* **6**, 645 (1938).

³ C. C. J. Roothaan and R. G. Parr, *J. Chem. Phys.* **17**, 1001 (1949).

⁴ R. G. Parr, D. P. Craig, and I. G. Ross, *J. Chem. Phys.* **18**, 1561 (1950).

⁵ J. W. Moskowitz and M. P. Barnett, *J. Chem. Phys.* **39**, 1557 (1963).

⁶ J. Koutecký, J. Čížek, J. Dubský, and K. Hlavaty, *Theoret. Chim. Acta* **2**, 462 (1964).

⁷ R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466 (1953).

⁸ R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 767 (1953).

⁹ J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953).

¹⁰ R. Pariser, *J. Chem. Phys.* **21**, 568 (1953).

¹¹ Computed using hydrogenlike $2p$ orbital with effective nuclear charge 3.18.

¹² Computed using the 3P carbon Hartree-Fock AO of E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.* **127**, 1618 (1961).

eV,^{10,13-16} to believe literally in atomic orbitals is clearly to court disaster.

But could a major fault with the "nonempirical theory" have been an inappropriate $2p\pi$ AO? We propose to attack this $2p\pi$ -AO problem and related problems in π -electron theory through the valence-state model, rather than by calculations on sample molecules because of the conceptual and computational simplicity. As already reported,¹⁷ the $2p\pi$ AO obtained by minimizing the energy of carbon in a valence state appropriate for alternant-hydrocarbon ground states differs considerably from the conventional Slater-type orbital (STO) with nuclear charge 3.18.

In this paper we discuss the specification of the valence state in detail [the energy expression we eventually work with is not the same as Van Vleck's¹⁸ because we explicitly treat the π electrons by molecular-orbital (MO) theory], we study the effect of including MO character for both σ and π electrons, and we also study the effect of basis size on the valence-state atomic orbitals of carbon in the ground state of an alternant hydrocarbon. In Paper II¹⁹ we shall discuss the changes in the valence-state AO's brought about by π -electron excitation and ionization (including the species of Pariser's²⁰ disproportionation reaction).

II. THEORY OF VALENCE STATES

The "valence state" is not a well-defined concept. "Valence state" is meant to refer to the "state" of an atom in a molecule.²⁰ But since atoms in molecules do have their own observable properties, their valence states cannot be specified by nature.

"Valence state" does take on a precise meaning only within the context of a particular atom-oriented scheme for representing the molecular wavefunction, i.e., a scheme whereby the wavefunction is written entirely in terms of subunits assigned to definite atoms. The original valence state of Van Vleck¹⁸ is a natural part of the molecule only within the classical valence-bond theory. Moffitt's atoms-in-molecules theory^{21,22} and Hurley's method of intra-atomic correlation corrections^{23,24} each have their own valence states [see Ref. 22, Eq. (3.6), and Ref. 24, Eqs. (25) and (26)].

¹³ R. Pariser, J. Chem. Phys. **24**, 250 (1956).

¹⁴ (a) J. R. Hoyland and L. Goodman, J. Chem. Phys. **36**, 12 (1962); (b) L. Goodman and J. R. Hoyland, J. Chem. Phys. **39**, 1068 (1963); (c) N. Mataga and K. Nishimoto, Z. Physik. Chem. Frankfurt **13**, 140 (1957).

¹⁵ G. Pilcher and H. A. Skinner, J. Inorg. Nucl. Chem. **24**, 937 (1962).

¹⁶ J. Hinze and H. H. Jaffé, J. Am. Chem. Soc. **84**, 540 (1962).

¹⁷ H. J. Silverstone, H. W. Joy, and M. K. Orloff, J. Am. Chem. Soc. **88**, 1325 (1966).

¹⁸ J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

¹⁹ H. W. Joy and H. J. Silverstone, "Valence States of Carbon in π -Electron Systems. II. Excited States and Ions," Mol. Phys. (to be published).

²⁰ R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).

²¹ W. Moffitt, Proc. Roy. Soc. (London) **A210**, 245 (1951).

²² W. Moffitt, Rep. Prog. Phys. **17**, 173 (1954).

²³ A. C. Hurley, Proc. Phys. Soc. (London) **A69**, 49 (1956).

²⁴ A. C. Hurley, J. Chem. Phys. **28**, 532 (1958).

The common spirit of the valence states of Van Vleck, Moffitt, and Hurley is embodied in the following recipe:

(a) Write an approximate (or exact) wavefunction for the molecule. It is essential that this wavefunction be expressed in terms of functions assigned to definite atoms, (e.g., atomic orbitals).

(b) Write the energy expression.

(c) Separate from the energy the integrals involving functions assigned to a particular atom, but not assigned to any other. This energy is called the valence-state energy of that atom in the molecule.

In an approximate molecular calculation involving valence states, the schemes adopted for Rules (a) and (c) depend on the *aims* of the calculation, the validity of picturing the molecule in terms of atoms, and the amount of effort one is willing to spend on the calculation. (The most frequent use of the valence-state idea has been to incorporate experimental atomic data into molecular calculations.)

Specification of the Molecular Wavefunction

Our aim here is to obtain atomic orbitals for non-empirical π -electron theory. We write the approximate wavefunction in accordance with the π -electron approximation²⁵ as an antisymmetrized product of a σ -electron wavefunction Ψ_σ and a π -electron Ψ_π ,

$$\Psi = \mathcal{A}\{\Psi_\sigma\Psi_\pi\}. \quad (2)$$

For Ψ_π we take the conventional¹ simple product (or linear combination of simple products) of LCAO (linear combination of atomic orbitals)-type molecular orbitals $\phi_i^\pi(\mathbf{r})$ and spin functions α and β :

$$\phi_i^\pi(\mathbf{r}) = \sum_{\text{C atoms } a} C_{ia} 2p\pi(\mathbf{r} - \mathbf{r}_a), \quad (3)$$

$$2p\pi(\mathbf{r}) = R_\pi(r) Y_l^m(\theta, \phi). \quad (4)$$

$R_\pi(r)$ is a radial function to be determined by the calculation, and Y_l^m denotes a spherical harmonic.

Ψ_σ , which is usually irrelevant in semiempirical π -electron theory,¹ must be treated explicitly. We consider the following simple form for Ψ_σ :

$$\Psi_\sigma = B_1 B_2 \cdots B_M (1s_1)^2 (1s_2)^2 \cdots (1s_N)^2, \quad (5)$$

where $(1s_i)$ represents an $1s$ orbital on carbon atom i , and B_j represents a two-electron wavefunction for the j th bond. For simplicity, we treat only alternant hydrocarbons and assume all C-C and all C-H bond distances are respectively equal and that all bond angles are equal to 120° .

We take B_j to be a linear combination of a simple-valence-bond and molecular-orbital wavefunction for

²⁵ P. G. Lykos and R. G. Parr, J. Chem. Phys. **28**, 361 (1958).

bond j . For a CH bond

$$B_{\text{CH}} = \left[a \frac{\sigma(1)\sigma(2) + h(1)h(2)}{\sqrt{2}} + b \frac{\sigma(1)h(2) + h(1)\sigma(2)}{\sqrt{2}} \right] \alpha(1)\beta(2), \quad (6)$$

where σ is an sp^2 trigonal hybrid orbital pointing from the carbon to the hydrogen, and h is a $1s$ orbital on the hydrogen:

$$\sigma = (1/\sqrt{3})(2s) + (\sqrt{2}/\sqrt{3})(2p\sigma). \quad (7)$$

The $(2s)$ must be orthogonal to the carbon inner shell $(1s)$, and

$$(2p\sigma) = R_\sigma(r) Y_1^\sigma, \quad (8)$$

$$R_\sigma \neq R_r. \quad (9)$$

Similarly, for the C-C σ bond between Atoms A and B,

$$B_{\text{CC}^{\text{AB}}} = \left[a \frac{\sigma^{\text{A}}(1)\sigma^{\text{A}}(2) + \sigma^{\text{B}}(1)\sigma^{\text{B}}(2)}{\sqrt{2}} + b \frac{\sigma^{\text{A}}(1)\sigma^{\text{B}}(2) + \sigma^{\text{B}}(1)\sigma^{\text{A}}(2)}{\sqrt{2}} \right] \alpha(1)\beta(2), \quad (10)$$

where σ_{A} is an sp^2 hybrid on A pointing toward B. For simplicity, we use the same values of a and b for all σ bonds. Note that $(a=0, b=1)$ corresponds to the simple valence-bond-type function, and $(a=b=1/\sqrt{2})$ corresponds to the simplest possible localized molecular-orbital function, e.g.,

$$B_{\text{CC}^{\text{AB}}} |_{a=b=1/\sqrt{2}} = [\sigma^{\text{A}}(1) + \sigma^{\text{B}}(1)/\sqrt{2}] [\sigma^{\text{A}}(2) + \sigma^{\text{B}}(2)/\sqrt{2}] \alpha(1)\beta(2). \quad (11)$$

One would therefore expect

$$0 \leq a \leq 1/\sqrt{2}. \quad (12)$$

Specification of the Valence-State Energy

The final part of the valence-state recipe is to determine all the terms in the energy coming from a single carbon atom using Ψ [Eqs. (2) and (3)-(10)]. In doing so we neglect all overlap integrals, i.e.,

$$\langle 2p\pi(\mathbf{r}-\mathbf{r}_a) | 2p\pi(\mathbf{r}-\mathbf{r}_b) \rangle = \delta_{ab}, \quad (13)$$

$$\langle \sigma^{\text{A}} | \sigma^{\text{B}} \rangle = \delta_{\text{AB}}, \quad (14)$$

$$\langle \sigma | h \rangle = 0. \quad (15)$$

[Equations (13)-(15) are not valid in the strict sense. However, they permit the theory to be developed much more easily, have sometimes been justified by other considerations,^{26,27} and define the valence state in the sense of Moffit's "nonadiabatic dissociation."²²] With some algebraic manipulation, we obtain the following

²⁶ I. Fischer-Hjalmars, *J. Chem. Phys.* **42**, 1962 (1965).

²⁷ I. Fischer-Hjalmars, in *Modern Quantum Chemistry-Istanbul Lectures*, O. Sinanoğlu, Ed. (Academic Press Inc., New York, 1965), Pt. I.

expression for the valence-state energy of carbon described by the wavefunction (2) when Ψ_r corresponds to a single determinant:

$$E_{\text{CVS}} = E_{\text{C}^+} + (q_+ + q_-)\alpha + q_+q_-\gamma, \quad (16)$$

$$E_{\text{C}^+} = 2I_{1s} + 3I_{\sigma_1} + J_{1s1s} + 6J_{1s\sigma_1} - 3K_{1s\sigma_1} + 3J_{\sigma_1\sigma_2} - \frac{3}{2}K_{\sigma_1\sigma_2} + \frac{3}{2}a^2J_{\sigma_1\sigma_1}, \quad (17)$$

$$\alpha = I_{2p\pi} + 2J_{1s2p\pi} - K_{1s2p\pi} + 3J_{\sigma_12p\pi} - \frac{3}{2}K_{\sigma_12p\pi}, \quad (18)$$

$$\gamma = J_{2p\pi2p\pi}, \quad (19)$$

$$q_+ = \sum_{i(\alpha\text{spin}, \pi\text{electrons})} |C_{i0}|^2, \quad (20)$$

$$q_- = \sum_{j(\beta\text{spin}, \pi\text{electrons})} |C_{j0}|^2, \quad (21)$$

$$I_\psi = \langle \psi | -\frac{1}{2}\nabla^2 - (6/|\mathbf{r}-\mathbf{r}_0|) | \psi \rangle \quad (22)$$

$$J_{\psi\psi'} = \langle \psi(1)\psi'(2) | 1/r_{12} | \psi(1)\psi'(2) \rangle, \quad (23)$$

$$K_{\psi\psi'} = \langle \psi(1)\psi'(2) | 1/r_{12} | \psi'(1)\psi(2) \rangle. \quad (24)$$

The σ_1 and σ_2 are two sp^2 σ orbitals [Eq. (7)] at 120° to one another. The q_+ and q_- are the charge densities of the α and β π electrons, respectively. When Ψ_r corresponds to a linear combination of Slater determinants, q_+ and q_- retain their meanings as π charge densities, but the coefficient of γ in Eq. (16) will in general be different from q_+q_- . For concreteness, we have labeled the carbon atom of interest by the number "0" in Eqs. (20)-(22).

Alternant-Hydrocarbon Ground States

We immediately specialize Eq. (16) for alternant-hydrocarbon ground states (AHC-GS) by setting^{9,28}

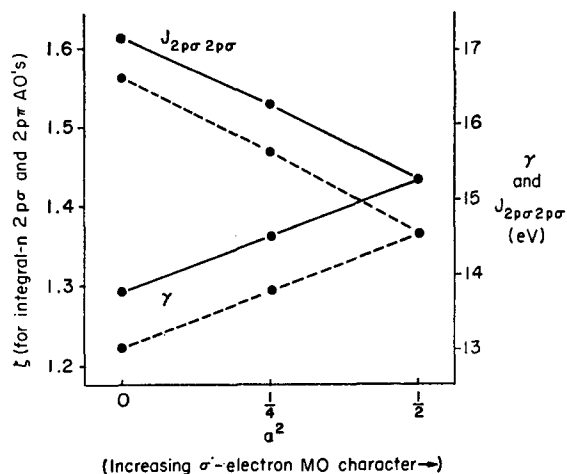
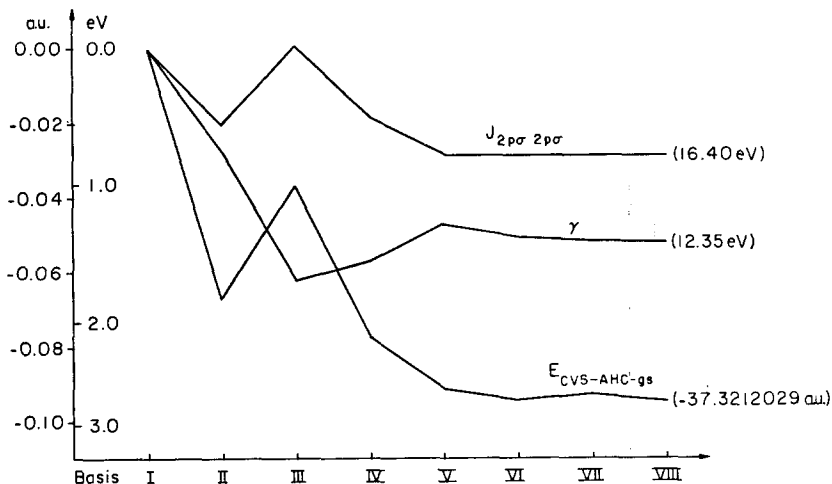


FIG. 1. Effect of σ -electron molecular-orbital character on the $2p\sigma$ and $2p\pi$ atomic orbitals. Solid lines give the orbital exponents (left-hand scale) and Coulomb self-repulsion integrals γ and $J_{2p\sigma 2p\sigma}$ (right-hand scale) for the integral- n minimal-basis orbitals. Dashed lines give γ and $J_{2p\sigma 2p\sigma}$ (but not ζ) for the nonintegral- n minimal basis.

²⁸ C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.* **36**, 193 (1940).

FIG. 2. Changes in total energy, γ , and $J_{2p\sigma 2p\sigma}$ as the basis is improved. The numbers in parentheses give the final values of these quantities.



$$q_+ = q_- = \frac{1}{2}:$$

$$E_{CVS-AHC-GS} = E_C + \alpha + \frac{1}{4}\gamma. \quad (25)$$

This result differs from that of Van Vleck by the $\frac{1}{4}\gamma$ in Eq. (25) and the α^2 term in E_C [Eq. (17)]. Both these terms are brought in by the molecular-orbital description and are absent from the simple (no ionic structures) valence-bond description.

Minimization of E_{CVS} ?

To determine the valence-state orbitals, we minimize E_{CVS} . Minimizing valence-state energies was originally suggested by Goepfert-Mayer and Sklar² and is not without precedent,²⁹⁻³³ but since valence states are not *bona fide* states, the variational principle is not strictly applicable. Hopefully, the atomic valence-state energies constitute a substantial part of the total molecular energy. A justification for minimization could be given if the entire molecular energy using Ψ [Eq. (2)] were minimized and the resulting orbitals turned out substantially the same as those obtained by minimizing the valence-state energy. Such a molecular calculation would be much more difficult than the present one, so we leave the justification to the future; thus, at this stage, minimizing E_{CVS} must be considered (from the viewpoint of rigor) as another ingredient of the valence-state model.

It should be noted that minimization of the analogous valence-state energy for hydrogen in the simple MO treatment of H_2 gives a $1s$ orbital further from the "best-scaled" $1s$ AO than is the atomic-hydrogen AO. For H_2 , the valence-state minimization is thus inappropriate. It is not felt, however, that H_2 is necessarily typical.

²⁹ O. Sinanoğlu and M. K. Orloff, in *Modern Quantum Chemistry-Istanbul Lectures*, O. Sinanoğlu, Ed. (Academic Press Inc., New York, 1965), Pt. I.

³⁰ M. K. Orloff and O. Sinanoğlu *J. Chem. Phys.* **43**, 49 (1965).

³¹ R. B. Hermann, *J. Chem. Phys.* **42**, 1027 (1965).

³² K. Ohno, *Theoret. Chim. Acta* **2**, 219 (1964).

³³ K. Ruedenberg, *J. Chem. Phys.* **34**, 1907 (1961).

III. METHODS OF COMPUTATION

Our approach is entirely analogous to the treatment of the atomic Hartree-Fock problem by the expansion method of Roothaan.³⁴ We first rewrite the valence-state energy formulas of Eqs. (17)–(19) by inserting

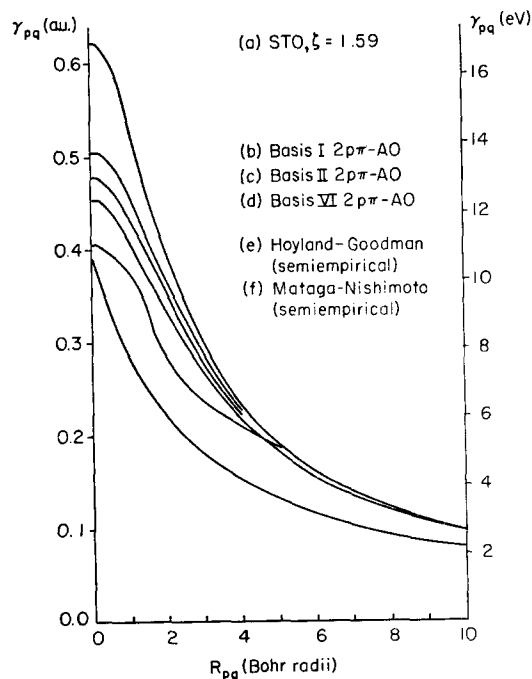


FIG. 3. γ_{pq} vs R_{pq} computed with (a) STO with $\zeta=1.59$ and $n=2$ (uppermost curve); (b) integral- n minimal basis AO; (c) nonintegral- n minimal basis AO; (d) nonintegral- n double basis AO; (e) semiempirical curve of Hoyland and Goodman, estimated from Fig. 1 of Ref. 14(a); (f) semiempirical formula of Mataga and Nishimoto (lowermost curve). In all six cases, γ_{pq} was calculated for R (in Bohr radii) = 0, 0.5, 1, 2, 3, 4, 5, 7, and 10, and then a smooth curve was drawn.

³⁴ C. C. J. Roothaan and P. S. Bagus, *Methods Computational Phys.* **2**, 47 (1963).

TABLE I. Minimization of alternant-hydrocarbon-ground-state carbon valence-state energy with and without $\frac{1}{4}\gamma$.

Energy expression	Basis type and total energy*	γ	Basis functions	n Principal quantum number	ζ Orbital exponent	Coefficient for atomic orbitals			
						1s	2s	2p σ	2p π
$E_{CVS-AHC-GS} = E_C^* + \alpha + \frac{1}{4}\gamma (a^2 = 0)$	Minimal; integral n -37.2264492 a.u.	0.5061 a.u. 13.77 eV	s	1	5.6787	-0.24872			
			s	2	1.6649	1.02763			
			p σ	2	1.6136		1.00000		
			p π	2	1.2929				1.00000
$E_C^* + \alpha (a^2 = 0)$	Minimal; integral n -37.3655152 a.u.	0.6023 a.u. 16.39 eV	s	1	5.6779	-0.24450			
			s	2	1.6462	1.02662			
			p σ	2	1.5666		1.00000		
			p π	2	1.5387				1.00000

* 1 a.u. = 1 hartree = 27.21 eV.

the explicit forms of the σ -hybrid orbitals:

$$E_C^* = 2I_{1s} + I_2 + 2I_{2px} + J_{1s1s} + 2J_{1s2s} - K_{1s2s} + 4J_{1s2px} - 2K_{1s2px} + \frac{1}{6}(a^2 + 1)J_{2s2s} + \frac{1}{6}(4a^2 + 1)J_{2px2px} + \frac{1}{6}(4a^2 + 10)J_{2s2px} + J_{2px2py} + \frac{1}{6}(8a^2 - 10)K_{2s2px} - \frac{1}{2}K_{2px2py}, \quad (26)$$

$$\alpha = I_{2p\pi} + 2J_{1s2p\pi} + J_{2s2p\pi} + 2J_{2px2p\pi} - K_{1s2p\pi} - \frac{1}{2}K_{2s2p\pi} - K_{2px2p\pi}, \quad (27)$$

$$\gamma = J_{2p\pi2p\pi}, \quad (28)$$

where we have taken the radial parts of the $2px$ and $2py$ orbitals to be equal. We then attempt to construct the atomic orbitals [$1s$, $2s$, $2px$, $2py$, $2p\pi (=2pz) =$ the set ϕ_i] of Eqs. (26)–(28) as analytic Hartree-Fock-type orbitals; that is, they will be a set of orthonormal orbitals which are expanded in terms of a basis of ordinary real Slater-type orbitals (STO's) (=the set f_j): $\phi_i = \sum_j C_{ij}f_j$, $i=1, \dots, 5$, $j=1, \dots, k \geq 5$, where the expansion coefficients C_{ij} are to be determined variationally.

The coefficients (those which are not zero by symmetry) could in principle be determined by Roothaan's method, but they are instead found here by the more direct numerical technique of minimum energy orthogonalization.³⁶ We have collected all the nonzero C_{ij} 's and all the adjustable factors (n and ζ) of each STO basis orbital [$f_j = N r^{n-1} e^{-\zeta r} S_l^m(\theta, \phi)$] into a single set of parameters to be varied by computer to give a minimum E_{CVS} at several different values of a^2 . We carried out parameter optimization for both noninteger and integer values of n and, in order to assess more fully the rate of convergence to true Hartree-Fock-type orbitals, for several different basis-set sizes.

Most of the calculations were performed with integer- and noninteger- n "minimal" basis sets ($k=5$), but selected cases were done for the minimal sets with an extra $p\pi$ ($k=6$), for the "double" sets ($k=10$), and for the double sets with an extra $p\pi$ ($k=11$). For the $k=11$ basis sets (Bases VII and VIII) the core AO's were "frozen" at their double basis values (Bases V and VI) and only the three-term $2p\pi$ AO was re-optimized. Note that the noninteger- n double basis has been improved slightly over the earlier result.¹⁷

IV. RESULTS AND DISCUSSION

First consider the importance of the $\frac{1}{4}\gamma$ in Eq. (25). We minimized $E_{CVS-AHC-GS}$ with $a^2=0$ (VB wavefunction for σ electrons) using a minimal basis set of STO's. We also minimized the same expression (25) without the $\frac{1}{4}\gamma$ (VB Ψ_π vs MO Ψ_π). Table I contains the results. [The species without the $\frac{1}{4}\gamma$ is the valence state used previously^{18,29-32} to represent carbon in alternant hydrocarbons and corresponds to Eq. (16)

³⁶ H. W. Joy, L. J. Schaad, and G. S. Handler, J. Chem. Phys. **41**, 2026 (1964).

TABLE II. Minimization of $E_{CVS-AHC-GS}$. Effect of adding MO character to the σ -electron description. Minimal basis.

Integral #	Basis type and total energy	d^2	γ	$J_{2p\sigma-2p\pi}$	Basis functions	# Principal quantum number	ζ Orbital exponent	Coefficients for atomic orbitals			
								1s	2s	2p σ	2p π
Integral # -37.2264492 a.u.	0	0	0.5061 a.u.	0.6316 a.u.	s	1	5.6787	0.99715	-0.24872		
			13.77 eV	17.19 eV	s	2	1.6649	0.012074	1.02763		
-36.9623757 a.u.	$\frac{1}{2}$	$\frac{1}{2}$	0.5336 a.u.	0.5984 a.u.	p σ	2	1.6136			1.00000	
					p π	2	1.2929				
			14.52 eV	16.28 eV	s	1	5.6805	0.99728	-0.23836		
					s	2	1.6222	0.011979	1.02530		
-36.7100776 a.u.	$\frac{1}{2}$	$\frac{1}{2}$	0.5612 a.u.	0.5612 a.u.	p σ	2	1.5288			1.00000	
					p π	2	1.3633				
			15.27 eV	15.27 eV	s	1	5.6821	0.99739	-0.22991		
					s	2	1.5870	0.011901	1.02348		
Non-integral # -37.2938082 a.u.	0	0	0.4785 a.u.	0.6114 a.u.	s	0.98595	5.5965	0.99783	-0.23300		
					s	2.2417	1.8540	0.009742	1.02463		
			13.02 eV	16.64 eV	p σ	1.6609	1.3468			1.00000	
					p π	1.4803	0.96325				1.00000
-37.0652786 a.u.	$\frac{1}{2}$	$\frac{1}{2}$	0.5064 a.u.	0.5749 a.u.	s	0.98594	5.5965	0.99788	-0.22834		
					s	2.1727	1.7583	0.009721	1.02362		
			13.78 eV	15.64 eV	p σ	1.6053	1.2329			1.00000	
					p π	1.5118	1.0363				1.00000
-36.7900777 a.u.	$\frac{1}{2}$	$\frac{1}{2}$	0.5345 a.u.	0.5344 a.u.	s	0.98594	5.5965	0.99793	-0.22492		
					s	2.1116	1.6786	0.009618	1.02292		
			14.54 eV	14.54 eV	p σ	1.5434	1.1114			1.00000	
					p π	1.5435	1.1115				1.00000

TABLE III. Effect of improvement of basis on AHC-GS carbon valence state.

Basis type and total energy	γ	$J_{2p\sigma 2p\sigma}$	Basis functions	Principal quantum number n	ζ Orbital exponent	Coefficients for atomic orbitals			
						ϕ_{1s}	ϕ_{2s}	$\phi_{2p\sigma}$	$\phi_{2p\pi}$
I. Integral n , minimal -37.2264492	0.5061 a.u. 13.77 eV	0.6316 a.u. 17.19 eV	s	1	5.6787	0.99715	-0.24872		
			s	2	1.6649	0.01207	1.02763		
			$p\sigma$	2	1.6136			1.00000	
			$p\pi$	2	1.2929				1.00000
II. Nonintegral n , minimal -37.2938082	0.4785 a.u. 13.02 eV	0.6114 a.u. 16.64 eV	s	0.98595	5.5965	0.99783	-0.23300		
			s	2.2417	1.8540	0.00974	1.02463		
			$p\sigma$	1.6609	1.3468			1.00000	
			$p\pi$	1.4803	0.9633				1.00000
III. Integral n , minimal plus an extra $p\pi$ -37.2635631	0.4434 a.u. 12.06 eV	0.6348 a.u. 17.27 eV	s	1	5.6771	0.99708	-0.25029		
			s	2	1.6701	0.01229	1.02794		
			$p\sigma$	2	1.6219			1.00000	
			$p\pi$	2	0.8675				0.75523
		$p\pi$	2	2.3016					0.35578
IV. Nonintegral n , minimal plus an extra $p\pi$ -37.3040042	0.4488 a.u. 12.21 eV	0.6128 a.u. 16.67 eV	s	0.9859	5.5962	0.99781	-0.23330		
			s	2.2472	1.8609	0.00983	1.02467		
			$p\sigma$	1.6646	1.3522			1.00000	
			$p\pi$	1.7325	0.7529				0.69841
		$p\pi$	1.8195	1.9046					0.39425
V. Integral n , double -37.3179739	0.4587 a.u. 12.48 eV	0.6027 a.u. 16.40 eV	s	1	5.866	0.96613	-0.22372		
			s	2	1.500	-0.01345	0.80043		
			s	3	3.278	0.312614	0.01356		
			s	4	3.950	-0.26133	0.22907		
		$p\sigma$	2	1.323			0.80696		
		$p\sigma$	2	2.778			0.24884		
		$p\pi$	2	0.9042				0.75372	
		$p\pi$	2	2.331					0.35138
VI. Nonintegral n , double -37.3209653	0.4551 a.u. 12.38 eV	0.6026 a.u. 16.40 eV	s	0.9957	5.829	0.96841	-0.21571		
			s	2.417	1.718	-0.01033	0.79134		
			s	3.123	3.548	0.28634	0.19626		
			s	4.047	4.185	-0.23904	0.06708		
		$p\sigma$	1.869	1.221			0.73161		
		$p\sigma$	1.864	2.265			0.31343		
		$p\pi$	1.741	0.7724				0.70065	
		$p\pi$	1.823	1.924					0.38942

TABLE III (Continued)

Basis type and total energy	γ	$J_{2p\pi 2p\sigma}$	Basis functions	n Principal quantum number	d Orbital exponent	Coefficients for atomic orbitals			
						ϕ_{1s}	ϕ_{2s}	$\phi_{2p\sigma}$	$\phi_{2p\pi}$
VII. Integral n , double plus an extra $p\pi$ -37.3191210	0.4543 a.u. 12.36 eV	0.6027 a.u. 16.40 eV	s	1	5.866	0.96613	-0.22372		
			s	2	1.500	-0.01345	0.80043		
			s	3	3.278	0.31261	0.01356		
			s	4	3.950	-0.26133	0.22907		
			$p\sigma$	2	1.323			0.80696	
			$p\sigma$	2	2.778			0.24884	
			$p\pi$	2	0.7709				0.59114
			$p\pi$	2	3.132				0.21186
			$p\pi$	2	2.106				0.35145
			VIII. Nonintegral n , double plus an extra $p\pi$ -37.3212029	0.4539 a.u. 12.35 eV	0.6026 a.u. 16.40 eV	s	0.9957	5.829	0.96841
s	2.417	1.718				-0.01033	0.79134		
s	3.123	3.548				0.28634	0.19626		
s	4.047	4.185				-0.23904	0.06708		
$p\sigma$	1.869	1.221						0.73161	
$p\sigma$	1.864	2.265						0.31343	
$p\pi$	1.937	0.7072							0.50569
$p\pi$	1.892	2.197							0.40507
$p\pi$	3.567	1.847							0.23788

with $q_+ = 1, q_- = 0$.) The effective nuclear charge (2ζ) of the AHC-GS valence-state $2p\pi$ AO is 2.59 vs 3.08 for the all VB valence state,³⁶ (and vs 3.18 for Zener's³⁷ atomic carbon and 3.25 for Slater's³⁸ rules). The minimal-basis-set AHC-GS orbital is considerably more expanded than the all-VB orbital and yields a γ of 13.77 eV. That it is important to let $\zeta_{2p\pi}$ differ³⁶ from ζ_{2p} can also be seen from Table I.

Second, consider the effect of a^2 , i.e., the description of the σ electrons, on the valence state. In Table II and Fig. 1, the results of minimizing $E_{CVS-AHC-GS}$ with $a^2 = 0, \frac{1}{4},$ and $\frac{1}{2}$ (VB, intermediate, and MO descriptions) are given both for integral- n and nonintegral- n minimal bases of STO's. Both sets of calculations indicate that as the MO character of Ψ_σ is increased (1) the $1s$ orbital contracts slightly, (2) the $2s$ orbital expands, and (3) the $2p\sigma$ orbital expands and the $2p\pi$ orbital contracts, the two coinciding at $a^2 = \frac{1}{2}$. The coincidence of the $2p\pi$ and $2p\sigma$ AO's in the all-MO case comes about from the symmetrical way the three $2p$ orbitals enter the energy expression. Note that even in the all-MO case, the $2p\pi$ effective charge (2.87) is still significantly less than the atomic 3.18. Moreover, the nonintegral- n $2p\pi$ AO's give values of γ about 6% smaller than in the integral- n cases.

Next consider the effect of improvement of the basis. We choose (somewhat arbitrarily) the VB description of the σ electrons. (At present there is no simple way to select the best value of a^2 .) In Table III we list the results obtained with several progressively more flexible bases, and in Fig. 2 we plot the energy lowering and the lowering in γ as the basis set is improved. One notices that:

(1) Going from an integral- n to a nonintegral- n minimal basis gives a much greater energy lowering than the next step of doubling the nonintegral- n basis.

(2) The lowering in γ on going from the integral- n STO to the nonintegral- n STO is as great as the subsequent lowering on going to two STO's.

(3) Introduction of an extra $2p\pi$ basis function has very little effect on the σ electrons but does improve the $2p\pi$ AO significantly.

(4) The difference between the integral- n and nonintegral- n double-basis results is much less than that for the minimal basis. This suggests that these results are fairly close to the convergence limit.

(5) The introduction of a third $2p\pi$ basis orbital gives little further improvement in the energy and almost no change in γ .

(6) The best $2p\pi$ AO, i.e., the Basis VIII AO, yields a γ of 12.35 eV, which is surprisingly close to the experimental values.

³⁶ Minimization of a valence-state energy without the $\frac{1}{2}\gamma$ and with $\zeta_{2p\pi} \neq \zeta_{2p\sigma}$ was apparently carried out by Ohno (Ref. 32). However, we have not been able to reproduce Ohno's results or to guess his energy expression in terms of integrals over atomic orbitals.

³⁷ C. Zener, Phys. Rev. **36**, 51 (1930).

³⁸ J. C. Slater, Phys. Rev. **36**, 57 (1930).

TABLE IV. The two-center Coulomb integral γ_{pq} .

R_{pq} (Bohr radii)	γ_{pq}									
	Zener's AO		Basis I		Basis II		Basis VI		Mataga-Nishimoto	
	(a.u.)	(eV)	(a.u.)	(eV)	(a.u.)	(eV)	(a.u.)	(eV)	(a.u.)	(eV)
0	0.6223	16.93	0.5061	13.77	0.4785	13.02	0.4551	12.38	0.3985	10.84
1	0.5400	14.69	0.4591	12.49	0.4349	11.83	0.4122	11.22	0.2849	7.753
2	0.4015	10.92	0.3667	9.978	0.3517	9.570	0.3347	9.107	0.2217	6.034
2.6457	0.3305	8.994	0.3115	8.477	0.3020	8.216	0.2896	7.880	0.1940	5.278
3	0.2994	8.147	0.2855	7.769	0.2781	7.568	0.2680	7.294	0.1815	4.939
4	0.2343	6.376	0.2278	6.198	0.2242	6.100	0.2187	5.950	0.1536	4.180
5	0.1915	5.211	0.1878	5.110	0.1859	5.058	0.1828	4.973	0.1332	3.623
7	0.1396	3.798	0.1381	3.757	0.1373	3.735	0.1361	3.702	0.1052	2.861
10	0.09885	2.690	0.09828	2.674	0.09799	2.666	0.09753	2.654	0.07994	2.175

One concludes that the $2p\pi$ AO is poorly represented by a single STO and that the value of γ is much closer to the experimental values than had previously been supposed. [This last conclusion should hold even when $\sigma^2 > 0$, although the γ would be a little larger (see Table II and Fig. 1).] Furthermore this value of γ is obtained without benefit of any attempt to allow for electron correlation,^{10,29-31} as would be done in the SPO method of Dewar,³⁹ or for σ -electron rearrangements.^{10,29,30} It is also worth noting that although the differences between integer- and noninteger- n results do indeed disappear⁴⁰ as the convergence limits are approached, those calculations which must use severely limited basis sets probably ought to be done with noninteger- n orbitals.

Finally, in Table IV and Fig. 3 the values of the two-

³⁹ A. L. H. Chung, M. J. S. Dewar, and N. L. Sabelli, *Molecular Orbitals in Chemistry, Physics and Biology, A Tribute to R. S. Mulliken*, P.-O. Löwdin and B. Pullman, Eds. (Academic Press, Inc., New York, 1964), p. 395.

⁴⁰ H. W. Joy and G. S. Handler, *J. Chem. Phys.* **42**, 3047 (1965).

center Coulomb repulsion integrals γ_{pq} (which also play an important role in π theory) calculated with (a) a STO with $\zeta = 1.59$, and $n = 2$; (b)-(d) the $2p\pi$ AO's of Bases I, II, and VI; (e) the semiempirical curve of Hoyland and Goodman^{14a,b}; and (f) the semiempirical formula of Mataga and Nishimoto,^{14c}

$$\gamma_{pq}(\text{Mataga-Nishimoto}) = (2.510 + R_{pq})^{-1}, \quad (29)$$

are compared. (The noninteger- n integrals were calculated using the Fourier-transform convolution theorem.)⁴¹

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⁴¹ H. J. Silverstone, *J. Chem. Phys.* **45**, 4337 (1966).