

what quantities or attributes of a charge distribution or wave function make up the basic building blocks of a molecular system? The results presented here suggest

that the molecular fragments as defined by planes through the nuclei may be the basic units for the understanding of additivity.

## Parametrization of Semiempirical $\pi$ -Electron Molecular Orbital Calculations. $\pi$ Systems Containing Carbon, Nitrogen, Oxygen, and Fluorine<sup>1</sup>

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**Abstract:** A uniform parametrization is suggested for  $\pi$ -electronic structure calculations of conjugated systems containing carbon, nitrogen, oxygen, and fluorine. All parameters are related directly to atomic data. The parametrization scheme is substantiated by comparing computed and observed uv spectral data and proton hyperfine coupling constants for a large number of different  $\pi$ -electron systems. The good correlations obtained suggest that  $\pi$ -electronic structure calculations, in conjunction with the proposed parametrization scheme, can be used reliably for the prediction of uv spectra and proton hyperfine coupling constants. Arguments are presented that singlet-triplet transition energies, as well as ionization potentials, cannot be predicted with equal reliability using the scheme proposed.

The application of semiempirical  $\pi$ -electron molecular orbital calculations to the study of chemical and spectroscopic properties of unsaturated hydrocarbons has been extensive and in general successful. The method of calculation used commonly is the semiempirical scheme of Pariser, Parr, and Pople, which is an SCF-LCAO procedure based on the independent-particle model, grossly simplified by the assumption of  $\Sigma$ - $\Pi$  separability and the approximation of "zero differential overlap" between atomic orbitals on different centers.<sup>2</sup> The effect of these rather severe approximations is hopefully compensated somewhat by the introduction of semiempirical parameters into the calculation. Computations following the PPP method result in  $\pi$ -electron molecular wave functions, describing many important phenomena not accommodated by the simpler Hückel theory, such as separations between excited states of different multiplicity, excitation energies for electronic transitions giving rise to  $\alpha$  and  $\beta$  bands in the absorption spectra of aromatic hydrocarbons, and positive as well as negative spin densities in free radicals and ions. Although computations using the PPP method are in principle no more difficult than Hückel calculations, the choice of suitable parameters for PPP calculations is more arduous, especially if hetero systems are to be treated.

Often, when  $\pi$ -electron calculations are performed for a limited group of similar molecules, a parametrization is effected such as to give good agreement between computed and experimental data for some molecules in the group considered. Proceeding in this manner results in a certain loss of objectivity, such as is commonly en-

countered in Hückel theory. In addition, it is more difficult to judge the relative reliability of calculations from different sources, when different approximations have been made in the selection of the basic parameters. If the PPP theory is general enough that it allows correlation of computed results with experimental data over a wide variety of unsaturated compounds, there must be at least one consistent choice of parameters which will yield a general and wide-reaching correlation. It is felt that there exists a need for such a unified parametrization scheme which is generally applicable, without additional modifications, to all types of atoms routinely encountered in different  $\pi$ -electron systems.

In order to deal with this problem we propose herein a generalized parameter scheme for PPP type calculations and detail its application to  $\pi$ -electron systems containing carbon, nitrogen, oxygen, and fluorine. Owing to the empirical nature of  $\pi$ -electron theory, it was felt that a direct theoretical parameter choice was not feasible, but the validity of an empirical parameter scheme, though derived with some theoretical reasoning, had to be demonstrated by showing its capability to predict or correlate observables. Therefore in section 3 a number of representative calculations of electronic energies and proton isotopic hyperfine coupling constants for different types of unsaturated systems are presented to substantiate the parameter scheme proposed in section 2. To clarify our notation and to avoid confusion, section 1 allows for a brief review of the  $\pi$ -electron formalism as it is used here.

### 1. Semiempirical $\pi$ -Electron Theory

In the  $\pi$ -electron approximation the  $\Sigma$  part of the total electronic wave function of a molecule is assumed to be invariant to changes in the  $\pi$ -electron distribution and therefore considered as constant and disregarded. A molecular wave function,  $\Psi_s$ , of a stationary state, de-

(1) Research supported in part by the National Science Foundation.  
 (2) (a) J. A. Pople, *Proc. Phys. Soc., London, Ser. A*, **68**, 81 (1955);  
 (b) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953);  
 (c) for additional references, see general reviews, e.g., L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966; K. Jug, *Theor. Chim. Acta*, **14**, 91 (1969).

scribing the  $\pi$ -electron cloud only, is then written in general as a sum of configurational functions,  $\Phi_n$ . The configurational functions are Slater determinants constructed from molecular orbitals  $\psi_i$ . These MO's are given as linear combinations of basis functions  $\varphi_\mu$  as

$$\psi_i = \sum_\mu \varphi_\mu c_{\mu i} \quad (1)$$

where the  $c_{\mu i}$ 's are linear expansion coefficients. As a basis set  $\varphi_\mu$ , atomic  $2p\pi$  orbitals are chosen, centered one on each atom which is participating in the  $\pi$  structure of the system.

(a) **Closed-Shell Ground State.** The  $\pi$ -electron molecular wave function for a closed-shell ground state of a molecule with  $n$  ( $n = \text{even}$ )  $\pi$  electrons is written as a single Slater determinant, constructed from  $m = n/2$  doubly occupied spatial orbitals

$$\Psi_0 = \Phi_0 =$$

$$\frac{1}{\sqrt{n!}} \det\{\psi_1(1)\bar{\psi}_1(2) \dots \psi_i(2i-1)\bar{\psi}_i(2i) \dots \bar{\psi}_m(n)\} \quad (2)$$

where barred orbitals are  $\beta$  spin, unbarred,  $\alpha$  spin.  $\Psi_0$  is an eigenfunction of  $S^2$  and  $S_z$  with the eigenvalues 0, representing a singlet state.

The  $\psi_i$ 's in eq 2 are determined by the eigenvectors of the Fock equation

$$\mathbf{F}\mathbf{c} = \mathbf{S}\mathbf{c}\epsilon \quad (3)$$

where  $\epsilon$  is diagonal.

In the zero differential overlap approximation of Pariser, Parr, and Pople we have  $\varphi_\mu \varphi_\nu d\tau = 0$  unless  $\nu = \mu$ . Thus  $\mathbf{S}$  is a unit matrix, and the matrix elements of  $\mathbf{F}$  are given by

$$F_{\mu\nu} = H_{\mu\nu} - (1/2)p_{\mu\nu}\gamma_{\mu\nu} + \delta_{\mu\nu}\sum_\sigma p_{\sigma\sigma}\gamma_{\mu\sigma} \quad (4)$$

where

$$\gamma_{\mu\nu} = \iint \varphi_\mu(1)\varphi_\nu(2)(1/r_{12})\varphi_\mu(1)\varphi_\nu(2)d\tau_1d\tau_2 \quad (5)$$

$$H_{\mu\mu} = -I_\mu(V, n) - \sum_{\sigma \neq \mu} Z_\sigma \gamma_{\mu\sigma} \quad (6)$$

and

$$p_{\mu\nu} = 2 \sum_i^m c_{\mu i} c_{\nu i} \quad (7)$$

The  $\gamma_{\mu\nu}$ 's are one- and two-center Coulomb repulsion integrals,  $I_\mu(V, n)$  is the  $n$ th ionization potential of atom  $\mu$  in valence state  $V$ ,  $Z_\sigma$  is the core charge of atom  $\sigma$  (equal to the number of electrons contributed to the  $\pi$ -electron system), and  $p_{\mu\nu}$  represents an element of the charge density-bond order matrix  $\mathbf{P}$ .  $H_{\mu\nu}$  ( $=\beta_{\mu\nu}$ ) for  $\mu \neq \nu$  is known as a core resonance integral and enters as a parameter, as do  $I_\mu(V, n)$  and  $\gamma_{\mu\nu}$ .

(b) **Open-Shell Ground States.** For open-shell systems of  $\pi$ -electron free radicals and radical anions and cations, we choose the spin-unrestricted Hartree-Fock description, because we would like to retain the simplicity of a single determinantal wave function, but at the same time be able to describe negative spin densities, central in the description of electron spin resonance spectroscopy.

An unrestricted molecular wave function for  $p$   $\alpha$  electrons and  $q$   $\beta$  electrons (putting arbitrarily  $p > q$ ) has the form

$$\Psi_0^u = (1/\sqrt{n!}) \det\{\psi_1^\alpha(1)\psi_2^\alpha(2) \dots \psi_p^\alpha(p)\psi_{p+1}^\beta(p+1) \dots \psi_{p+q}^\beta(p+q)\} \quad (8)$$

where the molecular orbitals comprising the elements of the determinant form two different orthonormal sets

$$\psi_i^\alpha \sum_\mu = \varphi_\mu c_{\mu i}^\alpha \quad \psi_i^\beta \sum_\mu = \varphi_\mu c_{\mu i}^\beta \quad (9)$$

determined by the solutions of

$$\mathbf{F}^\alpha \mathbf{c}^\alpha = \mathbf{S} \mathbf{c}^\alpha \epsilon^\alpha, \quad \mathbf{F}^\beta \mathbf{c}^\beta = \mathbf{S} \mathbf{c}^\beta \epsilon^\beta \quad (10)$$

with

$$F_{\mu\nu}^\alpha = H_{\mu\nu} - p_{\mu\nu}^\alpha \gamma_{\mu\nu} + \delta_{\mu\nu} \sum_\sigma (p_{\sigma\sigma}^\alpha + p_{\sigma\sigma}^\beta) \gamma_{\mu\sigma} \quad (11)$$

and

$$p_{\mu\nu}^\alpha = \sum_i^{\text{occ}} c_{\mu i}^\alpha c_{\nu i}^\alpha \quad (12)$$

The matrix elements  $\mathbf{F}^\beta$  are obtained by interchanging the superscripts  $\alpha$  with the superscripts  $\beta$  in eq 11 and 12. The  $\pi$  electronic energy of the system is

$$E_0^u = (1/2) \sum_{\mu\nu} [p_{\mu\nu}^\alpha (H_{\mu\nu} + F_{\mu\nu}^\alpha) + p_{\mu\nu}^\beta (H_{\mu\nu} + F_{\mu\nu}^\beta)] \quad (13)$$

The wave function  $\Psi_0^u$  is an eigenfunction of  $S_z$  but not of  $S^2$  and contains, in addition to the state of the multiplicity desired, contamination from spin components of higher multiplicity. However, the extent of contamination from higher multiplets is generally not large and  $\Psi_0^u$  may usually be considered a reasonable approximation to the state desired. By annihilating contaminating states of higher multiplicity one can obtain a ground-state function from  $\Psi_0^u$ , which is an eigenfunction of  $S^2$ . Such an annihilation will in general change the energy and charge distribution little; however, it may have a marked effect on spin densities (see Results).

(c) **Excited States.** A simple formulation of the molecular wave function for an excited singlet or triplet state, arising from a single excitation of a closed-shell ground state, may be given as the sum or difference of two determinantal functions.

$${}^{3,1}\Phi_{i \rightarrow k} =$$

$$(1/\sqrt{2n}) [\det\{\psi_1(1)\bar{\psi}_1(2) \dots \psi_k(2i-1)\bar{\psi}_i(2i) \dots \bar{\psi}_m(n)\} \pm \det\{\psi_1(1)\bar{\psi}_1(2) \dots \psi_i(2i-1)\bar{\psi}_k(2i) \dots \bar{\psi}_m(n)\}] \quad (14)$$

Equation 14 describes a spin-proper configuration arising from a single excitation of an electron out of the orbital  $\psi_i$ , occupied in the ground state, into a virtual (unoccupied) orbital  $\psi_k$ . The positive sign refers to a singlet and the negative sign to a triplet configuration. A single configuration represented by eq 14 will be in general a poor approximation to an excited state. A better, and frequently a sufficiently good approximation to an excited state, is obtained by writing the excited-state wave function as a linear combination of many such spin-proper configurations of a given multiplicity

$$\Psi_p = \sum_n \Phi_n A_{np} \quad (15)$$

and determining the linear expansion coefficients  $A_{np}$  by the variational method (configuration-interaction calculation). In this investigation the summation in eq 15 will be limited to singly excited configurations from the restricted Hartree-Fock ground-state function of eq 2, and the parametrization will be effected accordingly. The energies of the electronic excited states and the linear expansion coefficients

$A_{np}$  are the eigenvalues and eigenvectors respectively of the matrix  $\mathbf{H}$  of the total  $\pi$ -electron operator  $\mathcal{H}^\pi$  of the system, having the elements  $\langle \Phi_m | \mathcal{H}^\pi | \Phi_n \rangle$ . Since the orbitals from which the spin-proper configurations are constructed are Hartree-Fock orbitals, the interaction elements between ground state and singly excited configurations will vanish, and the  $\mathbf{H}$  matrix elements may be written for singlets as

$$\langle {}^1\Phi_m | \mathcal{H}^\pi | {}^1\Phi_n \rangle = \langle {}^1\Phi_{i \rightarrow k} | \mathcal{H}^\pi | {}^1\Phi_{i \rightarrow l} \rangle = \delta_{ij} \delta_{kl} E_0 + \delta_{kl} \epsilon_k - \delta_{ij} \epsilon_i - (jk|il) + 2(jk|li) \quad (16)$$

and for triplets as

$$\langle {}^3\Phi_m | \mathcal{H}^\pi | {}^3\Phi_n \rangle = \langle {}^3\Phi_{i \rightarrow k} | \mathcal{H}^\pi | {}^3\Phi_{i \rightarrow l} \rangle = \delta_{ij} \delta_{kl} E_0 + \delta_{kl} \epsilon_k - \delta_{ij} \epsilon_i - (jk|il) \quad (17)$$

where  $\delta_{ij}$  is the Kronecker delta. Due to the "zero differential overlap" approximation, we have

$$(ij|kl) = \iint \psi_i(1)\psi_j(2)(1/r_{12})\psi_k(1)\psi_l(2)d\tau_1d\tau_2 \approx \sum_{\mu\nu} c_{\mu i}c_{\mu j}c_{\nu k}c_{\nu l}\gamma_{\mu\nu} \quad (18)$$

By subtracting the ground-state energy,  $E_0$ , from the diagonal matrix elements, the eigenvalues obtained will be the excitation energies.

Analogously excited doublet and quartet states could be constructed from the unrestricted Hartree-Fock functions of ions and radicals, eq 8; however, this possibility is not considered in this work.

## 2. Parametrization

From the preceding review of the formalism of semiempirical  $\pi$ -electron molecular orbital theory, it is seen that the same basic parameters enter into each type of calculation considered, namely the valence-state ionization potentials  $I_\mu$ , the Coulomb repulsion integrals  $\gamma_{\mu\nu}$ , and the core resonance integrals  $\beta_{\mu\nu}$ . We proceed now to a detailed discussion and specification of the particular parameter choice proposed for the atoms carbon, nitrogen, oxygen, and fluorine.

(a) **Valence-State Ionization Potentials and One-Center Coulomb Repulsion Integrals.** The valence-state ionization potentials and the one-center Coulomb repulsion integrals are interrelated through the elegant argument due to Pariser,<sup>3</sup> who pointed out that the energetics of a charge-transfer disproportionation of two identical neutral atoms into an ion pair require approximately

$$\gamma_{\mu\mu} = I_\mu - A_\mu \quad (19)$$

where  $I_\mu$  and  $A_\mu$  are the proper ionization potential and electron affinity of atom  $\mu$ . The validity of Pariser's argument has been questioned frequently; it has been criticized particularly because the rearrangement in the electronic core (analogous to the  $\Sigma$  core in  $\pi$ -electron theory) of the atoms is not considered. Neglect of core rearrangement, however, is consistent with the entire framework of  $\pi$ -electron theory. Equation 19 is attractive by its simplicity and especially through the fact that with it good results can be obtained. To our knowledge there is in semiempirical  $\pi$  theory no procedure of obtaining the one-center Coulomb integral, which yields results significantly better; there-

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

fore, eq 19 has been adopted for the determination of the one-center Coulomb repulsion integrals.

The determination of valence-state ionization potentials and electron affinities is accomplished by combining the proper valence-state promotional energies with the corresponding ground-state ionization potentials and electron affinities, respectively. For example, the valence-state ionization potential and electron affinity for carbon in its (tr tr tr  $\pi$ ) valence state is given by

$$I_C(\text{tr tr tr } \pi, 1) = I_C + P_C^+(\text{tr tr tr}) - P_C^0(\text{tr tr tr } \pi)$$

$$A_C(\text{tr tr tr } \pi, 1) =$$

$$A_C + P_C^0(\text{tr tr tr } \pi) - P_C^-(\text{tr tr tr } \pi^2)$$

where  $P_C(v)$  is the promotion energy to valence state  $v$ . For an atom contributing two electrons to the  $\pi$ -electron system of a molecule, it is necessary to have the second valence-state ionization potential and corresponding electron affinity, *i.e.*, the first ionization potential. As an example for a pyrrole nitrogen, with a valence state tr tr tr  $\pi^2$ , it is

$$I_N(\text{tr tr tr } \pi^2, 2) = I_N^2 + P_N^{2+}(\text{tr tr tr}) - P_N^+(\text{tr tr tr } \pi)$$

$$A_N(\text{tr tr tr } \pi^2, 2) = I_N^1 +$$

$$P_N^+(\text{tr tr tr } \pi) - P_N^0(\text{tr tr tr } \pi^2)$$

Selection of the ground-state ionization potentials and electron affinities and calculations of the appropriate promotion energies has been considered in detail in an earlier publication,<sup>4</sup> and the valence-state quantities employed herein are based on these results.

It is in general not necessary to consider fine details in the hybridization of the underlying core of the atoms considered, since such changes affect the  $p\pi$ -electron ionization potential and electron affinity only little. As an example,  $I_C(\text{tr tr tr } \pi, 1) = 11.16$  eV and  $A_C(\text{tr tr tr } \pi, 1) = 0.03$  eV, while for acetylene-type carbon the values would be  $I_C(\text{di di } \pi \pi, 1) = 11.19$  eV and  $A_C(\text{di di } \pi \pi, 1) = 0.10$  eV. It is therefore sufficient to use general  $p\pi$ -electron ionization potentials and electron affinities. In Table I the required

**Table I.** Valence-State Ionization Potentials, Electron Affinities, and One-Center Coulomb Integrals Used<sup>a</sup>

Atom	Valence-state electronic configuration	Valence-state ionization potential, eV	Valence-state electron affinity, eV	One-center Coulomb integral, eV
C	tr tr tr $\pi$	11.16	0.03	11.13
N(I)	tr <sup>2</sup> tr tr $\pi$	14.12	1.78	12.34
N(II)	tr tr tr $\pi^2$	28.72	11.96	16.76
O(I)	tr <sup>2</sup> tr <sup>2</sup> tr $\pi$	17.70	2.47	15.23
O(II)	tr <sup>2</sup> tr tr $\pi^2$	34.12	15.30	18.82
F(II)	sp <sup>2</sup> p <sup>2</sup> p <sup>2</sup>	40.70	18.52	22.18

<sup>a</sup> See ref 6.

$p\pi$ -electron ionization potentials and electron affinities are listed together with the corresponding one-center Coulomb repulsion integrals, evaluated from eq 19, for the atoms considered in this investigation. The values

(4) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962); J. Hinze, Ph.D. Dissertation, University of Cincinnati, 1962.

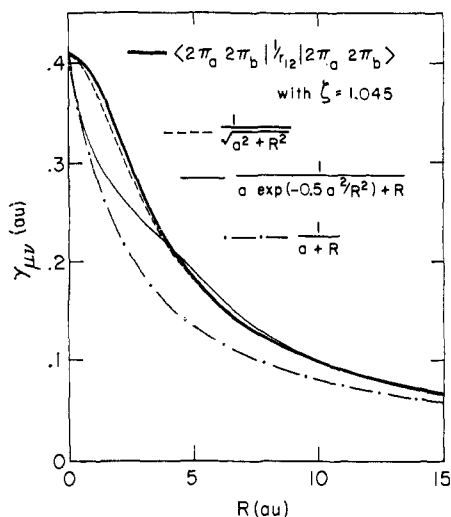


Figure 1. Dependence of  $\gamma_{\mu\nu}$  on  $r_{\mu\nu}$  as computed for  $2p\pi$  orbitals, and as given by different approximate formulas.

given correspond to an underlying trigonally hybridized core, as it is most commonly encountered.

(b) **Two-Center Coulomb Repulsion Integrals.** The one-center Coulomb repulsion integrals, when determined semiempirically from eq 19, are lower than the corresponding theoretical values, computed from Slater-type orbitals using Slater-Zehner exponents or from atomic Hartree-Fock orbitals, and thus correspond to somewhat more diffuse orbitals. The two-center Coulomb integrals must be determined with recognition of their proper limiting values; *i.e.*, they should join smoothly the purely electrostatic value  $r_{\mu\nu}^{-1}$  for large distances  $r_{\mu\nu}$  and also go to  $\gamma_{\mu\mu}$  at  $r_{\mu\nu} = 0$  in the homonuclear case. A general formula for  $\gamma_{\mu\nu}$  may be obtained by treating the problem purely theoretically and evaluating the Coulomb integral using Slater-type functions with an exponent that would give the empirical  $\gamma_{\mu\mu}$  for the one-center case. Such a procedure would complicate  $\pi$ -electron calculations considerably, and not necessarily yield better results than the alternative method of treating the integrals empirically. This can be done by choosing a flexible function with the required limiting behavior and implementing it from experience. We have chosen the latter method, and our suggested general formula for  $\gamma_{\mu\nu}$  in atomic units is

$$\gamma_{\mu\nu} = 1/[a \exp(-r_{\mu\nu}^2/2a^2) + r_{\mu\nu}] \quad (20)$$

where

$$a = 2/(\gamma_{\mu\mu} + \gamma_{\nu\nu}) \quad (21)$$

with the  $\gamma$ 's in hartrees and  $r$  in bohrs. (Atomic units are chosen here to avoid the appearance of conversion factors in the formulas.)

This expression is similar to a suggested formula by Mataga and Nishimoto,<sup>5</sup> and has been inspired by it. An equation of similar form has been suggested by Knowlton and Carper.<sup>6</sup> The exponential factor introduced into the denominator was found necessary to dampen the influence of  $a$  at intermediate values of  $r_{\mu\nu}$ , because Mataga-type formulas, without the

(5) K. Nishimoto and N. Mataga, *Z. Phys. Chem. (Frankfurt am Main)*, **12**, 335 (1957); **13**, 140 (1957).

(6) P. Knowlton and W. R. Carper, *Mol. Phys.*, **11**, 213 (1966).

exponential factor, result in the prediction of triplet states which are in general more than 1 eV too low. The reason for this is apparently that Mataga-type  $\gamma_{\mu\nu}$ 's show initially a too rapid decrease of  $\gamma_{\mu\nu}$  with  $r_{\mu\nu}$ , giving too large differences between one-center Coulomb integrals and nearest-neighbor Coulomb integrals. Another formula for  $\gamma_{\mu\nu}$  tested in this work has been

$$\gamma_{\mu\nu} = 1/\sqrt{a^2 + r^2} \quad (22)$$

as suggested by Ohno.<sup>7</sup> However, results obtained with such  $\gamma_{\mu\nu}$ 's were completely unacceptable. In Figure 1 the dependence of different  $\gamma_{\mu\nu}$  formulas on  $r_{\mu\nu}$  is illustrated for  $C(2\pi)$ - $C(2p\pi)$  Coulomb repulsion.

(c) **Core Resonance Integrals.** A semitheoretical method of estimating  $\beta_{\mu\nu}$  has been proposed by Ohno.<sup>7</sup> Using Löwdin orbitals and assuming that the major contribution to  $\beta_{\mu\nu}$  comes from the region near the midpoint of internuclear separation, he derives

$$\beta_{\mu\nu} = (1/2)(Z_\mu + Z_\nu)S_{\mu\nu}\{\gamma_{\mu\nu} - (2C/r_{\mu\nu})\} \quad (23)$$

where  $C$  is a disposable parameter. We have chosen to implement eq 23 in its present form into the overall parametrization scheme proposed herein, choosing the basic functions for the evaluation of  $S_{\mu\nu}$  in a manner consistent with the semiempirical  $\gamma_{\mu\nu}$ . This is accomplished by evaluating  $S_{\mu\nu}$  over Slater orbitals, using the theoretical value of the orbital exponents corresponding to the semiempirical value for the one-center Coulomb repulsion integral; *i.e.*, evaluating the one-center Coulomb repulsion integral  $\gamma_{\mu\mu}$  from a  $2p\pi$  orbital, which is represented by a single  $2p$  Slater-type basis function with exponent  $\zeta_\mu$ , gives the relation

$$\zeta_\mu = (1280/501)\gamma_{\mu\mu} \quad (24)$$

which is used to obtain the  $\zeta_\mu$ 's required for the determination of the overlap integrals  $S_{\mu\nu}$ . This procedure leads to relatively large values for the overlap integrals, but has the advantage of leaving the parameter scheme proposed internally consistent, and based entirely on the atomic energy data. That  $S_{\mu\nu}$  used in eq 23 may be too large is remedied by the parameter  $C$ , which is left unspecified to this point. This parameter has been chosen empirically such as to give the best overall fit to the electronic excitation energies in a small set of selected compounds, namely ethylene, benzene, and the monocyclic azines. The best value found is  $C = 0.545$ , and this value has been used in all following calculations performed, to substantiate the parameter scheme proposed herein.

### 3. Results of Sample Calculations

As pointed out in the introduction, the authors feel that a rigorous theoretical justification of a parameter scheme in the Pariser-Parr-Pople method cannot be achieved, owing to the many approximations in this semiempirical MO procedure. Numerical experimentation is therefore the only method to test the merits of the parametrization scheme proposed in section 2. Any parameter scheme is useful only if with it several experimental observables can be calculated reliably for a large class of molecules. It is, however, asking too much to expect a particular scheme to overcome the limitations inherent in the Pariser-Parr-Pople

(7) K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964).

method. The method is based on the independent-particle model and is therefore incapable of yielding effects which depend critically on electron correlation. Fortunately, it appears possible to compensate some of this shortcoming by an appropriate parameter choice. However, if parameters are chosen to compensate for one particular error, one should not expect the same parameters to compensate other correlation errors. To be more specific, let us discuss correlation errors in the description of electron excitation and ionization.

A particular singly excited configuration of a closed-shell molecule gives rise to a singlet and a triplet state. We ask what the electron correlation error is, if we calculate term values, *i.e.*

$$\Delta E = E^* - E^0$$

Identifying the correlation energy as  $\epsilon$  (a negative quantity), we obtain

$$\Delta\epsilon = \epsilon^* - \epsilon^0$$

If the transition energy is calculated within the framework of the independent-particle model, we should get  $\Delta E_{\text{HF}}$  which in general will be smaller than  $\Delta E$ , since  $\epsilon^0$  is in general smaller than  $\epsilon^*$  ( $\epsilon^0$  and  $\epsilon^*$  are negative energy quantities), and

$$\Delta E = \Delta E_{\text{HF}} + \Delta\epsilon$$

If we effect the parametrization such that we obtain  $\Delta E^{(1)}$ , for singlet states, directly, in the frame of the independent-particle model, then we should expect to obtain values for  $\Delta E^{(3)}$  for triplet states, which are too low, because we calculate approximately

$$\Delta E^{(3)} = \Delta E^{(3)}_{\text{HF}} + \Delta\epsilon^{(1)}$$

the corrections  $\Delta\epsilon^{(1)}$  resulting from our parameter choice; however,  $\Delta\epsilon^{(1)}$  is in general smaller than  $\Delta\epsilon^{(3)}$ , since the Fermi hole in the triplet state results in  $\epsilon^{*(1)} < \epsilon^{*(3)}$  ( $\epsilon$ 's are negative quantities).

The parametrization scheme suggested in this paper is adjusted so as to yield good correlation between experimental and computed values for singlet-singlet transition energies and for ground-state properties, *i.e.*, proton isotopic hyperfine coupling constants. It must be expected therefore that singlet-triplet excitations will be calculated consistently too low. Such a consistent discrepancy has been observed in all cases where experimental singlet-triplet transition energies are known.

It can be concluded from an argument quite analogous to the one presented above that ionization potentials calculated from orbital energies, following Koopmans' theorem, should be too large, if the orbital energies are obtained with parameters chosen for singlet-singlet transitions. This is also consistent with the results obtained in this work. Thus the parameter scheme presented here will reliably yield only ground-state properties and singlet-singlet transition energies. We believe, because of the arguments presented above, that such limitations should apply to any general parameter scheme for the Pariser-Parr-Pople method. The arguments presented above apply only if, as is done here, the ground state is described by a single, spin-restricted HF function, and the excited states are expressed as combinations of Slater determinants, singly

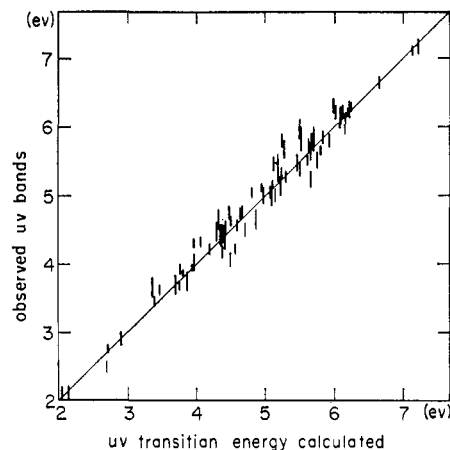


Figure 2. Observed uv absorption bands *vs.* computed singlet-term energies for molecules given in Table II.

excited with respect to the ground state. If doubly and higher excited configurations are used in the expansion of the total wave function, these shortcomings of the conventional Pariser-Parr-Pople method can be overcome. Work along these lines is in progress.

**Results for Singlet-Singlet Excitations.** Singlet-singlet excitation energies were calculated for organic  $\pi$ -electron systems containing the atoms C, N, O, and F. The results are given in Figure 2 and Table II. All systems were assumed to be planar and, if known, the ground-state bond distances and angles were used; otherwise, idealized structures were assumed with standard internuclear distances. It was found that the results did not depend critically on these assumed geometries. The computed transition energies should correspond to the energies of the absorption maxima, since these Franck-Condon maxima in general correspond to excitations from the zeroth vibrational state, which corresponds most closely to the ground-state geometry assumed in our calculations. Unfortunately, most of the observed absorption maxima are rather broad; therefore, we have compared an observed absorption range with the computed transition energies. This we believe is more meaningful than comparing the exact observed absorption maxima. Frequently weak absorptions, which are symmetry or overlap forbidden, do not show up in the system as absorption maxima. If such absorptions appeared as shoulders of stronger peaks, we have included them in Table II together with the corresponding computed excitation energies. If, however, symmetry- or overlap-forbidden excitations resulted in the computation of energy values where neighboring strong lines completely obscured the appearance of a weak absorption, then such computed excitations are left out in Table II, since no meaningful comparison would be possible. It should be kept in mind that the purpose of this presentation is to compare computed and observed spectra to justify a parameter scheme, and we do not even attempt to interpret in detail any one particular uv spectrum of a compound. Only in the latter case would it be necessary to also report computed weak transition energies which clearly are obscured in the observed spectrum. It is seen from Table II and from the correlation diagram, Figure 2, that the computed transition energies correlate well with the observed absorption maxima ranges.

Table II. Computed and Experimental Uv-Excitation Energies (eV)

Type	Compound	Ref	Excitation 1		Excitation 2		Excitation 3		Excitation 4		Excitation 5	
			Calcd	Exptl	Calcd	Exptl	Calcd	Exptl	Calcd	Exptl	Calcd	Exptl
Hydrocarbons												
Alternant	<i>trans</i> -Butadiene	<i>a</i>	5.51	5.80-6.10	6.64	6.60-6.70	7.13	7.05-7.15				
	Styrene	<i>b</i>	4.39	4.30-4.50	4.82	5.00-5.10	5.83	5.75-5.90	6.08	5.95-6.30		
	Naphthalene	<i>b</i>	3.97	3.90-4.15	4.36	4.40-4.60	5.80	5.60-5.70	6.17	5.90-6.20		
	Phenanthrene	<i>b</i>	3.71	3.55-3.85	4.21	4.15-4.30	5.14,	4.85-5.10	5.56,	5.70-6.00		
						5.16		5.71				
Nonalternant	Azulene	<i>b, d</i>	2.03, 2.13	2.00-2.20	3.36	3.50-3.80	4.31	4.35-4.60	4.98	5.05-5.15		
	Acenaphthylene	<i>c, e</i>	2.90	2.80-3.00	3.77	3.65-3.75	3.81	3.80-3.90	4.87	4.50-4.80	5.55	5.30-5.50
N <sup>+</sup>	Pyrazine	<i>b</i>		3.95-4.05	4.67	4.70-4.85	6.18	6.15-6.25	7.22	7.05-7.25		
	Isoquinoline	<i>f</i>	3.77	3.85-4.00	4.31	4.50-4.80	5.22	5.25-5.40	5.61,	5.60-5.80		
									5.66			
	Acridine	<i>c</i>	3.38	3.40-3.50	3.47	3.55-3.70	4.15,		5.11,	4.90-5.10		
						4.85		5.12				
								5.15				
N <sup>2+</sup>	Aniline	<i>b, c</i>	4.41	4.25-4.40	5.30	5.20-5.35	6.22,	6.20-6.35				
							6.23					
	Pyrrrole	<i>b, g</i>	5.12	5.10-5.20	5.47	5.35-5.60						
	Indole	<i>b</i>	2.38		3.97	4.25-4.35	4.50	4.55-4.70	5.28	5.55-5.80		
O <sup>+</sup>	<i>o</i> -Benzoquinone	<i>h</i>	2.79	2.40-2.55	3.87	3.60-3.90	5.22	5.00-5.30				
	<i>p</i> -Benzoquinone	<i>c, h</i>	2.71	2.70-2.80	4.07	4.25-4.40	5.67	5.10-5.35				
	Benzaldehyde	<i>b</i>		3.65-3.85	4.34	4.30-4.50	4.97	4.90-5.15	5.94	5.75-5.90		
O <sup>2+</sup>	Phenol	<i>b, c</i>	4.61	4.50-4.65	5.64	5.50-5.75						
	Hydroquinone	<i>b, i</i>	4.58	4.15-4.30	5.60	5.45-5.60						
	Furan	<i>b, j</i>	4.71	4.40-4.60	5.67	5.60-5.80						
F <sup>2+</sup>	Fluorobenzene	<i>b</i>	4.62	4.65-4.80	5.67	5.80-5.90						
	$\alpha$ -Fluoro- naphthalene	<i>k</i>	3.95	3.90-4.00	4.34	4.30-4.50						
	$\beta$ -Fluoro- naphthalene	<i>k</i>	3.95	3.90-4.05	4.34	4.30-4.50						
Mixed	<i>p</i> -Aminopyridine	<i>l</i>	4.36	4.35-4.50	5.10	4.95-5.15						
	Benzoic acid	<i>b, j</i>	3.84		4.42	4.40-4.60	5.16	5.35-5.55	6.11,	6.15-6.30		
									6.20			
	Nitrobenzene	<i>b</i>	4.49,	4.65-4.85	5.26	5.70-5.85	6.01,	6.10-6.30				
			4.56				6.20					
	<i>p</i> -Nitroaniline	<i>m</i>	4.37,	4.10-4.30	5.76	5.40-5.65						
			4.53									
<i>p</i> -Nitrophenole	<i>m</i>	4.48,	3.85-4.15	5.19	5.25-5.60	5.94,	6.20-6.35					
		4.55				6.16						

<sup>a</sup> L. C. Jones, Jr., and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955). <sup>b</sup> J. R. Platt, "Systematics of Electronic Spectra of Conjugated Molecules," Wiley, New York, N. Y., 1964. <sup>c</sup> R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, N. Y., 1951. <sup>d</sup> E. K. Jensen, E. Kovats, A. Eschenmoser, and E. Heilborner, *Helv. Chim. Acta*, **39**, 1051 (1956). <sup>e</sup> A. Pullman, *et al.*, *J. Chim. Phys. Physicochim. Biol.*, **48**, 359 (1951). <sup>f</sup> R. Müller and F. Dorr, *Z. Elektrochem.*, **63**, 1150 (1959). <sup>g</sup> S. Menezel, *Z. Phys. Chem.*, **125**, 161 (1927). <sup>h</sup> L. Horner and H. Lang, *Chem. Ber.*, **89**, 2768 (1956). <sup>i</sup> J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **37**, 1294 (1959). <sup>j</sup> "UV Atlas of Organic Compounds," Plenum Press, New York, N. Y., 1966. <sup>k</sup> T. Iredale and J. W. White, *Trans. Faraday Soc.*, **56**, 1719 (1960). <sup>l</sup> P. Grammaticakis, *Bull. Soc. Chim. Fr.*, 480 (1959). <sup>m</sup> L. Lang, Ed., "Absorption Spectra in the Ultraviolet and Visible Region," Academic Press, New York, N. Y., 1965.

It is clear that if a parameter scheme can be tailored so as to yield better results for a particular small class of compounds, the discrepancies for compounds outside this class would then surely be larger. In addition to the transition energies, we have also computed the transition moments, using the point-dipole approximation. The results obtained correlate rather well with the observed molar extinction coefficients. This permitted a less ambiguous assignment of computed and observed transition energies. Besides the results reported here, we computed the spectra of 40 more hydrocarbons and azines, and the results obtained agreed equally well with the observed spectra as did those reported here. We will report on these results in the future, with an attempt at detailed spectral assignments.

**Results for Proton Isotopic Hyperfine Coupling Constants.** It is clear that within the PPP method the proton hyperfine coupling constant, which depends on the electron spin probability at specific protons, cannot be obtained directly. The protons are generally located in the molecular plane where the  $\pi$ -electron wave function, which is the part of the electronic wave function considered explicitly, has a nodal plane. It is expected, however, that the proton hyperfine coupling constants,  $a_H$ , observed in esr spectra, correlate well with  $\rho_{C\pi}$ , the electron spin density in the  $\pi$  orbital of the carbon atom, to which the specific hydrogen atoms are bonded. This is generally known as the McConnell relation<sup>8</sup>

$$a_H = Q\rho_{C\pi}$$

(8) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

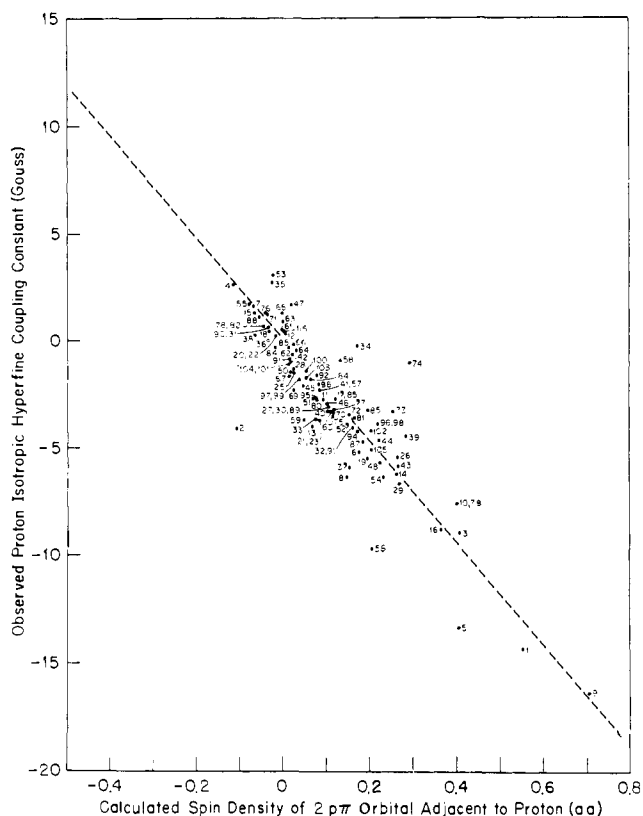
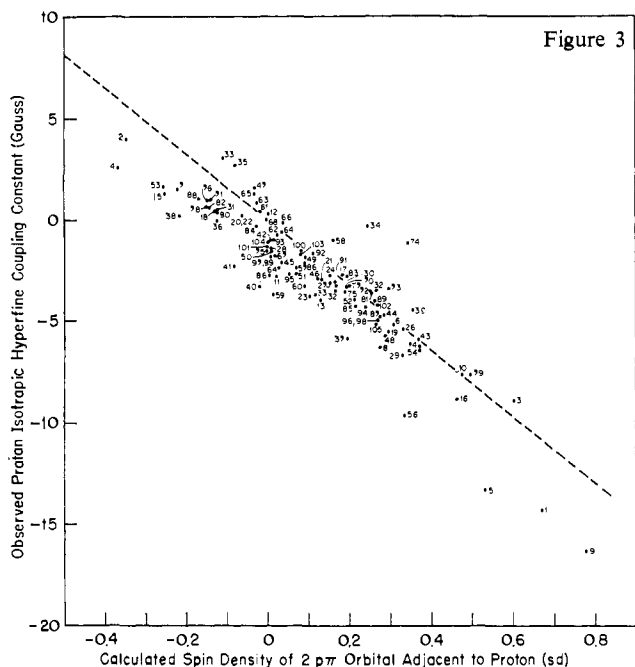


Figure 4. Observed proton isotropic hyperfine coupling constant vs. calculated  $2p\pi$  orbital spin density (aa = after annihilation of quartet contamination). Dotted line is linear-least-squares correlation line, constrained to origin. Key to Figure 3 applies also to Figure 4.

which can be justified theoretically.<sup>9</sup> Therefore, the calculated spin densities of the carbon atoms are correlated with the observed proton isotropic hyperfine coupling constants of the corresponding hydrogen atoms (see Figures 3 and 4).

(9) H. M. McConnell, *J. Chem. Phys.*, **28**, 1188 (1958).

Figure 3. Observed proton isotropic hyperfine coupling constant vs. calculated  $2p\pi$  orbital spin density (sd = single determinant). Dotted line is linear-least-squares correlation line, constrained to origin. Key: (1) allyl radical, 1 position;<sup>10</sup> (2) allyl radical, 2 position;<sup>10</sup> (3) pentadienyl radical, 1 position;<sup>10</sup> (4) pentadienyl radical, 2 position;<sup>10</sup> (5) pentadienyl radical, 3 position;<sup>10</sup> (6) benzyl radical, 2 position;<sup>11</sup> (7) benzyl radical, 3 position;<sup>11</sup> (8) benzyl radical, 4 position;<sup>11</sup> (9) benzyl radical, 7 position;<sup>11</sup> (10) *trans*-butadiene radical anion, 1 position;<sup>12</sup> (11) *trans*-butadiene radical anion, 2 position;<sup>12</sup> (12) azulene radical anion, 1 position;<sup>12</sup> (13) azulene radical anion, 2 position;<sup>12</sup> (14) azulene radical anion, 4 position;<sup>12</sup> (15) azulene radical anion, 5 position;<sup>12</sup> (16) azulene radical anion, 6 position;<sup>12</sup> (17) diphenyl radical anion, 2 position;<sup>13</sup> (18) diphenyl radical anion, 3 position;<sup>13</sup> (19) diphenyl radical anion, 4 position;<sup>13</sup> (20) biphenylene radical anion, 1 position;<sup>14</sup> (21) biphenylene radical anion, 2 position;<sup>14</sup> (22) biphenylene radical cation, 1 position;<sup>15,16</sup> (23) biphenylene radical cation, 2 position;<sup>15,16</sup> (24) anthracene radical anion, 1 position;<sup>17,18</sup> (25) anthracene radical anion, 2 position;<sup>17,18</sup> (26) anthracene radical anion, 9 position;<sup>17,18</sup> (27) anthracene radical cation, 1 position;<sup>17,18</sup> (28) anthracene radical cation, 2 position;<sup>17,18</sup> (29) anthracene radical cation, 9 position;<sup>17,18</sup> (30) perylene radical anion, 1 position;<sup>17,18</sup> (31) perylene radical anion, 2 position;<sup>17,18</sup> (32) perylene radical anion, 3 position;<sup>17,18</sup> (33) dibenzobiphenylene radical cation, 1 position;<sup>14</sup> (34) dibenzobiphenylene radical cation, 5 position;<sup>14</sup> (35) *m*-dinitrobenzene, 2 position;<sup>19</sup> (36) pyridazine radical anion, 3 position;<sup>20</sup> (37) pyridazine radical anion, 4 position;<sup>20</sup> (38) *s*-tetrazine radical anion, 3 position;<sup>21</sup> (39) *m*-dinitrobenzene, 4 position;<sup>19</sup> (40) 1,4-diazanaphthalene radical anion, 2 position;<sup>22</sup> (41) 1,4-diazanaphthalene radical anion, 5 position;<sup>22</sup> (42) 1,4-diazanaphthalene radical anion, 6 position;<sup>22</sup> (43) phthalazine radical anion, 1 position;<sup>21</sup> (44) phthalazine radical anion, 5 position;<sup>21</sup> (45) phthalazine radical anion, 6 position;<sup>21</sup> (46) 1,5-diazanaphthalene radical anion, 2 position;<sup>20</sup> (47) 1,5-diazanaphthalene radical anion, 3 position;<sup>20</sup> (48) 1,5-diazanaphthalene radical anion, 4 position;<sup>24</sup> (49) phenazine radical anion, 1 position;<sup>20</sup> (50) phenazine radical anion, 2 position;<sup>20</sup> (51) 1,4,5,8-tetraazaanthracene radical anion, 2 position;<sup>22</sup> (52) 1,4,5,8-tetraazaanthracene radical anion, 9 position;<sup>22</sup> (53) dihydropyrazine radical cation, 2 position;<sup>23</sup> (54) phenoxy radical, 2 position;<sup>24</sup> (55) phenoxy radical, 3 position;<sup>24</sup> (56) phenoxy radical, 4 position;<sup>24</sup> (57) *p*-benzoquinone radical anion, 2 position;<sup>25,26</sup> (58) *o*-benzoquinone radical anion, 3 position;<sup>25,27,28</sup> (59) *o*-benzoquinone radical anion, 4 position;<sup>25,27,28</sup> (60) 1,4-naphthoquinone radical anion, 2 position;<sup>25</sup> (61) 1,4-naphthoquinone radical anion, 5 position;<sup>25</sup> (62) 1,4-naphthoquinone radical anion, 6 position;<sup>25</sup> (63) 9,10-anthraquinone radical anion, 1 position;<sup>25</sup> (64) 9,10-anthraquinone radical anion, 2 position;<sup>25</sup> (65) 9,10-phenanthrenequinone radical anion, 1 position;<sup>29</sup> (66) 9,10-phenanthrenequinone radical anion, 2 position;<sup>29</sup> (67) 9,10-phenanthrenequinone radical anion, 3 position;<sup>29</sup> (68) 9,10-phenanthrenequinone radical anion, 4 position;<sup>29</sup> (69) hydroquinone radical cation, 2 position;<sup>30</sup> (70) nitrobenzene radical anion, 2 position;<sup>31</sup> (71, 72) nitrobenzene radical anion, 4 position;<sup>31</sup> (73) 1-nitro-4-aminobenzene radical anion, 2 position;<sup>31</sup> (74) 1-nitro-4-aminobenzene radical anion, 3 position;<sup>31</sup> (75) 1-nitro-4-fluorobenzene radical anion, 2 position;<sup>32</sup> (76) 1-nitro-4-fluorobenzene radical anion, 3 position;<sup>32</sup> (77) 1-nitro-4-hydroxybenzene radical anion, 2 position;<sup>33</sup> (78) 1-nitro-4-hydroxybenzene radical anion, 3 position;<sup>33</sup> (79) *cis*-butadiene radical anion, 1 position;<sup>12</sup> (80) *cis*-butadiene radical anion, 2 position;<sup>12</sup> (81) phenanthrene radical anion, 1 position;<sup>34</sup> (82) phenanthrene radical anion, 2 position;<sup>34</sup> (83) phenanthrene radical anion, 3 position;<sup>34</sup> (84) phenanthrene radical anion, 4 position;<sup>34</sup> (85) phenanthrene radical anion, 9 position;<sup>34</sup> (86) pyrene radical anion, 1 position;<sup>16</sup> (87) pyrene radical anion, 3 position;<sup>16</sup> (88) pyrene radical anion, 4 position;<sup>16</sup> (89) perylene radical cation, 1 position;<sup>17,18</sup> (90) perylene radical cation, 2 position;<sup>17,18</sup> (91) perylene radical cation, 3 position;<sup>17,18</sup> (92) dibenzobiphenylene radical anion, 1 position;<sup>14</sup> (93) dibenzobiphenylene radical anion, 2 position;<sup>14</sup> (94) dibenzobiphenylene radical anion, 5 position;<sup>14</sup> (95) pyrazine radical anion, 2 position;<sup>35</sup> (96) naphthalene radical anion, 1 position;<sup>13</sup> (97) naphthalene radical anion, 2 position;<sup>13</sup> (98) naphthalene radical cation, 1 position;<sup>13</sup> (99) naphthalene radical cation, 2 position;<sup>13</sup> (100) tetracene radical anion, 1 position;<sup>13</sup> (101) tetracene radical anion, 2 position;<sup>13</sup> (102) tetracene radical anion, 5 position;<sup>13</sup> (103) tetracene radical cation, 1 position;<sup>13</sup> (104) tetracene radical cation, 2 position;<sup>13</sup> (105) tetracene radical cation, 5 position.<sup>13</sup>

It is well known that PPP calculations within the restricted SCF frame, *i.e.*, each spatial orbital occupied with spin- $\alpha$  and spin- $\beta$  electrons except on singly occupied orbitals, cannot yield negative spin densities. It is therefore necessary to resort to an unrestricted SCF formalism, as outlined above, if spin densities at the carbon atoms are to be computed in a more realistic manner. It is well known also that unrestricted SCF functions are not eigenfunctions of the  $S^2$  operator. Thus the wave functions which are obtained directly by solving eq 10 will in general not represent pure doublet states as they should for the radicals and positive and negative ions considered here. In principle, it is possible to project out the components of the wave function which corresponds to states of higher multiplicity. This, however, is rather arduous, and it is in general sufficient to annihilate the next higher multiplicity component, here a quartet. This is so because the higher spin components are in general only small contaminations of the wave functions, which in our case are in general of more than 98% doublet character. It should in general not be expected that the projected wave function or the function with the dominant contamination, here the quartet, annihilated yield a more true representation of the electron or spin distribution. Because the orbitals of the projected function were obtained by solving eq 10, in which the electron interaction potential is obtained from the unprojected total wave function, the projected or annihilated functions are in general no longer self-consistent functions. In addition, the generation of wave functions which are eigenfunctions of  $S^2$  from the unrestricted SCF function is necessarily arbitrary. The mechanical procedures of projection or annihilation do not always yield functions which give a potential in the SCF equations which is most closely related to the potential used when solving the SCF equations. Thus, the unrestricted SCF functions are afflicted with inadequacies if used directly or after projection or annihilation of the contaminating spin components. Fortunately, these inadequacies are in general not serious, since the contribution of high-spin components to the unrestricted SCF functions is rather small. Inspection and statistical evaluation of the correlations in Figures 3 and 4 show that the correlation of experimental and computed results before

and after annihilation of quartet states is equally good. For the spin-density proton hyperfine coupling constant correlation derived from a single determinantal function (Figure 3)<sup>10-35</sup> the slope is  $Q = -17.09$ , and the standard error is 1.05 G, while for the function after quartet annihilation (Figure 4)<sup>10-35</sup> the slope is  $Q = -23.66$ , with the standard error 0.84 G. Thus we conclude that our parameter scheme is adequate to reliably yield proton hyperfine coupling constants within the unrestricted SCF frame of the PPP approximation and the McConnell relation. It may be concluded further that a projection or annihilation of contaminating high multiplicity in the wave function is unnecessary labor if esr spectral data are to be correlated or predicted.

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