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Calculations of Ground- and Excited-State Potential Surfaces for Conjugated Heteroatomic Molecules

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Abstract: The QCFF/PI method is extended to conjugated heteroatomic molecules. The extension is based on a new formalism for σ–π separability which starts from the all-valence-electron Hamiltonian, fixes the σ-electron charge distribution, and introduces it as an effective potential in the Hamiltonian of the σ electrons. The semiempirical parameters are obtained by fitting calculated and observed atomization energies, ionization energies, excitation energies, equilibrium geometries, dipole moments, and vibrational frequencies of nitrogen- and oxygen-containing conjugated molecules. The method provides a useful tool for calculating equilibrium conformations, electronic spectra, and resonance Raman spectra of large biological chromophores and for studying the effect of solvent or protein environments on such properties.

I. Introduction

Conjugated molecules containing nitrogen and oxygen "heteroatoms" are important parts of most biological chromophores, including such molecules as porphyrins, chlorophylls, nucleic acids, retinal, and flavins. Detailed theoretical studies of such systems might help in understanding more deeply the mechanism of important biological processes. Thus, for example, there is currently significant interest in interpretation of resonance Raman (RR) spectra of biological molecules,[1-3] in the effect of proteins on the absorption spectra of their prosthetic groups,[4-6] and in the factors that control electron transfer in proteins.[7,8] Studies of such problems require methods capable of reliable evaluation of ground- and excited-state equilibrium geometries and vibrational frequencies. Such methods should be flexible enough to allow incorporation of the effects of solvent and/or protein environment. While ab initio quantum mechanical approaches can treat small heteroatom molecules, they are too expensive to be used for detailed studies of large conjugated molecules. It is possible to use all-valence-electron semiempirical approaches (e.g., extended Hückel,[9] CNDO,[10-12]INDO,[13] PCILO,[14] PRDDO,[15] and MINDO[16]). However, although very promising and very useful in many cases, these methods have not been developed to the degree of reliability and efficiency needed for calculations of ground- and excited-state equilibrium geometries and vibrational frequencies of large molecules. The other possibility is to assume σ–π separability and represent the σ potential surface by empirical potential functions and the π-electron potential surfaces by a semiempirical approach. Many calculations of these types have been performed (see, for example, ref 17 and 18) and considerable success has been achieved in evaluation of electronic properties of rigid molecules. In general, the potential surfaces provided by these methods do not allow detailed conformational and vibrational studies.

A possible approach for detailed studies of large conjugated molecules is the quantum mechanical extension of the consistent force field to conjugated molecules (QCFF/PI).[19-21] This method is based on a formal separation of σ and π electrons, with the former represented by analytical empirical potential functions and the latter by a second-order analytical representation of a semiempirical model of the Pariser–Parr–Pople type corrected for orbital overlap. The method provides both ground- and excited-state potential surfaces for large conjugated molecules, allowing one to evaluate many molecular properties including equilibrium geometries, vibrational frequencies, and resonance Raman intensities.[20] In view of the previous success of the QCFF/PI method in treating conjugated hydrocarbons, it seems quite natural to extend this method to conjugated heteroatomic molecules. The basic problem is that in heteroatom systems the σ-electron core is no longer constant; the changes in the σ charges strongly influence the local potentials of the π electrons. Thus, in order to retain the advantages of the QCFF/PI approximation one must reformulate the σ–π separability approach. This is done here using a new approach based on a formal all-valence-electron treatment in which the σ-electron densities are evaluated empirically and constitute the core potential for the π-electron calculations, while the back polarization of the σ electrons by the π electrons is neglected.

Section II describes the reformulation of the σ–π separability approximation, Section III considers the refinement of the energy parameters for heteroatomic molecules and compares the final refined set of calculated properties with observed properties. Section IV describes several applications of the method including calculations of resonance Raman spectra of porphyrins and environmental effects on absorption spectra of chromophores in proteins.

II. Theoretical Approach

(a) Reformulation of the σ–π Separability Approximation. In the case of conjugated hydrocarbons the QCFF/PI potentials surface of the Nth electronic state is given by

$$V^N(\mathbf{r}) = V_\sigma^0(\mathbf{r}) + V_\pi^0(\mathbf{r}) + \Delta V_\pi^N(\mathbf{r}) \qquad (1)$$

where $\mathbf{r}$ is the Cartesian coordinate vector, $V_\sigma^0(\mathbf{r}) + V_\pi^0(\mathbf{r})$ is the sum of the σ- and π-electron energies for the gound state, and $\Delta V_\pi^N(\mathbf{r})$ is the π-electron[20] excited energy. The surface $V_\sigma(\mathbf{r})$ is represented by empirical potential functions. The evaluation of the π surface is based on a SCF–MO CI method.[20] In this method

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it is assumed that the σ-electron distribution is identical for all carbon atoms. Conjugated molecules with O and N heteroatoms require a more sophisticated approach since the σ electrons may be strongly polarized and this will alter the corresponding π-electron core potentials. In order to extend the QCFF/PI approach to heteroatom systems, we reformulated the π-electron treatment to include the interaction with the σ electrons while retaining the σ–π separability assumption. Our treatment is based on considering the all-valence-electron Hamiltonian, fixing the σ-electron distribution, and constructing an effective π-electron Hamiltonian. The starting LCAO wave function is given by

$$\Phi_n = \sum\nolimits_\mu v_{n\mu}{}^\pi \chi_\mu{}^\pi + \sum\nolimits_\mu v_{n\nu}{}^\sigma t_\nu{}^\sigma \tag{2}$$

where the $\chi_\mu{}^\pi$'s are $2p_z$ Slater atomic orbitals, and the $t_\nu{}^\sigma$'s are sp^2 hybrid σ orbitals. Following ref 19 we actually work with Löwdin orbitals. (The index λ is omitted for simplicity.) It is assumed formally that the t^σ and χ^π orbitals are orthogonal. The coefficients $\mathbf{v}_n{}^\pi$ and $\mathbf{v}_n{}^\sigma$ are obtained by solving the all-valence-electron SCF equation.

$$\mathbf{F}\mathbf{v}_n = \epsilon_n \mathbf{v}_n \tag{3}$$

The appropriate $\mathbf{F}$ matrix is of the following form:

$$\begin{vmatrix} \mathrm{F}^{\pi} & \mathrm{F}^{\pi\text{-}\sigma} \\ \mathrm{F}^{\pi\text{-}\sigma} & \mathrm{F}^{\sigma} \end{vmatrix} \tag{4}$$

The assumption of σ–π orthogonality implies that $\mathbf{F}^{\pi-\sigma} = \mathbf{0}$ and yields two sets of solutions to the SCF equation, $\mathbf{v}_n{}^\pi = (\mathbf{v}_n{}^\pi, \mathbf{0})$ and $\mathbf{v}_m{}^\sigma = (\mathbf{0}, \mathbf{v}_m{}^\sigma)$ (all the $\mathbf{v}_{n\nu}{}^\sigma$ are zero for $\Phi_n{}^\pi$ and all the $\mathbf{v}_{n\mu}{}^\pi$ are zero for $\Phi_n{}^\sigma$).

Assuming that the complete $\mathbf{F}$ matrix is treated with a CNDO-type all-valence-electron approximation, we obtain (in the notation of ref 11):

$$F_{\mu\mu} = U_{\mu\mu} + (P_A - \tfrac{1}{2}P_{\mu\mu})\gamma_{AA} + \sum_{B\neq A}^{\substack{\text{atoms with}\\ \pi\text{ electrons}}} (P_B\gamma_{AB} - V_{AB}) + \sum_{C\neq A}^{\substack{\text{atoms with only}\\ \sigma\text{ electrons}}} (P_C\gamma_{AC} - V_{AC}) \tag{5}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \tag{6}$$

where the μth orbital is attached to the Ath atom, U is the resonance integral, γ is the two-electron repulsive integral, V is the penetration integral, P is the bond order, and

$$P_A = \Big(\sum_{\nu}^{\substack{\text{all } \sigma \text{ orbitals}\\ \text{on A}}} P_{\nu\nu}\Big) + P_A{}^\pi = P_A{}^\pi + P_A{}^\sigma \tag{7}$$

Next, we modify $\mathbf{F}_{\mu\mu}{}^\pi$ to a form similar to the one used in π-electron calculations. This is done by the following: (i) defining for each atom a total core charge $\bar{Z} = Z^\pi + Z^\sigma$ as the number of valence electrons where Z^π is taken arbitrarily as 1 for C, O, and pyridine nitrogen and 2 for pyrrole-type nitrogen; (ii) defining the net σ and π charges by $Q_A{}^\sigma = (Z_A{}^\sigma - P_A{}^\sigma)$ and $Q_A{}^\pi = (Z_A{}^\pi - P_A{}^\pi)$, assuming Q^σ is constant (as implied by solving $\mathbf{F}^{\sigma-\sigma}$ first and then keeping the resulting π bond order constant); (iii) using the usual approximation $V_{AB} = Z_B\gamma_{AB}$, and defining $W_\mu = (U_{\mu\mu} + Z_A{}^\sigma\gamma_{AA})$. The diagonal element of $\mathbf{F}^\pi$ becomes

$$F_{\mu\mu}{}^\pi = [W_\mu - Q_A{}^\sigma\gamma_{AA}] + \Big[(P_A{}^\pi - \tfrac{1}{2}P_{\mu\mu})\gamma_{AA} - \sum_{B}^{\substack{\text{atoms with}\\ \pi\text{ electrons}}}{}' Q_B{}^\pi\gamma_{AB}\Big] - \Big[\sum_{B}^{\substack{\text{atoms with}\\ \pi\text{ electrons}}}{}' Q_B{}^\sigma\gamma_{AB} + \sum_{C}^{\substack{\text{atoms with}\\ \sigma\text{ electrons}}} Q_C{}^\sigma\gamma_{AC}\Big] \tag{8}$$

The off-diagonal elements of $\mathbf{F}^\pi$ are not modified.

Three different components are present in the final $F_{\mu\mu}$: (i) the "effective" core of a π electron on atom A which includes the Q^σ charge contribution, (ii) the usual π–π electron interaction term, and (iii) the contribution arising from the interaction between a π electron on atom A and the electric field generated by the "σ-core" charges of the surrounding atoms. Defining the "effective" core (W_μ) as $U_{\mu\mu} + Z_A{}^\sigma\gamma_{AA}$ is particularly useful for determining the parameters of different states of the same atomic species. For example, the nitrogen atom in pyrrole ($Z^\pi = 2$) and pyridine ($Z^\pi = 1$) compounds will have the same $U_{\mu\mu}$, but their core will differ by γ_{AA} because their values for Z^σ differ ($Z^\sigma = 4$ for pyridine; $Z^\sigma = 3$ for pyrrole).

In the present approximation the total energy can be expressed as:

$$E = \sum_A E_A + \sum_{A>B} E_{AB} \tag{9}$$

where E_A and E_{AB} are given by:

$$E_A = P_A{}^\pi(W_\mu - \tfrac{1}{2}Q_A{}^\sigma\gamma_{AA}) + \tfrac{1}{4}(P_A{}^\pi)^2\gamma_{AA} + E_A{}^\sigma \tag{10}$$

$$E_{AB} = \sum_\mu\sum_\nu [2P_{\mu\nu}{}^\pi\beta_{\mu\nu} - \tfrac{1}{2}(P_{\mu\nu}{}^\pi)^2\gamma_{AB}] + (Q_A{}^\pi + Q_A{}^\sigma)(Q_B{}^\pi + Q_B{}^\sigma)\gamma_{AB} + E_{AB}{}^\sigma$$

μ and ν are on atoms A and B, respectively, and the terms $E_A{}^\sigma$ and $E_{AB}{}^\sigma$ are defined as

$$\begin{aligned} E_A{}^\sigma &= \sum_{\mu}^{\substack{\sigma\text{ orbitals}\\ \text{on A}}} P_{\mu\mu}{}^\sigma U_{\mu\mu} + \tfrac{1}{2} \sum_{\mu}^{\substack{\sigma\text{ orbitals}\\ \text{on A}}} \sum_\nu (P_{\mu\mu}{}^\sigma P_{\nu\nu}{}^\sigma - \tfrac{1}{2}(P_{\mu\nu}{}^\sigma)^2)\gamma_{AA} \\ E_{AB}{}^\sigma &= \sum_{\mu}^{\substack{\sigma\text{ orbitals}\\ \text{on A}}} \sum_{\nu}^{\substack{\sigma\text{ orbitals}\\ \text{on B}}} (2P_{\mu\nu}{}^\sigma\beta_{\mu\nu} - \tfrac{1}{2}(P_{\mu\nu}{}^\sigma)^2\gamma_{AB}) \end{aligned} \tag{11}$$

These terms represent the energy due to the σ- electron interaction. This energy is absorbed in the empirical potential functions of the σ- potential surface.

(b) QCFF/PI Calculations for Heteroatom Systems. Using the formulation of the previous section, we perform the π-electron calculation by assigning a set of fixed σ charges (that depend only on the bonding topology) and solving the SCF equation:

$$\mathbf{F}^\pi\mathbf{v}^\pi = \epsilon\mathbf{v}^\pi \tag{12}$$

The $\mathbf{F}^\pi$ matrix elements (eq 6 and 8) are given as

$$\begin{aligned} F_{\mu\mu}{}^\pi &= \bar{W}_\mu + (P_A{}^\pi - \tfrac{1}{2}P_{\mu\mu})\gamma_{AA} - \sum_B{}' \bar{Q}_B\gamma_{AB} \\ F_{\mu\nu}{}^\pi &= \beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \end{aligned} \tag{13}$$

where $\bar{W}_\mu = W_\mu - K^W Q_A{}^\sigma\gamma_{AA}$, $\bar{Q} = Q^\pi + Q^\sigma$, B runs over all atoms, and Q^π is zero for atoms without π electrons. γ_{AB} for interaction of π atoms with σ atoms is taken as e^2/r. K^W in $\bar{W}_\mu$ is a screening parameter ($K^W \leq 1$) needed for simultaneous fitting of dipole moments and ionization potentials (see below). The functional form of the integrals W_μ, β, and γ are the same used in ref 19.

The π-electron ground-state potential surface is given by eq 9 and 10, which can be rewritten as:

$$V_\pi{}^0(\mathrm{r}) = \sum_A [P_A{}^\pi(W_\mu - \tfrac{1}{2}Q_A{}^\sigma\gamma_{AA}) + \tfrac{1}{4}(P_A{}^\pi)^2\gamma_{AB}] + \sum_{A>B}\sum_\mu\sum_\nu [2P_{\mu\nu}{}^\pi\beta_{\mu\nu} - \tfrac{1}{2}(P_{\mu\nu}{}^\pi)^2\gamma_{AB}] + \sum_{A>B} \bar{Q}_A\bar{Q}_B\gamma_{AB} + \sum_{A,C} [\bar{Q}_A Q_C{}^\sigma]e^2/r_{AC} \tag{14}$$

where A and B run over π atoms and C runs over σ atoms. The last term represents the electrostatic interaction between atoms with π electrons (A) and atoms without π electrons (C). the bond orders, $P_A{}^\pi$, and the π charges, $Q_A{}^\pi$, are evaluated by solving eq 12.

The σ-electron potential surface is given by:

$$V_\sigma{}^0(\mathbf{r}) = \sum_i M(b_i) + \tfrac{1}{2}\sum_i [K_a(a_i - a_0)^2 + 2D_i] + \tfrac{1}{2}\sum_i K_\theta(\theta_i - \theta_0)^2 + \tfrac{1}{2}\sum_i F(q_i - q_0)^2 + \tfrac{1}{2}\sum_i K_\phi{}^{(1)} \cos\phi_i + \tfrac{1}{2}\sum K_\phi{}^{(2)} \cos 2\phi_i + \tfrac{1}{2}\sum_i K_\chi(\chi_i - \chi_0)^2 + \sum_{i>j} f(r_{ij}) + \sum_{k>l} (Q_k{}^\sigma Q_l{}^\sigma)e^2/r_{kl} \tag{15}$$

where M is a Morse potential function, b_i are bond lengths between atoms with π electrons, and the a_i are bond lengths between pairs of atoms which include at least one atom without π electrons. θ_i, ϕ_i, and χ_i are respectively bond angles, torsion angles, and out-of-plane angles (see ref 20), q_i are the 1–3 nonbonded distances, while r_{ij} are nonbonded distances between atoms separated by more than one atom. The nonbonded function $f(r_{ij})$ is the exp-6 function

Table I. Parameters for π-Electron Integrals[a]

λ_W

atom	W^0, eV	β', eV	Z^π	Z^σ	K^W
N	−31.60	0.10	2	3	1.0
N^P	−17.39	0.20	1	4	0.8
O	−18.88	0.20	1	5	0.8
C^P	−10.47	0.20	1	3	1.0

λ_β

atom pairs	β^0, eV	μ_β, Å^{-1}	K_β, Å^{-1}	ϵ_T	$b_0{}^1$, Å
C^P N	−2.400	1.954	0.1039	−0.20	1.397
C^P N^P	−2.465	1.728	0.8884	−0.20	1.397
C^P O	−2.450	2.700	2.8000	0.0	1.230
N N^P	−2.400	1.700	0.4054	−0.20	1.397
N^P N^P	−2.400	1.700	0.4054	−0.20	1.397

λ_γ

atom pairs	$(\overline{\text{I-A}})$, eV	G_0, eV	G_S, eV	μ_γ, Å^{-1}
C^P N	12.70	11.00	0.3	0.45
C^P N^P	12.70	11.68	0.6	0.07
C^P O	13.50	8.00	0.6	0.43
N N	16.00	11.0	0.6	0.24
O O	17.64	10.0	0.0	0.35

[a] The functional form of the integrals W, β, and γ as well as the notation of their different parameters is the same as in ref 20. The parameters for C^P C^P are given in ref 20. I–A is taken as the average of the I–A of the corresponding isolated atoms. Unsaturated carbons are designated by C^P, pyrrole-like nitrogen (-NH-) by N, pyridine-like nitrogen (-N-) by N^P. K^W is the screening parameter in $\overline{W}$ ($\overline{W} = W - K^W Q_A{}^\sigma \gamma_{AA}$).

used in ref 20. The last term represents the electrostatic interaction between all pairs of atoms which have no π electrons (these include bonded atoms). The term E_A of eq 10 is not included as an atomic constant since it is effectively absorbed in the corresponding Morse potentials.

The treatment of excited π potential surfaces is identical with that for hydrocarbon molecules,[19] where the excitation energy $\Delta V_\pi{}^N(\mathbf{r})$ (eq 1) is obtained by the standard SCF–CI treatment using the modified $\mathbf{F}^\pi$ matrix of eq 13. Note that the present treatment does not evaluate n → π^* transitions.

The applications of the QCFF/PI potential surfaces to calculations of ground- and excited-state equilibrium geometries and vibrational frequencies are described in detail elsewhere.[19,20] Here we apply the same procedure to the potential surfaces of conjugated heteroatomic molecules.

(c) Potential Parameters. The parameters of the π-electron integrals and the σ-potential functions are given in Tables I and II, respectively. These parameters were obtained by extensive least-squares fits of different calculated and observed properties (see next section). In addition to the above parameters the present treatment requires the σ core charges (Q^σ). These charges can be evaluated by an all-valence-electron approach. Here we evaluate the σ charges by the method proposed by Del Re.[22] In this method the net σ-charge on atom A is given by

$$Q_A = \sum_B q_A{}^{(B)} \tag{16}$$

where B runs on all atoms connected to A and $q_A{}^{(B)}$ is the charge on atom A resulting from an A–B covalent bond. $q_A{}^{(B)}$ is defined by

$$q_A{}^{(B)} = D_A{}^{(B)}(1 + (D_A{}^{(B)})^2)^{-1/2} \tag{17}$$

where

$$D_A{}^{(B)} = (\delta_B - \delta_A)/(2\epsilon_{AB})$$

The δ_A's are computed by solving the following set of linear equations (for all atoms in the molecule)

$$\delta_A = \delta_A{}^0 + \sum_B \delta_B \bar{\gamma}_{AB} \tag{18}$$

Table II. Parameters for the σ Potential Functions[a]

bond	D	α	$^1/_2K_b$	b_0
C^P-N	65.0	2.10		1.340
C-N	88.0		88.0	1.450
C^P-N^P	65.0	2.00		1.255
N-H	93.0		414.0	1.000
N-N^P	40.0	2.90		1.309
N^P-N^P	35.0	2.67		1.360
C^P-O	75.0	1.80		1.235

bond angle	$^1/_2K_\theta$	θ_0	$^1/_2F$	q_0
C^PC^PN	58.3	2.094	32.4	2.56
C^PNC^P	58.3	2.094	32.4	2.56
C^PNH	24.0	2.094	29.5	2.18
NC^PH	24.0	2.094	29.5	2.18
N^PC^PH	24.0	2.094	29.5	2.18
$N^PC^PC^P$	52.8	2.094	29.5	2.56
$C^PN^PC^P$	52.8	2.094	29.5	2.56
NC^PN^P	52.8	2.094	32.4	2.74
$N^PC^PN^P$	52.8	2.094	32.4	2.74
$C^PN^PN^P$	52.8	2.094	32.4	2.56

torsion	$^1/_2K_\phi$	torsion	$^1/_2K_\phi$
X-C^P-N-X	7.80	X-N-N^P-X	6.50
X-C^P-N^P-X	5.73	X-N^P-N^P-X	5.73

out of plane	$^1/_2K_\chi$
N	3.0

nonbonded[b]	A	B	μ
HN	41 579	117	4.25
HO	12 786	79	4.19
CN	1 189 937	718	4.31
CO	395 890	573	4.28
NO	399 408	562	4.28

[a] Units used are: energies in kcal/mol, lengths in angstroms, angles to radians; force constants are expressed correspondingly. [b] The nonbonded potential functions used are $A\exp(-\mu r) - Br^{-6}$; the C–C and C–H parameters are as in ref 20. The nonbonded parameters for N and N^P are assumed to be equal.

Table III. Parameters for σ Charges[a]

	C	C^P	H	N	N^P	O
$\delta_A{}^0$	0.07	0.12	0.00	0.40	0.30	0.40

$\bar{\gamma}_{AB}$

	B					
A	C	C^P	H	N	N^P	O
C	0.1	0.1	0.4	0.1	0.1	0.1
C^P	0.1	0.1	0.4	0.1	0.1	0.1
H	0.3	0.3	0.1	0.3	0.3	0.3
N	0.1	0.1	0.4	0.1	0.1	0.1
N^P	0.1	0.1	0.4	0.1	0.1	0.1
O	0.1	0.1	0.4	0.1	0.1	0.1

$\epsilon_{A\text{-}B}$

	B				
A	C	C^P	H	N	N^P
C	1.0				
C^P	0.320				
H	1.000	1.00			
N	1.000	0.750	0.690		
N^P	1.000	0.700	0.450	0.500	
O	0.950	1.050	0.450	0.950	0.950

[a] Notation for atoms as in Table I.

The parameters $\delta_A{}^0$, $\bar{\gamma}_{AB}$, and ϵ_{AB} are given in Table III. These parameters were refined, together with all other energy parameters, by the least-squares fitting procedure.

(d) Possible Simplifications. The approach described in the previous sections, and used in the calculations reported in this paper, requires substantial modifications of the original QCFF/PI method. A less rigorous (and less reliable) treatment can be used in order to avoid modifications. It is possible to assign σ charges

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Table IV. Parameter Set for Simplified Calculations[a]

atom	$\overline{W}$	$\overline{Z}$	Q^σ
N	−15.1	0.90	−0.15
N^PH	−28.6	1.80	−0.20
O	−17.3	0.90	−0.10
C^P	−9.97	$1.0 + Q_C^\sigma$	(Q_C^σ)[b]

[a] All other parameters are taken without change from Tables I and II. [b] The σ charge of the carbon atoms is evaluated by taking $-Q^\sigma$ of the corresponding heteroatom and distributing it over the nearest neighboring carbon atoms. For example, in pyrrole the σ charge of C_5 and C_2 is $(0.2)/2 = 0.1$.

only on the basis of atom type, regardless of the bonding arrangement. In this case, the diagonal SCF matrix element are approximated by

$$\bar{W}_\mu = W_\mu - Q_A{}^\sigma\gamma_{AA} \qquad \bar{Q}_\mu{}^\pi = (\bar{Z}_\mu{}^\pi - P_A{}^\pi) \\ \bar{Z}_\mu{}^\pi = Z_\mu{}^\pi + Q_A{}^\sigma \tag{19}$$

This simplified treatment can be incorporated directly into the orginal QCFF/PI program.[21] The corresponding parameters are given in Table IV.

The π-electron energy surface in the simplified approach is given by:

$$V_\pi{}^0(\mathbf{r}) \simeq \sum_\mu P_{\mu\mu}[\bar{W}_\mu + {}^1\!/\!_4 P_{\mu\mu}\gamma_{AA}] + 2\sum_{\nu>\mu} P_{\nu\mu}\beta_{\mu\nu} - \\ \sum_{\nu>\mu}[{}^1\!/\!_2 P_{\mu\nu}{}^2 - \bar{Q}_\mu{}^\pi\bar{Q}_\nu{}^\pi]\gamma_{\mu\nu} + \sum_{\mu,C}\bar{Q}_\mu{}^\pi Q_C\, e^2/r_{\mu C} \tag{20}$$

This energy expression which (excluding the last term) is the one used in the original QCFF/PI program gives reasonable equilibrium energies and relative energies, but unreliable atomization energies for heteroatom systems.

In general the simplified approach is recommended for qualitative studies while the nonsimplified approach (which was used in all the studies reported here) is recommended for quantitative studies.

III. Determination of Semiempirical Parameters

Section II describes a procedure for calculating the total energy surface $V^N(\mathbf{r})$ (relative to the separated atoms) of a conjugated heteroatomic molecule in the Nth electronic state. Since the expression $V^N(\mathbf{r})$ involves a mixture of semiempirical concepts implemented in terms of rather complicated functions that depend on many parameters, the results can be regarded as meaningful only if they apply to a significant number of independent properties for a variety of molecules. Here we determine the parameters by the CFF least-squares procedure.[20,23] This method determines a set of parameters which yield satisfactory agreement between the calculated and experimental properties depending on the zeroth, first, and second derivative terms in a Taylor expansion of the potential energy surfaces of various molecules. The effectiveness of the procedure is based on the availability of analytic expressions for the potential energy and its first and second derivatives with respect to the atomic Cartesian coordinates (see ref 20 for more details). A large number of experimental data were employed in the fitting procedure. They include: ionization energies, excitation energies, atomization energies, dipole moments, equilibrium conformations, and vibrational frequencies of conjugated molecules containing nitrogen and/or C=O groups. The molecules included in this data base are shown in Figure 1. The next sections give additional information about the properties included in the least squares.

The nonbonded interaction parameters were determined by an independent procedure because the data included above are not sufficiently sensitive to these interactions. For C–H and C–C interactions we used the previous QCFF/PI parameters.[20] For interactions involving N and O we employ a modified form of the potential functions of ref 37; that is, these potentials were fitted by exp-6 potentials over a series of distances and orientations. This fitting involves a decrease of 0.1 Å in all the r^* of ref 37 to account for the difference between unit cell parameters at room temperature and at 0 K.

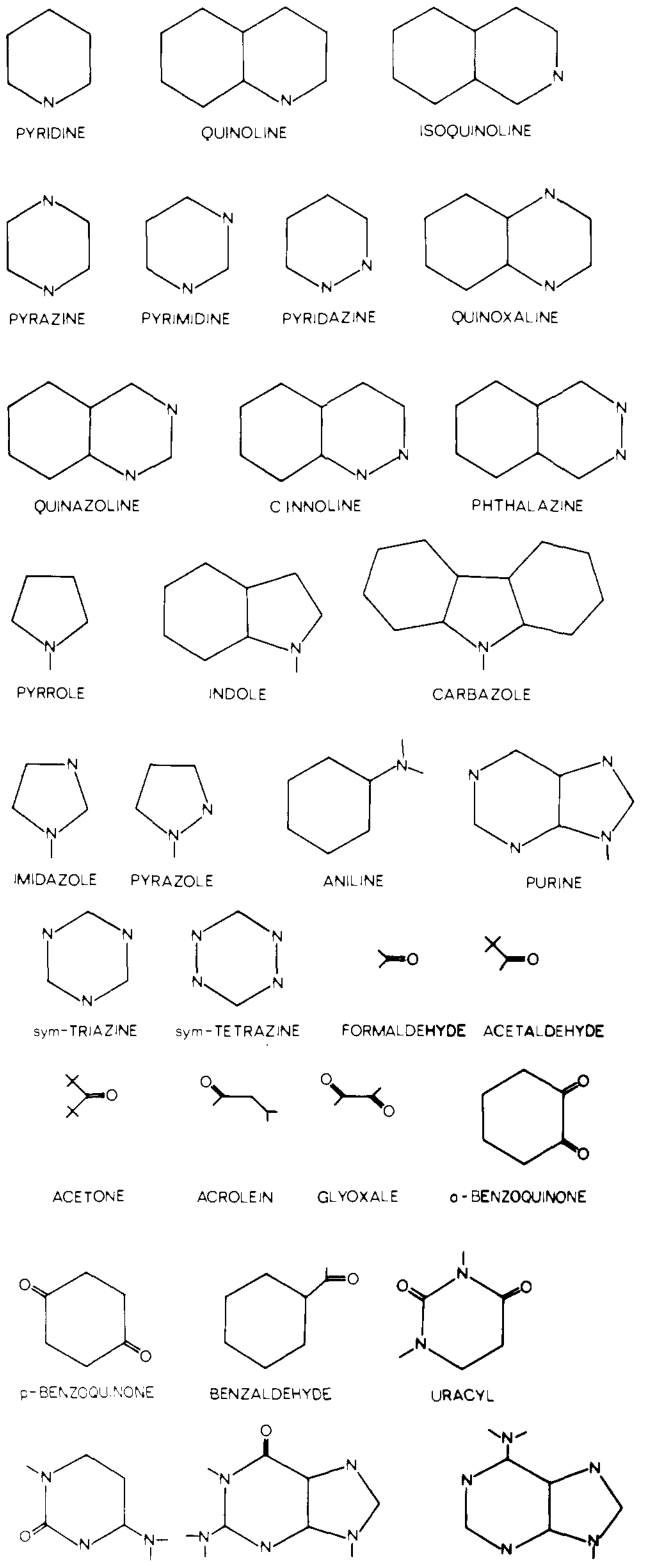

Figure 1. Molecular diagrams of the molecules included in the QCFF/PI refinement procedure.

(a) Ionization Energies. The calculated ionization energies (obtained in the last iteration of the least-squares procedure) and the corresponding experimental results are given in Table V. The agreement between the calculated and observed values is good, and all the deviations are smaller than 0.6 eV. In some cases (e.g., the first ionization of pyridine) there is a large range of experimental values for a given property. In such cases we assign a low

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(23) S. Lifson, and A. Warshel, *J. Chem. Phys.*, **49**, 5116 (1968).

Table V. Calculated and Observed Ionization Energies (in eV) Included in the Optimization of the QCFF/PF Parameters

compound	calcd	obsd	compound	calcd	obsd
pyridine	9.74	9.00,^{c} 9.28,^{b} 9.31,^{g} 9.70,^{d} 9.80^{a}	cinnoline	9.22	8.51,^{g,h} 8.95^{l}
	10.12	10.45,^{g} 10.5,^{a} 10.5^{c}		9.78	9.03^{g,h}
	12.93	12.30,^{g} 12.6^{a}		11.05	10.83,^{g,h} 9.75^{g}
quinoline	8.73	8.62,^{g} 8.67,^{m} 8.90^{d}		12.31	12.04,^{g,h} 10.83^{g}
	9.23	9.00,^{m} 9.07^{g}		14.00	13.85,^{g,h} 12.04^{g}
	10.67	10.63,^{m} 10.64^{g}	aniline	7.9	7.71^{b}
	11.60	11.37,^{m} 11.42^{g}		9.1	8.95^{b}
	13.22	13.07^{g}		10.9	10.49^{b}
isoquinoline	8.66	8.53,^{m} 8.54^{g}	formaldehyde	12.9	13.99,^{b} 14.09^{k}
	9.24	9.16,^{m} 9.24^{g}	acetaldehyde	12.6	12.75,^{b} 13.90^{b}
	10.52	10.32,^{m} 10.50^{g}	acetone	12.3	12.16,^{b} 14.15^{b}
	11.73	11.43,^{m} 11.60^{g}	acrolein	10.6	10.82,^{b} 10.93^{k}
	13.20	13.26^{g}		13.0	13.19,^{b} 13.20^{k}
pyrimidine	10.24	9.35,^{b} 9.42,^{g} 9.47,^{b} 9.91^{d}	glyoxal	12.6	12.19^{k}
	10.46	10.39,^{g} 10.39^{b}		14.1	13.85^{k}
	13.37	13.60,^{b} 13.62^{g}	*p*-benzoquinone	10.4	10.49^{k}
pyridazine	10.23	8.71,^{d} 8.90,^{g} 8.91,^{b} 9.86,^{d} 10.15^{c}		11.2	11.25^{k}
	10.79	10.53,^{b} 10.55^{b}		13.2	13.43^{k}
	13.85	13.59,^{b} 13.63^{g}	benzaldehyde	9.7	9.46,^{i} 9.51^{b}
quinazoline	9.73	9.02^{g}		9.9	
	10.99	10.72^{g}		12.2	11.48^{i}
	12.01	12.02^{g}	formamide	10.6	10.13^{k}
	13.61	13.78^{g}	pyrrole	8.57	8.20,^{b} 8.22,^{b} 8.23,^{o} 8.90,^{d} 8.97^{d}
quinoxaline	9.67	9.02^{g}		9.62	9.03,^{b} 9.22^{o}
	11.25	10.72^{g}		14.50	12.38,^{b} 14.70^{o}
	11.90	11.58^{g}	imidazole	9.06	8.78^{o}
	13.56	13.98^{g}		10.44	10.3^{o}
phthalazine	8.97	8.68,^{h} 8.68^{g}		14.64	14.7^{o}
	9.99	9.17,^{h} 9.17^{g}	pyrazole	9.09	9.15^{o}
	10.90	10.77,^{h} 9.68^{g}		9.67	9.88^{o}
	12.37	12.07,^{h} 10.77^{g}		14.88	14.70^{o}
	13.84	14.09,^{h} 12.07^{g}			
pyrazine	10.19	9.27,^{b} 9.29,^{d,e} 9.16,^{g} 9.62,^{f} 10.01^{d}			
	10.79	10.11,^{b} 10.15,^{g} 10.16^{d}			
	13.23	13.10,^{b} 13.13,^{g} 13.60^{f}			

[a] C. Batich, E. Heilbronner, V. Hornung, A. J. Ashe III, D. T. Clark, U. T. Cobely, D. Kilcast, and I. Scanlan, *J. Am. Chem. Soc.*, **95**, 928 (1973). [b] D. W. Turner, *Adv. Phys. Org. Chem.*, 4, 31 (1966). [c] M. N. Pisanias, L. G. Christophorou, J. G. Carter, and D. L. McCorkle, *J. Chem. Phys.*, **58**, 2110 (1973). [d] R. P. Blaunstein and L. G. Christophorou, *Radiat. Res. Rev.*, **3**, 69 (1971). [e] J. E. Parkin and K. K. Innes, *J. Mol. Spectrosc.*, **15**, 407 (1965). [f] J. H. D. Eland, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 471 (1969). [g] M. J. S. Dewar and S. C. Worley, *J. Chem. Phys.*, 51, 263 (1969). [h] M. Sundbom, *Acta Chem. Scand.*, **25**, 487 (1971). [i] K. Watanabe, *J. Chem. Phys.*, **25**, 542 (1957). [j] S. Cradock, R. H. Findlay, and M. H. Palmer, *Tetrahedron*, 29, 2173 (1973). [k] D. W. Turner, "Molecular Photoelectron Spectroscopy", Wiely, New York, 1970. [l] J. H. D. Eland and C. J. Danby, *Z. Naturforsch., Teil A*, **23**, 335 (1968). [m] A. J. Yencha and M. A. El-Sayed, *J. Chem. Phys.*, 48, 3469 (1968).

weight (P in eq 12 of ref 20) for the particular observable in the least-squares refinement procedure. In the case of cinnoline and phthalazine the calculations support the assignment of Sundbom[18] rather than that of Dewar and Worley.[24]

It appears that the high ionization potentials, which correspond to orbitals with major components on nitrogen atoms, are very useful in providing information about the corresponding W and γ. In order to obtain a reasonable fit of the calculated and observed values of these ionization energies, while retaining a reasonable agreement between the calculated and observed dipole moments, we had to introduce the screening parameter K^W (see Table I) for oxygen and pyridine nitrogen. This might reflect the effect of the lone-pair electrons.

It is encouraging to note that the carbonyl compounds reproduce nicely the experimental trend of the ionization potentials in formaldehyde, acetaldehyde, and acetone where the decrease in the energy of the occupied orbitals was reached by means of a purely σ charge effect. This effect is due to the σ charge donation from the methyl groups that make the unsatuated carbon progressively more negative, and therefore decrease its affinity to the π electrons.

(b) Excitation Energies. The refined calculated excitation energies and the corresponding observed values are given in Table VI. The table also compares the calculated and observed oscillator stengths. The agreement between the calculated and observed results for the nitrogen compound is quite satisfactory. The refinement procedure for the oxygen-containing compounds involved a large statistical weight for molecules with a single nonconjugated $C{=}O$ bond. This resulted in a significant discrepancy between the calculated and observed excitation energies of glyoxal. This inconsistency cannot be resolved in the present level of approximations.

(c) Atomization Energies. The calculated atomization energy is given by the difference between the molecular energy of eq 10 and the energies of the isolated atoms. The energy of an isolated atom does not include the term $E_A{}^\sigma$ of eq 10 since this term is incorporated in the Morse potential.

The refined set of atomization energies and the corresponding observed values are given in Table VII. The atomization energies depend strongly on the diagonal π bond orders which are very sensitive to the σ charges. As the σ charges are also important for the dipole moment and ionization energies, our fitting procedure represents a compromise. However, it should be noted that the present agreement between the calculated and observed atomization energies is similar to that obtained in all-valence-electron calculations.[12,16]

(d) Dipole Moments. The final set of calculated dipole moments and the corresponding observed values are given in Table VIII. A negative correlation was found between the calculated magnitude of the dipole moments and the calculated ionization energies. A similar but less pronounced behavior appears in the correlation between the calculated dipole moments and the calculated atomization and excitation energies. Thus, it appears that good calculated dipole moment could be obtained only at the expense of poorer agreement in other properties. Since our main

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(24) M. J. S. Dewar, and S. D. Worley, *J. Chem. Phys.*, **51**, 263 (1969).

Table VI. Calculated and Observed Excitation Energies (in eV) Included in the Refinement of the QCFF/PI Parameters (Oscillator Strength in Parentheses)

compound	calcd	obsd
pyridine	4.91 (0.02)	4.75-4.97 (0.04)^{a,i,l}
	5.93 (0.22)	6.17-6.37 (0.18)
	6.54 (1.03)	6.70-7.13 (0.66)
	6.93 (0.80)	7.10
quinoline	4.20 (0.04)	3.95 (0.02)^{f,l,p}
	4.60 (0.18)	4.46-4.62 (0.12)
	5.66 (1.71)	5.35-5.50 (0.54)
	5.82 (0.46)	6.08-6.11 (0.93
isoquinoline	4.26 (0.03)	3.86-4.03 (0.02)^{b,c,q,l}
	4.52 (0.26)	4.58-4.66 (0.11)
	5.64 (0.56)	5.35-5.39
	5.76 (1.13)	5.70-5.75 (1.02)
	5.92 (0.69)	5.86-6.32 (s)
pyrimidine	4.83 (0.00)	5.00-526 (0.05)^{a,d,l,m}
	6.12 (0.56)	6.45-6.71 (0.16)
	6.81 (1.04)	6.89-7.44 (0.43)
	6.99 (0.42)	7.25-7.68
pyrazine	5.30 (0.02)	4.49-4.93 (0.10)^{a,d,l,m}
	5.85 (0.24)	6.06-6.59 (0.14)
	6.87 (1.00)	7.15-7.67 (vs)
pyridazine	5.14 (0.00)	4.90-5.13 (0.02)^{a,d,m}
	5.01 (0.33)	6.15-6.67 (0.01)
	7.03 (0.41)	7.10-7.33 (1.0)
phthalazine	4.39 (0.00)	4.06-4.27 (0.01)^{b,q,r,s}
	4.79 (0.20)	4.64-4.78 (0.10)
	6.05 (1.56)	5.78-5.86 (1.18)
cinnoline	4.31 (0.01)	3.91-3.93^{l,t,x}
	4.33 (0.35)	4.37-4.65
	6.04 (1.97)	5.49-5.65
	6.42 (0.25)	6.28
quinazoline	4.20 (0.02)	3.99-4.05 (0.03)^{l,v}
	4.67 (0.27)	4.56-4.65 (0.09)
	5.66 (1.60)	5.58-5.66 (0.86)
	5.84 (0.06)	6.28 (0.84)
quinoxaline	4.34 (0.02)	3.90-3.95 (0.13)^{b,f,j}
	4.74 (0.17)	4.20-4.34 (0.13)
	5.74 (1.73)	5.30-5.44 (0.30)
	5.69 (0.69)	5.88-5.99
	6.31 (0.10)	6.36 (0.61)
sym-triazine	5.65 (0.40)	5.45-5.70^{b,e,n}
tetrazine	5.55 (0.04)	5.01^{o,u,w}
	5.84 (0.32)	6.47
pyrrole	5.73 (0.36)	5.70^{g}
	6.07 (0.00)	6.50
	7.47 (0.90)	7.10
indole	4.50 (0.05)	4.21-4.27^{j,x}
	5.00 (0.29)	4.40-5.71
	5.76 (0.84)	5.55-5.78
	6.17 (0.81)	5.69
	6.16 (0.12)	6.44
carbazole	4.58 (0.02)	3.71-4.24^{j,x}
	4.85 (0.33)	4.27-4.85
	5.31 (0.51)	4.81-5.29
	5.65 (1.23)	5.29-5.88
	5.73 (0.84)	5.95-6.15
	6.03 (0.02)	
imidazole	5.94 (0.36)	5.90^{w}
aniline	4.6 (0.05)	4.4 (0.33)^{k,gg}
	5.5 (0.18)	5.4 (0.14)
	6.2 (0.86)	6.3 (0.51)
	6.3 (1.05)	6.8 (0.57)
		7.8 (0.68)
purine	4.32 (0.17)	4.71^{bb,cc}
	5.31 (0.33)	5.10
	6.08 (1.00)	6.10
	6.24 (0.51)	6.60
formaldehyde	8.04 (0.47)	7.97^{z}
acetaldehyde	8.03 (0.47)	7.52^{z,ee,ff}
acetone	8.08 (0.47)	8.05^{aa}
acrolein	5.79 (0.67)	5.89^{z,hh}
glyoxal	6.41 (0.86)	7.44^{y}
benzaldehyde	4.53 (0.02)	4.52 (0.02)^{dd}
	5.15 (0.44)	5.35 (0.26)
	5.90 (0.55)	6.35 (1.7)
	6.22 (0.84)	6.68 (1.7)
	6.37 (0.18)	6.97 (1.7)
	7.12 (0.30)	7.50 (1.7)
p-benzoquinone	3.7 (0.00)	4.28 (0.01)^{h}
	4.6 (0.80)	5.17 (0.15)
o-benzoquinone	3.59 (0.2)	3.3 (0.66)^{h}
	5.29 (0.2)	4.9 (0.26)
	6.5 (0.9)	6.2 (s)
uracyl	5.25 (0.45)	4.70^{cc}
	6.14 (0.20)	5.10
	6.34 (0.35)	6.10
	6.81 (0.36)	6.80
cytosine	4.43 (0.17)	4.50^{cc}
	5.32 (0.07)	5.20
	6.16 (1.32)	6.10
	6.68 (0.23)	6.70
guanine	4.23 (0.54)	4.50^{cc}
	5.02 (0.33)	5.20
	6.01 (0.09)	6.00
	6.18 (0.00)	6.60
adenine	4.30 (0.26)	4.80^{cc}
	4.78 (0.20)	5.90
	5.69 (0.96)	6.70

[a] K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectrosc.*, **22**, 125 (1967). [b] H. Baba and I. Yamazaki, *J. Mol. Spectrosc.*, 44, 118 (1972). [c] J. E. Ridley and M. C. Zerner, *J. Mol. Spectrosc.*, 50, 457 (1974). [d] J. E. Parkin and K. K. Innes, *J. Mol. Spectrosc.*, 15, 407 (1965). [e] J. S. Brinen, R. C. Hirt, and R. G. Schmitt, *Spectrochim. Acta*, 18, 863 (1962). [f] R. W. Glass, L. C. Robertson, and J. A. Merritt, *J. Chem. Phys.*, **53**, 3857 (1970). [g] W. C. Price and A. D. Walsh, *Proc. R. Soc. London, Sci. A*, 179, 201 (1941). [h] L. Horner and H. Long, *Chem. Ber.*, 89, 2768 (1965). [i] L. W. Pickett, M. E. Corning, G. M. Wieder, D. A. Semenow, J. M. Buckley, *J. Am. Chem. Soc.*, 75, 1618 (1953). [j] H. V. Schutt and H. Zimmerman, *Ber. Bunsenges. Phys. Chem.*, 67, 54 (1963). [k] K. Kimura and S. Nagakura, *Mol. Phys.*, 9, 117 (1965). [l] G. Favini and I. R. Bellobono, *Rend. Ist. Lomb. Sci. Lett. A*, 99, 380 (1965). [m] M. N. Pisanias, L. G. Christophorou, J. G. Carter, D. L. McCorkle, *J. Chem. Phys.*, 58, 2110 (1973). [n] R. C. Hirt, F. Halverson, and R. G. Schmitt, *J. Chem. Phys.*, **22**, 1148 (1954). [o] G. H. Spencer, P. C. Cross, and K. B. Wiberg, *J. Chem. Phys.*, **35**, 1925 (1962). [p] N. Mataga, and S. Tsuno, *Bull. Chem. Soc. Jpn.*, 30, 368 (1957). [q] R. M. Hochstrasser and C. Marzzacco, *J. Chem. Phys.*, 48, 4079 (1968). [r] R. C. Hirt, F. T. King, and J. C. Cavagnoi, *J. Chem. Phys.*, **25**, 574 (1956). [s] R. Muller and F. Dorr, *Z. Elektrochem.*, 63, 1150 (1956). [t] S. C. Wait and F. M. Grogan, *J. Mol. Spectrosc.*, 24, 383 (1967). [u] G. A. Spencer, P. Cross, and K. B. Wiberg, *J. Chem. Phys.*, **35**, 1925 (1961). [v] A. R. Osborn, K. Schofield, and L. N. Short, *J. Chem. Soc.* 4191 (1956). [w] M. Gelus and J. M. Bonnier, *J. Chem. Phys.* 64, 1602 (1967). [x] H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, 17, 470 (1949). [y] A. D. Walsh, *Trans. Faraday Soc.*, 42, 66 (1946). [z] A. D. Walsh, *Trans. Faraday Soc.*, 41, 498 (1945). [aa] P. E. Stevenson, *J. Mol. Spectrosc.*, 17, 58 (1965). [bb] H. H. Chen and L. B. Clark, *J. Chem. Phys.*, 51, 1862 (1969). [cc] L. B. Clark and I. Tinoco, *J. Am. Chem. Soc.*, 87, 11 (1965). [dd] K. Kimura and S. Nagakura, *Theor. Chim. Acta*, 3, 164 (1965). [ee] A. D. Walsh, *Proc. R. Soc. London, Scr. A*, 185, 176 (1948). [ff] J. S. Lake and A. J. Harrison, *J. Chem. Phys.*, 30, 361 (1959). [gg] W. F. Forbes and I. R. Leckie, *Can. J. Chem.*, 36, 1371 (1958). [hh] W. F. Forbes and R. Shilton, *J. Am. Chem. Soc.*, 81, 786 (1959).

concern is in obtaining reliable potential surfaces, we gave a relatively small weight to the dipole moments in the least-squares fitting procedure. Yet, the agreement is similar to that obtained in all-valence-electron calculations.[16]

(e) Equilibrium Geometries. The refined calculated equilibrium geometries and the corresponding observed geometries are given in Table IX. The table includes only representative samples from each class of molecules. In general, the agreement is reasonable.

(f) Vibrational Frequencies. The least-squares refinement procedure includes the vibrational frequencies of pyridine and pyrrole. The refined calculated frequencies and the corresponding observed results are given in Table X. We will mention here

Table VII. Calculated and Observed Automization Energies (in kcal/mol) Included in the Optimization of the QCFF/PI Parameters[i]

compound	calcd	obsd
pyridine	1197.6	1194.3[a]
quinoline	1965.1	1964.3[b]
pyrimidine	1070.3	1071.0[c]
pyrazine	1072.0	1070.9[c]
pyridazine	1061.0	1051.3[c]
sym-triazine	970.1	965.7[f]
pyrrole	1027.0	1031.2[d]
carbazole	2584.0	2580.0[d]
indole	1803.0	1800.1[d]
imidazole	908.0	914.6[e]
pyrazole	902.3	905.3[e]
aniline	151.7	1481.0[h]
formaldehyde	369.3	364.6[g]
actaldehyde	641.0	649.4,[g] 695.3[f]
acetone	914.1	936.7[g]
acrolein	793.4	805.9[f]
glyoxal	620.1	615.1[g]
p-benzoquinone	1375.5	1382.2[b]
benzaldehyde	1569.7	1574.3[h]
formamide	520.0	544.2,[f] 561.3[f]

[a] J. D. Cox, A. R. Challoner, and A. R. Meetham, *J. Chem. Soc.*, 265 (1954). [b] G. W. Wheland, "Resonance in Organic Chemistry", Wiley, New York, 1955. [c] J. Tjebbes, *Acta Chem. Scand.*, 16, 916 (1962). [d] H. Zimmerman and H. Geisenfender, *Z. Elektrochem.*, 65, 368 (1961). [e] Based on heat of combustion given by Zimmerman and Geisenfender, footnote *d*. [f] Based on heat of formation at 25 °C given by G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969. [g] Based on the selected values of heat formation at 25 °C given by J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970. [h] S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965). [i] All the values reported are in kcal/mol and the calculated values were corrected for the vibrational enthalpies at 25 °C.

several points about the assignment: the vibrational spectra of pyridine was assigned previously by Corrsin et al.,[25] Kline and Turkevich,[26] Wilmshurt and Bernstein,[27] and McCullough et al.[28] For some frequencies the assignments are strikingly different. The QCFF/PI offers a possibility to reach more unique assignments since (a) the force constants are consistent with many properties and not only vibrational spectra, and (b) the calculation involves evaluation of infrared intensities.[20] This allows one to assign frequencies not only on the basis of symmetry but also on the basis of the agreement between the calculated and observed intensities. For the A_1 class the present assignment is consistent with that of Corrsin et al. except the line at 1139 cm^{-1} which is taken from Kline and Turkevich.[26] The assignment of this line is based on both the calculated frequency and the calculated intensity. The assignement of the B_1 and A_2 classes is the same as that of Corrsin et al. In the B_2 class the assignment of Corrsin et al. was modified where the 1043-cm^{-1} frequency (observed in the Raman spectrum of ref 25) was assigned as the highest frequency in this class. The very weak line at 675 cm^{-1} which is assigned by Corrsin et al. as a B_2 line might be a hot band (1375 − 703 = 672 cm^{-1}), since no weak intensity B_2 line is calculated for this region.

The vibrational spectrum of pyrrole was assigned by Lord and Miller,[29] Stern,[30] and Mirone.[31] There is significant descrepancy between the different assignments. Our assignment (based on calculated intensities, calculated frequencies, and examination of the deuterium effect) is somwhat different from that of ref 29.

Table VIII. Calculated and Observed Dipole Moments (in Debye) Included in the Optimization of the QCFF/PI Parameters

compound	calcd	obsd
pyridine	1.90	2.25[a]
quinoline	1.86	2.31[a]
isoquinoline	2.16	2.57[a]
pyrimidine	1.76	2.44[a]
pyridazine	3.82	3.97[b]
pyrrole	1.81	1.84[a]
indole	1.74	2.05[c]
carbazole	1.21	2.11[a]
imidazole	3.88	3.80[j]
pyrazole	2.64	2.21[a]
formaldehyde	2.95	2.34[d]
acetaldehyde	3.00	2.69[e]
acetone	3.60	2.90[g]
acrolein	3.51	3.11[f]
o-benzoquinone	5.41	5.1[h]
uracyl	4.47	5.18[k]
adenine	1.63	2.8[m]
benzaldehyde	3.55	3.0[a]
aniline	1.73	1.53[i]
purine	5.4	4.32[l]
cytosine	7.7	8.0[m]

[a] A. L. McClellan, in "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, 1963. [b] W. C. Schneider, *J. Am. Chem. Soc.*, 70, 627 (1948). [c] E. G. Cowley and J. R. Partington, *J. Chem. Soc.*, 47 (1936). [d] J. N. Shoolery and A. H. Sharbaugh, *Phys. Rev.*, 82, 95 (1951). [e] R. Kilb, C. C. Lin, and E. B. Wilson, *J. Chem. Phys.* 26, 1695 (1957). [f] R. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, *J. Chem. Phys.*, 26, 634 (1957). [g] J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, 31, 1562 (1959). [h] S. Nagakura and A. Kuboyama, *J. Am. Chem. Soc.*, 76, 1003 (1954). [i] C. W. N. Cumper, R. F. A. Ginman, D. G. Redford, and A. I. Vogel, *J. Chem. Soc.*, 1731 (1963). [j] K. Hoffmann in "Imidazole and Its Derivatives", Part I, Interscience, New York, 1953. [k] P. Mauret and J. P. Fayet, *C. R. Acad. Sci., Ser. C*, 264, 2081 (1967). [l] E. D. Bergmann and F. Weiler in "The Purines Theory and Experiment", Vol. 4, Eds., E. D. Bergmann and B. Pullmann. The Jerusalem Symposia on Quantum Chemistry and Biochemistry, p 21. [m] H. DeVoe and I. Tinoco, (estimated from the dipoles of the corresponding methylated compounds), *J. Mol. Biol.*, 4, 500 (1962).

The 1146-cm^{-1} mode, assigned in ref 29 to both A_1 and B_1 classes, is not included in the A_1 class. The very weak Raman line at 1237 cm^{-1}, assigned by ref 29 as an A_1 mode, is not included in the A_1 class in view of its uncertain polarization. The previous assignment of the strong line at 1146 cm^{-1} as a B_1 N–H bending mode[29] was found to be inconsistent with comparison of the calculated and observed frequency shift upon deuteration of the pyrrole nitrogen. The B_1 N–H was calculated in this work as a very weak line at 1364 cm^{-1} which cannot be assigned to the strong line at 1146 cm^{-1}.

IV. Applications

The method presented in this paper was used extensively in the past few years. Here we list several types of studies where the method was found to be particularly useful.

(a) Calculations of Resonance Raman (RR) Spectra. The calculation of ground- and excited-state equlibrium geometries and vibrational normal modes provides a powerful tool for evaluation of RR spectra of biological chromophores.[3] This was demonstrated in calculations of the RR spectrum of retinal and related molecules[32] and in analysis of the relation between "the spin state marker" frequencies and the heme geometry in metalloporphyrins.[3] In order to demonstrate the method we present

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(25) L. Corrsin, B. J. Fox, and R. C. Lord, *J. Chem. Phys.*, **21**, 1170 (1953).

(26) C. H. Kline, and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944).

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(29) R. C. Lord and F. A. Miller, *J. Chem. Phys.*, **10**, 328 (1942).

(30) A. Stern and K. Thalmayer, *Z. Phys. Chem. Abt. B*, **31**, 403 (1936).

(31) P. Mirone, *Gazz Chim. Ital.*, **86**, 165 (1956).

(32) A. Warshel, and P. Dauber, *J. Chem. Phys.*, **66**, 5477 (1977).

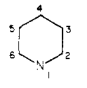
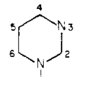
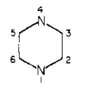
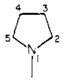
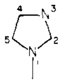
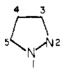
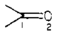
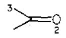
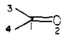
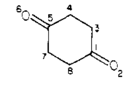
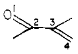
(33) A. L. Verma and H. J. Bernstein, *J. Chem. Phys.*, **61**, 2560 (1974).

(34) T. G. Spiro, and T. C. Strekas, *J. Am. Chem. Soc.*, **96**, 338 (1974).

(35) T. G. Spiro and T. C. Strekas, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2622 (1972).

(36) H. Ogoshi, Y. Saito, and K. Nakamoto, *J. Chem. Phys.*, **57**, 4194 (1972).

Table IX. Calculated and Observed Geometries[a,b] Included in the Optimization of the QCFF/PI Parameters

	bond	calcd	exptl	angle	calcd	exptl
 pyridine	N_1-C_2	1.335	1.340[c]	$C_2-N_1-C_6$	120.8	116.9
	C_2-C_3	1.419	1.354	$N_2-C_2-C_3$	121.2	123.9
	C_3-C_4	1.409	1.394	$C_2-C_3-C_4$	119.7	118.5
				$C_3-C_4-C_5$	117.1	118.3
 pyrimidine	N_1-C_2	1.360	1.355[d]	$C_2-N_1-C_6$	119.1	115.1
	C_4-C_5	1.425	1.395	$N_1-C_2-N_3$	123.9	128.5
	N_3-C_4	1.339	1.335	$C_4-C_5-C_6$	120.2	116.3
				$N_3-C_4-C_5$	118.3	122.6
 pyrazine	N_1-C_2	1.335	1.334[e]	$C_2-N_1-C_6$	119.4	115.8
	C_2-C_3	1.423	1.378	$N_2-C_2-C_3$	120.2	122.7
 pyrrole	N_1-C_2	1.344	1.370[f]	$C_2-N_1-C_5$	110.1	109.8
	C_2-C_3	1.385	1.380	$N_1-C_2-C_3$	108.9	107.1
	C_3-C_4	1.433	1.410	$C_2-C_3-C_4$	106.1	107.4
 imidazole	N_1-C_2	1.320	1.343[g]	$C_2-N_1-C_5$	108.1	107.2
	C_2-N_1	1.331	1.326	$N_1-C_2-N_3$	106.3	111.2
	N_3-C_4	1.351	1.378	$C_2-N_3-C_4$	107.6	105.3
	C_4-C_5	1.396	1.358	$N_3-C_4-C_5$	106.6	109.8
	N_1-C_5	1.328	1.369	$C_4-C_5-N_1$	107.0	106.3
 pyrazole	N_1-N_2	1.333	1.332[h]	$N_2-N_1-C_5$	110.5	111.7
	N_2-C_3	1.331	1.323	$N_1-N_2-C_3$	103.5	104.3
	C_3-C_4	1.420	1.391	$N_2-C_3-C_4$	107.1	111.7
	C_4-C_5	1.403	1.369	$C_3-C_2-C_5$	104.8	104.0
	N_1-C_5	1.311	1.339	$C_4-C_5-N_1$	107.5	107.5
 formaldehyde	C_1-O_2	1.229	1.212[i]	$H-C_1-O_2$	120.0	121.8
 acetaldehyde	C_1-O_2	1.230	1.216[j]	$C_3-C_1-O_2$	122.0	123.5
	C_1-C_3	1.492	1.501			
 acetone	C_1-O_2	1.233	1.222[k]	$C_3-C_1-O_2$	120.9	121.2
	C_1-C_3	1.499	1.507			
 *p*-benzoquinone	C_1-O_2	1.234	1.222[l]	$C_3-C_2-O_2$	121.1	121.1
	C_2-C_3	1.488	1.477	$C_1-C_3-C_4$	121.0	121.1
	C_3-C_4	1.348	1.322	$C_8-C_1-C_3$	117.6	117.1
 acrolein	C_2-O_1	1.231	1.219[m]	$C_3-C_2-O_1$	121.8	123.1
	C_2-C_3	1.473	1.470	$C_2-C_3-C_4$	122.4	119.5
	C_3-C_4	1.339	1.345			

[a] All bond lengths in Å. [b] All angles in degrees. [c] B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, 2, 361 (1958). [d] P. S. Wheatley, *Acta Crystallogr.* 13, 80 (1960). [e] P. S. Wheatley, *Acta Crystallogr.*, 10, 182 (1957). [f] D. H. Sutter and W. H. Flygare, *J. Am. Chem. Soc.*, 91, 6895 (1969). [g] S. Martinez-Carrera, *Acta Crystallogr.*, 20, 783 (1966). [h] F. Krebs Larsen, M. S. Lehmann, I. Sotofte, and S. E. Rasmussen, *Acta Chem. Scand.*, 84, 3248 (1970). [i] K. Takagi and T. Oka, *J. Phys. Soc. Jpn.*, 18, 1174 (1963). [j] R. Kilb, C. C. Lin, and E. B. Wilson, *J. Chem. Phys.*, 26, 1695 (1957). [k] R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, 18, 344 (1965). [l] J. Trotter, *Acta Crystallogr.*, 13, 86 (1960). [m] E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, 45, 104 (1966).

Table X. Experimental and Calculated Vibrational Frequencies Used in the Optimization of the Energy Parameters

Pyridine

	obsd[a]	calcd
A_1	3054	3093 (vw)
	3054 (s)	3090 (vw)
	3036 (vs)	3088 (vs)
	1580 (vs)	1555 (s)
	1482 (vs)	1440 (s)
	1139 (vvw)[b]	1140 (vvw)
	1068 (s)	1047 (m)
	1029 (vs)	1041 (s)
	992 (vs)	994 (vs)
	605 (s)	660 (m)
B_1	3083 (vs)	3090 (vs)
	3054	3087 (s)
	1572 (vs)	1545 (w)
	1439 (vs)	1439 (vs)
	1375 (m)	1331 (w)
	1217	1219 (s)
	1148 (s)	1142 (m)
	1068	1045 (w)
	652 (w)	666 (w)
A_2	981 (r)	1017
	886 (r)	848
	375 (r)	417
B_2	1043 (vvw)[c]	1049 (vvw)
	942 (vvw)	915 (vvw)
	749 (vvs)	738 (vvs)
	703 (vvw)	727 (vvs)
	403 (s)	462 (m)

Pyrrole

	obsd[d]	calcd
A_1	3400	3370 (vs)
	3133	3104 (m)
	3100	3103 (vs)
	1467	1470 (m)
	1418 (s)	1461 (vs)
		1123 (vvw)
	1076 (vs)	1086 (w)
	1015 (vs)	979 (m)
	711 (vs)	802 (vw)
B_1	3133	3108 (w)
	3111	3101 (vvs)
	1530 (vs)	1565 (s)
	1384 (m)	1396 (m)
		1364 (vvw)
	1146 (s)	1153 (w)
	1046 (vs)	1065 (s)
	768 (s)	782 (m)
A_2	1091 (r)[e]	1126 (r)
	868 (r)	896 (r)
	510 (r)[f]	523 (r)
B_2	1046 (m)	1117 (w)
	880 (w)	931 (w)
	647 (m)	676 (vvs)
	565 (w)	524 (w)

[a] All frequencies in cm^{-1}, intensity notation vs, s, m, w, vw, r for very strong, strong, medium, weak, very weak, and only Raman active, respectively. The observed frequencies are taken from ref 25 except when indicated otherwise (also see text). [b] Taken from ref 26. [c] See discussion in text. [d] The observed frequencies are taken from ref 29 except when indicated; otherwise for discussion of the assignment, see text. [e] Taken from ref 30. [f] Estimated in ref 29 with the help of the product rule.

in Table XI a complete normal mode analysis of a metalloporphyrin (where the metal is represented as an effective σ charge) and compare the calculated and observed RR intensities in Figure 2. This study provides the first analysis of the out-of-plane vibrations of porphyrins. Such an analysis could not have been accomplished by conventional normal mode approaches because of the complexity of the problem and the uncertainty about the proper force constants. The RR intensities calculations were found to be of great help in the assignment of the heme vibrations.

(b) Environmental Effects. The present method allows for a convenient evaluation of environmental effects on spectroscopic properties of conjugated molecules. The electrostatic potential from the charges and dipoles of the given environment is incorporated into the π-electron Hamiltonian in the same way as the electrostatic potential from the σ charge. That is, the diagonal SCF matrix element of the isolated molecule $(F_{\nu\nu}{}^{\pi})^0$ is modified by:

$$F_{\nu\nu}{}^{\pi} = (F_{\nu\nu}{}^{\pi})^0 - \sum_{C} Q_C e^2/r_{AC} + \sum_{D} \mu_D \mathbf{r}_{AD}/r_{AD}{}^3 \qquad (21)$$

where the νth π orbital is located on atom A, and Q and μ are

Table XI. Normal Mode Analysis of a Metalloporphyrin[a]

	calcd	obsd[b]	description
A_{1g}	3106		C-H
	3105		C-H
	1600	1562^1	b-b, m-a
	1395	$1370\ (1425)^2$	a-b, δ(CH)
	1363	1336^1	δ(CH), a-m
	1106	998^1	δ(CH)
	698	732^1	δ(ma)
	619	674^2	a-N, δ(ring)
	316	368^1	N-M
A_{2g}	3103		C-H
	1610	1587^1	a-m
	1409	1420^2	δ(CH), a-m
	1360	1322^1	δ(CH), a-N
	1180	1143^1	δ(CH), a-b
	820	802^1	δ(ring)
	695	604^3	δ(ring)
	363		δ(Na), δ(ring)
B_{1g}	3082		C-H
	1677	1631^1	a-m
	1545	$1547^2\ (1498)^1$	b-b
	1334	1352^1	δ(CH), a-N
	1207	1180^1	δ(CH), a-b
	1096	1059^1	δ(CH)
	780	760^2	δ(ring)
	559		δ(Na)
	238	206^1	N-M
B_{2g}	3107		C-H
	3082		C-H
	1470	1498^1	a-b
	1422	1380^1	a-N, a-m
	1243	1288^1	δ(CH), a-m, a-b
	858	853^1	δ(ring)
	650		a-N, δ(ring)
	426	426^1	δ(ring)
	107		δ(aN)
E_g	1064		χ_H
	851		$\chi_{H(m)}$
	787		χ_H
	591		χ_C
	556		χ_C
	373		χ_C
	172		χ_m
	130		χ_N
E_u	3106	3076^4	C-H
	3103	3062^4	C-H
	3082	3062^4	C-H
	1652	1690^4	m-a, a-b
	1575	1550^4	b-b, m-a
	1446	1520^4	a-b, δ(CH)
	1400	1389^4	a-N, a-m, δ(CH)
	1340	1302^4	δ(CH), a-N
	1310		δ(CH), a-b
	1180	1155^4	δ(CH), a-b
	1103	993^4	δ(CH)
	833	843^4	δ(ring)
E_u	770	740^4	a-N, δ(ma)
	645		a-N, δ(Na)
	631	703^4	a-N, δ(ring)
	460	385^4	N-M
	330	348^4	δ(ring)
	226	202^4	δ(Na)
A_{2u}	852	860	$\chi_{H(m)}$
	855		χ_H
	788	760	χ_C
	581	699^4	χ_C
	278		χ_m
	153	167^4	χ_M
	54		χ_M
A_{1u}	579		χ_C
	290		χ_C
B_{1u}	1063		χ_H
	788		χ_H
	594		χ_C
	414		χ_m
	77		
B_{2u}	1062		χ_H
	541		χ_C
	146		χ_N
	55		χ_a

[a] The assignment is based on comparing calculated and observed RR and IR intensities. Frequencies in cm^{-1}; the atom types a, b, m, N, and M designate respectively the carbon atoms bound to nitrogen, the pyrrole carbon atoms which are not bound to N, the meso atoms, the nitrogen atoms, and the metal atom. X-Y designate stretching frequency of an X-Y bond. δ designates bending frequency, δ(ring) designates bending of the whole porphyrin ring. χ_y designates out of plane deformation around atom y. [b] The observed frequencies are taken from ref 33, 34, 35, and 36 which are indicated here as 1, 2, 3, and 4, respectively.

the partial charges and induced dipoles of the atoms of the environment molecules.[37,38] If the environment molecules are represented by permanent dipoles (rather than point charges), they are included in the last term of this equation. The practical evaluation of the solvent dipoles for polar and nonpolar solvents was described in detail previously.[37,38]

As a demonstration of evaluation of environmental effects, we describe here calculations of the spectral shifts in hemoglobin upon allosteric transition; the hemoglobin molecule is characterized by two tertiary structures: high oxygen affinity form, (r) and low oxygen affinity form (t). Transition of the ligated hemoglobin from r to t shifts the absorption spectrum of the Q and Soret(s) bands to the red by 40–5 cm^{-1}.[39,40] In order to calculate the spectral shifts we evaluate the electrostatic potential from the protein at the heme atoms using the X-ray structures of methemoglobin and deoxyhemoglobin as representing the r and t states (see ref 41 for more details). The potentials from the protein tertiary structures, which are presented in Figure 4 of ref 41, were introduced into the SCF π-electron Hamiltonian of the heme atoms using eq 21. The calculated spectral shifts are compared to the observed one in Table XII. As seen from the table, the calculation reproduces red shifts of the same order as the observed shifts.

Table XII. Calculated Shifts of the Q and S Bands of the Porphyrins upon r → t Transition in Hemoglobin

protein electrostatic potential at the heme	band	ΔE, cm^{-1}	f
potential from the t state	Q	15 533	0.226
	S	28 333	3.040
potential from the r state	Q	15 566	0.403
	S	28 370	3.057

[a] ΔE and f are the transition energy and oscillator strength of the indicated electronic transitions. The degenerate S and Q transitions are split by the protein electric field and the ΔE presented here correspond to the average value of the split transition energies.

(c) Protonation Effects. Many biological processes involve protonated chromophores. These include protonated Schiff bases of retinal in rhodopsin and bacteriorhodopsin.[6] Calculations of

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(37) A. Warshel and M. Levitt, *J. Mol. Biol.*, **103**, 227 (1976).

(38) A. Warshel, *J. Phys. Chem.*, **83**, 1640 (1979).

(39) M. F. Perutz, E. J. Heidner, J. E. Ladner, J. G. Beetlestone, C. Ho, and E. F. Slade, *Biochemistry*, **13**, 2187 (1974).

(40) The spectral shifts upon the r → t transition in hemoglobin are caused by two opposing contributions: the interaction with the protein is expected to lead to a red shift and the displacement of the iron from the heme plane is expected to cause a blue shift. Spectral shifts in five-ligand systems are affected by the motion of the iron, and only in ligated systems, where the iron position is relatively fixed, do we expect the observed shift to reflect the change in interaction with the protein upon the r → t transition.

(41) A. Warshel and R. M. Weiss, *J. Am. Chem. Soc.*, **103**, 446 (1981).

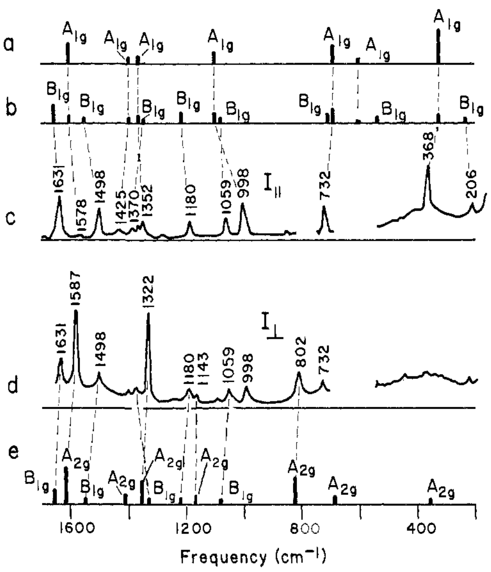

Figure 2. Calculated and observed[33] perpendicular and parallel contributions to the RR spectrum of the Q band of a typical porphyrin: (a) the calculated contribution of the A term to $I_{\parallel}$; (b) the calculated B term contribution to $I_{\parallel}$ of the B_{1g} and A_{1g} modes (the calculated intensities of the B_{2g} modes are much smaller); (c) the observed $I_{\parallel}$ of Cu-porphine[33] (the line at 1498 cm^{-1} is much weaker in other porphyrins where other strong B_g lines appear at ~1550 cm^{-1}); (d) the observed $I_{\perp}$ for Cu-porphine; (e) the calculated B term contribution to $I_{\perp}$.

the effect of protonation on absorption and resonance Raman spectra are straightforward. The proton charge is distributed as a σ charge between the proton and the atoms at the protonation site (the σ charge distribution can be determined by all-valence-electron calculations). This σ charge is treated simply as any other σ charge by eq 13, including the modifications of $\bar{W}_{\mu}$ by adding the $Q_{\mu}{}^{\sigma}\gamma_{AA}$ term associated with the new σ charge. This type of calculation was used extensively in studying the effect of protonation on the spectrum of protonated Schiff bases of retinal.[38,42]

V. Concluding Remarks

This paper presents an extension of the QCFF/PI method to heteroatom-containing conjugated molecules. The extension involves incorporation of the σ charges into the π-electron Hamiltonian by treating formally the SCF equation as an all-valence-electron problem, assuming zero σ–π overlap, and then fixing the σ-electron bond orders. The resulting submatrix of the π orbitals is the one used for the π-electron calculations. The incorporation of the potential from the σ atom of a given molecule in its π-electron Hamiltonian is generalized to incorporate potential from charges and induced dipoles of neighboring molecules (eq 21). This offers a simple and reliable way of incorporating environmental effects in calculations of spectroscopical properties of biological chromophores. This can be applied in detailed studies of spectral shifts of substrates or prosthetic groups in active sites of proteins with known X-ray structure. Such a study is demonstrated here for the spectral shift of hemoglobin upon r → t transition. Other related studies are now underway in our laboratory.

Incorporation of external potentials from neighboring molecules in π-electron calculations might be crucial for consistent study of the important class of charge-transfer crystals of TCNQ and related molecules.[43] In such cases, the present method can be implemented in the Molecular Crystal Analysis (MCA) program.[44,45]

The extension of the QCFF/PI method to conjugated molecules allows for interpretation of RR spectra of most biological chromophores. This is demonstrated here by the normal mode analysis of a porphyrin. Other studies are reported in ref 3. The present approach also offers the possibility of studying environmental effects on RR spectrum of biological chrmophores. Such studies may be done by simply using eq 21 in calculating RR spectrum of chromophores in protein active sites.

Acknowledgment. This work was supported by Grant EYO 1760 from the National Eye Institute and by the Alfred P. Sloan Foundation.

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Study of Additivity of Correlation and Polarization Effects in Relative Energies

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Abstract: Calculations are reported at the 6-31G and 6-31G** level with and without inclusion of all double excitations (CID/6-31G and CID/6-31G**). The relative effects of polarization *or* correlation are compared with calculations involving polarization *and* correlation. The error in additivity is ~2 kcal/mol for systems involving simple geometric changes and ~4 kcal/mol for systems involving dimerization and molecular combination. These results are especially interesting in electron-deficient systems involving relatively large corrections due to differences in classical vs. nonclassical bonding. We emphasize that additivity in total energies is neither expected nor observed.

As computers become more efficient and computer methods more effective, the problem of correlation is becoming more tractable. Several prominent groups in theoretical chemistry have recently[1,2] solved the problem of determining analytical gradients from correlated wave functions. Other groups are concerned with CI effects and geometries[3] notably Kutzelnigg[4-9] and Meyer.[10,11]

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