A Brief Review and Table of Semiempirical Parameters Used in the Hückel Molecular Orbital Method

WILLIAM P. PURCELL and JUDITH A. SINGER
Department of Medicinal Chemistry, College of Pharmacy, University of Tennessee, Memphis, Tenn. 38103

The application of the Hückel Molecular Orbital (HMO) method to the interpretation of experimental results in biochemistry and biology is discussed. Several methods of derivation and application of the semiempirical parameters used in the HMO technique are given, and a table listing the parameter values is included.

IN VIEW of the growing interest in the possibility of correlating Hückel Molecular Orbital (HMO) calculations (*38*) with biochemical and biological activities (*72, 75, 79, 94*), and the application of quantum chemistry to drug design (*89*), the authors have calculated electron charge distributions of selected cholinesterase inhibitors (*80*) and are in the process of applying quantum chemistry to our search for effective antimalarials. Two restrictions became apparent at the onset of these calculations: Parameters were assigned to a limited number of heteroatoms only, and the choice of parameters for a specific heteroatom was dependent upon the method of derivation. With this in mind, the authors decided that a useful contribution to the field would be the publication of a table of the currently available semiempirical parameters and their corresponding derivations and applications, so that other workers would not find it necessary to duplicate this relatively tedious search for the "right" parameter.

BACKGROUND

The HMO method has been described in detail previously (*24, 75, 85, 96*) and, therefore, the particulars and the approximations of the method will not be reported here. The HMO calculations deal with the mobile π electrons, assuming the σ electrons to be localized. The coulomb integral for atom x, α_x, is given in Equation 1, and the resonance integral for the bond between atom y and atom x, β_{yx}, is defined in Equation 2, where α_0 is a standard integral, usually of carbon, β_0 is a similar standard resonance integral—i.e., usually associated with the bond between two carbon atoms—and h and k are the semiempirical parameters under discussion.

$$\alpha_x = \alpha_0 + h\beta_0 \tag{1}$$

$$\beta_{yx} = k\beta_0 \tag{2}$$

The semiempirical parameters, h and k (Equations 1 and 2), have been determined from ionization potentials (*29*), electronegativities (*65*), nuclear magnetic resonance (*12*) and electron spin resonance (*103*), electric dipole moments (*51*), spectroscopic studies of charge transfer complexes (*46*), UV studies of bond length-bond energy relations (*70*), and bond orders (*48*). There are methods of selecting parameter values which give the best fit to a particular set of experimental data (*18*) and of evaluating and improving the parameters (*19, 93*).

The application of HMO calculations is widespread indeed, and one finds many examples in the disciplines of medicinal chemistry, biochemistry, and biology. Correlations of dipole moments, chemical reactivity, basic strengths, antitumor activity, electron transfer, and tautomerism with molecular orbital calculations of biologically important molecules have been discussed by Brown (*14*). Other selected examples include the application of quantum theory of the DNA molecule to the biological problems of heredity, mutations, aging, and tumors (*50, 52, 59, 73, 92*) and aspects of electronic structure and enzyme reactions (*68*), antimetabolite action (*67*), local anesthetic activity, (*108*), and antibacterial activity (*107*).

An example of the biological importance of studies on hydrogen bonding via quantum mechanics is reported by Rein and Harris (*84*), who investigated the guanine-cytosine complex in view of its probable role in the replication process in DNA. Along these same lines, a number of biological processes are believed to be functions of tautomeric equilibria; in particular, the theory of mutations (*72*) has been associated with tautomerism, and therefore, these equilibria have been examined quantum-mechanically (*74*).

EXPLANATION OF THE TABLE

The first column lists the elements under consideration in alphabetical order. The second column gives the atom which is associated with the coulomb integral, α, which, in turn, is associated with the parameter h. The third column gives the values for h corresponding to the atomic symbols in column two. The single and double dots over an atomic symbol—e.g., $\dot{\mathrm{N}}$ and $\ddot{\mathrm{N}}$—indicate situations in which the atom donates one or two electrons to the π electron system, respectively. The fourth column lists the bonds associated with the resonance integrals, β, and the fifth column gives the values of k defined in Equation 2. The dotted line bond—e.g., $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$—is used to indicate aromatic bonding. The sixth column contains comments considered pertinent and generally related to the method of parameter derivation and application, sometimes not separable. The applications are not meant to be complete; rather, representative applications have been selected. The last column gives the references associated with the entries in the first six columns.

Any particular entry is found only once in the table; therefore, for two heteroatoms—e.g., B-N—an entry is made under only one of the atoms. Also, although like atoms—e.g., all $\dot{\mathrm{O}}$—are generally grouped together, use of parameters specified for a particular group or molecule—e.g., benzoic acid—would necessitate listing certain parameters together— $\dot{\mathrm{O}}$ and $\ddot{\mathrm{O}}$ in the example.

Table I. Hückel Molecular Orbital Semiempirical Parameters

Element		h	Bonding	k	Derivation and Application	Ref.
Boron	B	-0.92^a	B—N	0.92^a	All parameters taken from the literature—groups *a* and *b* from (*8*) and group *c* from (*27*)—and used to study five-membered rings containing boron and nitrogen; results are similar using the parameters of Rasch (*81-83*).	(*4*)
		-1.08^b		0.72^b		
		-1.16^c		0.5^c		
	N	$+0.92^a$	B—B	0.8^a		
		$+1.08^b$		0.8^b		
		$+1.6^c$		0.8^c		
			N—N	0.6^a		
				0.6^b		
				0.6^c		
			C—B	0.7^a		
				0.7^b		
				0.9^c		
			C—N	0.8^a		
				0.8^b		
				0.9^c		
			C—C	0.9^a		
				0.9^b		
				0.9^c		
			C=C	1.1^a		
				1.1^b		
				1.1^c		
	B	-0.7	B—C	0.7 ($\beta_{C=C}$ as reference)	Correlation with known properties of dibutylethyleneboronate, with other parameters consistent with those suggested by Streitwieser (*96*)	(*58*)
	B	-1.5	B—C≡H_3	0.25	Calculations on vinyldimethylboron	(*57*)
			B—CH_3	0		
			C—B	0.7		
	B	≅1	C—B	≅0.7	Reactivity and spectral data of ethyleneboronic acid; results relatively insensitive to variation of the oxygen parameter	(*57*)
	B	-1	C—B	0.7	Recommended by Streitwieser	(*96*)
			C—B	0.61	For bond length of 1.4*A*.	(*81*)
			B—B	0.034	For bond length of 1.6A.	(*81*)
			B—N	0.62	For bond length of 1.41A.	(*81*)
			B—O	0.67	For bond length of 1.36A.	(*81*)
Carbon	C	0.07	C—H	1	For a simple LCAO-MO treatment of saturated molecules	(*25*)
	H	0	C—C	1		
	$\dot{C}$ (aromatic, adjacent to C=O)	0.2			Correlation with polarographic half-wave potentials and UV absorption spectra of ethyl esters of aromatic polycyclic carboxylic acids	(*42*)
	$\dot{C}$ (adjacent to N^+)	0.5			Tautomerism of *N*-hetero-aromatic hydroxy-compounds	(*53*)
	C (adjacent to *tert*-butyl)	-0.2			The *tert*-butyl group treated as purely inductive	(*61*)
			$C\overset{\cdots}{-}C$ (benzo-ring A of triphenylenes)	1	Bond orders of acenes	(*35*)
			$C\overset{\cdots}{-}C$ (extreme "single and double" bonds of triphenylenes)	0.8		
			C—C	0.8	Rather arbitrarily assigned on the basis of 0 [*sic*] and 1.20 for pure single and double bonds	(*34*)
			C=C (from benzologs of pyrene)	1.1		

			$\mathrm{C\overset{\cdots}{-}C}$ (triphenylenes)	1	Designated on basis of Clar's [Clar, McCallum and Robertson *(21)*] formulae for triphenylenes; values justified by crystal structure bond lengths *(1)*	*(35)*
			$\mathrm{C\overset{\cdots}{-}C}$ (extreme "single and double bonds" of triphenylenes)	0.8		
			$\mathrm{C\overset{\cdots}{-}C}$ (benzo-ring A of triphenylenes)	0.8, 1.1 (alternately)		
			$\mathrm{C\overset{\cdots}{-}C}$ (triphenylenes' alternating bonds)	0.737, 1.187	From a plot of the highest occupied molecular orbital energy as a function of β_2/β_1	*(35)*
			C—C	1	For bond length of 1.397A.	*(81)*
			C—C	0.9	Recommended by Streitwieser for a single sp^2-sp^2 bond of about 1.47A.	*(96)*
			$\mathrm{C\overset{\cdots}{-}C}$	1	Recommended by Streitwieser for an "aromatic" bond of about 1.40A.	*(96)*
			C=C	1.1	Recommended by Streitwieser for a double bond of about 1.34A.	*(96)*
			C—C	0	Used only between saturated carbons when no other bonds are present, including C—H bonds in substituents, as for alkyl radicals	*(95)*
			>C=C<	1.07	Overlap integral values for bond length of 1.34A. and correlation with ionization potentials	*(95)*
			=C—C=	0.90	Overlap integral value for bond length of 1.46A. and correlation with ionization potentials	*(95)*
			=C—C≡	0.97	Overlap integral value for bond length of 1.42A. and correlation with ionization potentials	*(95)*
			≡C—C≡	1.04	Overlap integral value for bond length of 1.38 A. and correlation with ionization potentials	*(95)*
			≡C—C	1.38	Value of *k* assumed; no bond length given	*(95)*
			$\mathrm{H_3C}$—C	0.75	Overlap integral value for bond length of 1.46A. and correlation with ionization potentials	*(95)*
			$\mathrm{H_3C}$—C=	0.7	Overlap integral value for bond length of 1.50A. and correlation with ionization potentials	*(95)*
			>C=C=	1.18	Overlap integral value for bond length of 1.30A. and correlation with ionization potentials	*(95)*
			=C=C=	1.24	Overlap integral value for bond length of 1.27A. and correlation with ionization potentials	*(95)*
			—C≡C—	1.40	Overlap integral value for bond length of 1.20A. and correlation with ionization potentials	*(95)*
			C—C	1.10	Absorption maxima and photoionization potentials for linear conjugated molecules	*(98)*
			C=C	1.45		
			$\mathrm{C\overset{\cdots}{-}C}$	1.02	Overlap integrals; used to calculate the electronic structure of thiazole	*(100)*
	H	−0.2	—C—	0.34	Used in a simple LCAO-MO treatment for saturated compounds	*(109)*
			C—H	1.1		
			—C=C—	1.27	Mulliken's method of overlap integrals for tetraphenylbutatriene; overlap neglected in the HMO calculations	*(111)*
			>C—C=	1.08	Mulliken's method of overlap integrals for tetraphenylbutatriene; overlap neglected in the HMO calculations	*(111)*
Halogens—Bromine	Br	1	C—Br	0.2	*h* from electronegativities; *k* to reproduce α-naphthalene results; results correlated with UV spectrum, which was relatively insensitive to parameter values	*(69)*
	Br	1.5	C—Br	0.3	Recommended by Streitwieser	*(96)*

Table I. Hückel Molecular Orbital Semiempirical Parameters (*Continued*)

Element		*h*	Bonding	*k*	Derivation and Application	Ref.
	Br	2.2	C—Br	0.2–0.3	*h* from ionization potentials of hydrides, used in the ω technique; *k* gives good correlation with ionization potentials when used with *h*	(*95*)
	Br	0.45	C—Br	0.58	Used in a simple LCAO-MO treatment for saturated compounds	(*109*)
	Br	2.4			Spectral data of bromobenzene, with overlap neglected	(*86*)
Chlorine	C—Cl	−0.015	C—C—Cl	0.90	MO treatment of substituted semiquinone hyperfine splitings with overlap neglected and the pseudo atom approach taken	(*12*)
	Cl C	0.35 0.07	C—Cl	0.65	For a simple LCAO-MO treatment of saturated molecules	(*25*)
	Cl C (adjacent)	2 0.5	C—Cl	0.8	Used to calculate the electronic structures of diethylphenylphosphates	(*32*)
	Cl	1	C—Cl	0.2	*h* from electronegativities; *k* to reproduce α-naphthalene results; results correlated with UV spectrum, which was relatively insensitive to parameter values	(*69*)
	Cl	2	C—Cl	0.4	Recommended by Streitwieser	(*96*)
	Cl	2.8	C—Cl CH_3—Cl	0.37, 0.38 0.26	*h* from ionization potentials of hydrides, used in the ω technique; $k_{C—Cl}$ gives good correlation with, respectively, ionization potential and electron impact potential when used with *h*; $k_{CH_3—Cl}$ the product of $k_{C—CH_3} \times k_{C—Cl}$	(*95*)
	Cl	0.5	C—Cl	0.65	Used in a simple LCAO-MO treatment for saturated compounds	(*109*)
	Cl	1.9			Ionization energy of hydrogen chloride	(*54*)
	Cl	1.4			Ionization energy of methyl chloride	(*54*)
	Cl	2.5			Chosen to give "best" fit to spectroscopic data and resonance energies	(*54*)
	Cl	2.5			Spectral data of chlorobenzene with overlap neglected	(*86*)
	Cl	1.6			Orientation effects in substitution in chlorobenzene	(*104*)
			C—Cl	1/3	No special derivation; calculations stated insensitive to this parameter, if it is small	(*6*)
Fluorine	F	0.57	C—F	0.85	For a simple LCAO-MO treatment of saturated molecules	(*25*)
	F	1.5	C—F	0.25	*h* from electronegativities; *k* to reproduce α-naphthalene results; results correlated with UV spectrum, which was relatively insensitive to parameter values	(*69*)
	F	3	C—F	0.7	Recommended by Streitwieser	(*96*)
	F	0.9	C—F	0.5	Used in a simple LCAO-MO treatment for saturated compounds	(*109*)
	F	2.6			Ionization energy of methyl fluoride	(*54*)
	F	5			Chosen to give "best" fit to spectroscopic data and resonance energies	(*54*)
	F	5			Spectral data of fluorobenzene, with overlap neglected	(*86*)
	F	4.5			Ionization potentials of hydrides, used in the ω technique	(*95*)

	F	2			Used in HMO calculations on para-substituted fluorobenzoyls, which were then combined with F^{19} shielding results to test shielding theories; used with $h_O = 1.5$	*(99)*
Iodine	I	0.4	C—I	0.53	Used in a simple LCAO-MO treatment for saturated compounds	*(109)*
Hydrogen Bonding	H-donor hetero-atom	−0.2			Recommended by Pullman	*(78)*
			hydrogen bond	0.2	Recommended by Pullman	*(78)*
	H-acceptor hetero-atom	+0.2			Recommended by Pullman	*(78)*
Hyperconjugation $=C <_{C \equiv H_3}$	$=C<$	−0.1	C—C	0.7	Recommended by Pullman	*(78)*
	$=C<$	0 to −0.1	C—C	0.7–1	Indicated by Streitwieser as frequently used	*(96)*
	$=C<$	−0.1			Attached methyl group treated as partly inductive and partly hyperconjugative	*(61)*
	$=C<$	−0.3 to −0.5			Derived from inductive model; range indicated by Streitwieser as working reasonably well	*(96)*
	$=C<$	−0.5 −0.9 −1.1			Inductive model of hyperconjugation, with, respectively, one, two, and three methyl groups on the carbon	*(97)*
	$—C\equiv$	−0.2	$C\equiv H_3$	2	Recommended by Pullman	*(78)*
	$—C\equiv$	0 to −0.1	$C\equiv H_3$	2–2.5	Indicated by Streitwieser as frequently used	*(96)*
	$—C\equiv$	−0.1			Chosen somewhat arbitrarily to reproduce the dipole moment of toluene	*(22)*
	$C\equiv H_3$	3	C—C	0.7	Used to calculate the electronic structures of diethylphenylphosphates	*(32)*
	$C\equiv H_3$	3	C—C	0.7	Methyl group treated as partly inductive and partly hyperconjugative	*(61)*
	$C\equiv H_3$	1.4–3.3	C—C	0.7–0.8	Derived from heteroatom model; indicated by Streitwieser as being frequently used	*(96)*
	$C\equiv H_3$	3	CH_3—O C—C	0.3 0.7	*h* from ionization potentials of hydrides, used in the ω technique; *k* gives good correlation with ionization potentials when used with *h*	*(95)*
	$C\equiv H_3$	2.0			Ionization energy of methane	*(54)*
	$C\equiv H_3$	1.4			Ionization energy of ethane	*(54)*
	$C\equiv H_3$	2.9			Chosen to give "best" fit to spectroscopic data and resonance energies	*(54)*
	$C\equiv H_3$	4			Hyperconjugation model with overlap included	*(63)*
	$C\equiv H_3$	3			Heteroatom model of hyperconjugation; appears suitable for the ω technique and cations	*(95)*
	$\equiv H_3$	−0.5			Chosen somewhat arbitrarily to reproduce the dipole moment of toluene	*(22)*
	$\equiv H_3$ (from deuterated toluene)	−0.46			To account for differences in energies and electron distributions effected by deuteration of toluene	*(37)*
	$\equiv H_3$	≅−0.3			Inclusion of ω as mentioned in *(62)* coupled with spectroscopically determined α_C and β_{CC}	*(39)*
	$\equiv H_3$ or $=H_2$	0, −0.25, −0.50			Comparison of calculated with experimental conjugation energies; (−0.50 considered best value)	*(47)*
	$\equiv H_3$	−0.50 −0.25 0.00 −0.25 0.50			Results of using the various values, with overlap included, compared with numerous experimental results	*(62)*
	$\equiv H_3$	−0.45			Dipole moment of toluene	*(66)*
	$\equiv H_3$	0 to −0.5			Indicated by Streitwieser as being frequently used	*(96)*

Table I. Hückel Molecular Orbital Semiempirical Parameters (*Continued*)

Element		*h*	Bonding	*k*	Derivation and Application	Ref.
	$C—C\equiv H_3$	−0.15	$C=C—C\equiv H_3$	0.93	MO treatment of substituted semiquinone hyperfine splittings, with overlap neglected and the pseudo atom approach taken	*(12)*
Metals	M	+1 −1 +3 −3	M—O M—N	0.4 0.4	Calculation of various values for metal chelates compared for *h* values; *k* from distance of the chelate bond and nature of the orbitals participating in π conjugation	*(31)*
Nitrogen	Ṅ C H	0.24 0.07 0	C—Al C—N N—H	0.67 1 0.45	For bond length of 1.63A. For a simple LCAO-MO treatment of saturated molecules	*(81)* *(25)*
	Ṅ	1.5	C—N	0.8, 0.6, 0.4, 0.2	Charge densities calculated for maleimide systems	*(56)*
	N̈ (amino)	1	C—N	0.4	*h* from electronegativities; *k* to reproduce α-naphthalene results correlated with UV spectrum, which was relatively insensitive to parameter values	*(69)*
	Ṅ	1	C—N	0.9	Recommended by Pullman	*(78)*
	Ṅ Ṅ (terminal)	0.8 0.4	C—N N—N	1.05 1.56	*k* from bond lengths, $h_{\dot{N}} = 0.8$ estimated, $h_{\dot{N}} = 0.4$ from literature *(76)*	*(90)*
	Ṅ	1.34	C—N	0.8	*h* from exploration of response surfaces for the determination of HMO parameters for phenol blue	*(93)*
	Ṅ	1.5	C—N	0.8	Recommended by Streitwieser	*(96)*
	Ṅ	1.7	C—N CH_3—N	0.7 0.4	*h* from ionization potentials of hydrides, used in the ω technique; *k* gives good correlation with ionization potentials when used with *h*	*(95)*
	Ṅ	0.1			Reproduction of results of advanced SCF calculation on methylenimonium ions	*(17)*
	Ṅ	1.2			Ionization energy of ammonia	*(54)*
	Ṅ	0.9			Ionization energy of methylamine	*(54)*
	Ṅ	1.6			Chosen to give "best" fit to spectroscopic data and resonance energies	*(54)*
	Ṅ	2			Selection of *h* values to give π moments too high by a factor of 1.6	*(64)* from *(96)*
	Ṅ	2			Indicated by Streitwieser as being at least consistent with substitution reactions on heterocyclic rings	*(96)*
			C—N	0.98	For bond length of 1.36A.	*(81)*
			N—N	0.98	For bond length of 1.31A.	*(81)*
Nitrogen	Ṅ	0.5	$C\overset{\cdots}{—}N$	1	Selected for study of 1,2-diaza-3,5,7-cyclooctatriene; MO results do not correlate with experiment	*(2)*
	Ṅ Ċ (adjacent)	0.5 0.05	$C\overset{\cdots}{—}N$	1	For pyridine, from substitution orientation of pyridine oxide	*(5)*
	Ṅ	0.5	$C\overset{\cdots}{—}N$	1	Radical reaction of pyridine	*(13)*
	Ṅ Ċ (adjacent to Ṅ)	0.5 0.08_5	$C\overset{\cdots}{—}N$	1	Reactions of quinoline	*(15)*
	Ṅ	1/2	$C\overset{\cdots}{—}N$	1	Correlation with experimental bond orders of pteridine	*(36)*
	Ṅ	≅0.25	$C\overset{\cdots}{—}N$	≅0.5	*h* assumed roughly halfway between h_C and h_O; *k* from pyrrole carbon-nitrogen bond energy	*(70)*

	Ṅ	0.4	$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$	1	Recommended by Pullman	*(78)*
	Ṅ	0.5	$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$	1	Recommended by Streitwieser	*(96)*
	Ṅ	2	$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$	1	Indicated by Streitwieser as being at least consistent with substitution reactions on heterocyclic rings	*(96)*
	Ṅ	1	$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$	0.9	*k* from overlap integrals; used to calculate the electronic structure of thiazole	*(100)*
	C (adjacent to Ṅ and both Ṅ and S)	0.1				
	Ṅ	0.2			Reproduction of SCF results	*(3)* from *(78)*
	Ṅ	0.5			Reactions of quinoline; selected from several trial values	*(15)*
	Ṅ	≅0.5			Reproduction of experimental dipole moments	*(26)*
	Ṅ	0.6			Reproduction of experimental dipole moments	*(51)*
	Ṅ	≅0.6			Acidity of heterocyclic phenols	*(53)*
	Ṅ	0.2			Reproduction of SCF results	*(60)* from *(78)*
	Ṅ	1			Selection of *h* values to give π moments too high by a factor of 1.6	*(64)* from *(96)*
	Ṅ	1			Exploration of response surfaces for the determination of HMO parameters for phenol blue	*(93)*
	Ṅ	≅0.5			Indicated by Streitwieser as being supported by numerous authors as reproducing experimental dipole moments	*(96)*
	Ṅ	0, 0.5			Both values correlated almost equally well with proton coupling constants for 4,4′-bipyridyl negative ion	*(103)*
	Ṅ	2			Resonance energies	*(105)*
	Ṅ	0.50			Agreement with resonance energies of the cyclazines (*h* values taken from the literature)	*(106)*
	C (adjacent)	0.17				
			$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$	1	Overlap integrals	*(78)*
			C=N	1.1 or 1.2	Resonance integrals' relation: $\frac{\beta_{C=X}}{\beta_{C=C}} = \frac{E_{C=X} - E_{C-X}}{E_{C=C} - E_{C-C}}$	*(78)*
	N̈ (pyrrole type)	2			Resonance energies	*(11)*
	Ṅ (cyano)	1	C≡N	1	Used to calculate the electronic structures of diethylphenylphosphates	*(32)*
	—C≡ (cyano)	0.1				
	C≡ (nitrile)	0.01- 0.1	C≡N	1.5	*k* from UV spectra of nitriles; *h* estimated by comparison with other parameters	*(71)*
	≡N (nitrile)	0.3				
	NH	2.5			Tautomerism of *N*-hetero-aromatic hydroxy-compounds	*(53)*
	N̈ (dimethylamino)	1	N—CH_3	0.7	Used to calculate the electronic structures of diethylphenylphosphates	*(32)*
	CH_3 (dimethylamino)	3	N—C	1		
	C (adjacent)	0.1				
	N̈ (indole)	≅1	$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ (indole)	≅0.9	Most suitable for discussion of electrophilic substitution and addition reactions of indole	*(87)*
Nitrogen	N+	2	N—O	≅0.7	Recommended by Streitwieser	*(96)*
	N (nitro)	1	C—N	1	Used to calculate the electronic structures of diethylphenylphosphates	*(32)*
	O (nitro)	1.5	N—O	1		
	C (adjacent)	0.2				

Table I. Hückel Molecular Orbital Semiempirical Parameters (*Continued*)

Element		*h*	Bonding	*k*	Derivation and Application	Ref.
	N+	1.0			For pyridinium ion, from substitution orientation of pyridine oxide	*(5)*
	C (adjacent)	0.1				
	N+	0.6	$N^+—O^-$	0.5	From substitution orientation of pyridine oxide	*(5)*
	C (adjacent)	0.06				
	O^-	1.0				
	N+	0.65	$N^+—O^-$	0.5	From substitution orientation of salt of pyridine oxide	*(5)*
	C (adjacent)	0.065				
	O^-	1.5				
	N+	2			Reactions of quinoline; selected from several trial values	*(15)*
	N+	1.4			Reproduction of results of advanced SCF calculations on methylenimonium ions	*(17)*
	N+	1.8, 1.1 over that of h_N			Acid-base equilibria of, respectively, amines and ortho amines, with approximate relation between pk_a and the charge density term	*(28)*
	N+	2			Jaffè's method based on the $\delta\rho$-correlation, applied to amine oxides	*(41)*
	O^-	1				
	N+	2.4			Reproduction of SCF results for pyridine cation	*(45)*
	C (adjacent)	0.4				
	N+	1.2, 1.85 over that of h_N			Acid-base equilibria of aromatic amines, first value without, and second value with, allowance for effect of the enhanced electronegativity of the adjacent carbons	*(53)*
	N+	2			Recommended by Pullman	*(78)*
			N—O	0.8	Correlation with moments of pyridine oxides	*(5)*
			N—O	0.6	Dipole moment of furazane	*(64)* from *(96)*
			N—O	1.17	For bond length of 1.18A.	*(81)*
			N—O	0.69	Assumed proportionality of overlap integrals	*(96)*
	N^-	−1.1			Reproduction of results of advanced SCF calculations on methylenimonium ions	*(17)*
Oxygen	Ö	0.40	C—O	0.95	For a simple LCAO-MO treatment of saturated molecules	*(25)*
	C	0.07	O—H	0.45		
	H	0				
	Ö	1.2	C—O	0.7	Correlation with polarographic half-wave potentials and UV absorption spectra of ethyl esters of aromatic polycyclic carboxylic acids	*(42)*
	Ö	0.51	C—O	0.57	Not given	*(61)*
	C (adjacent)	0.05 (from lit.)				
	Ö (hydroxyl)	1.3	C—O	0.4	*h* from electronegativities; *k* to reproduce α-naphthalene results; results correlated with UV spectrum, which was relatively insensitive to parameter values	*(69)*
	Ö	0.5	C—O	0.1-0.3	*h* from UV spectrum of furan; *k* from an assumed proportionality to the difference between single and double bond energies	*(70)*
	Ö	2	C—O	0.9	Recommended by Pullman	*(78)*
	Ö	2	C—O	0.8	Recommended by Streitwieser	*(96)*
	Ö	≅1			Oxidation potentials of phenols	*(30)*
	Ö	1.8			Ionization energy of water	*(54)*
	Ö	1.2			Ionization energy of methanol	*(54)*

Oxygen	$\ddot{O}$	1.8			Chosen to give "best" fit to spectroscopic data and resonance energies	*(54)*
	$\ddot{O}$	3.2			Selection of h values to give π moments too high by a factor of 1.6	*(64)* from *(96)*
	$\ddot{O}$	2.7			Ionization potentials of hydrides, used in the ω technique	*(95)*
			C—O	1.14	For bond length of 1.23A.	*(81)*
			C—O	1.1	Correlation with energies of $N\text{-}V_1$ transitions	*(110)*
	OCH_3	3	$C—OCH_3$	0.9	Used to calculate the electronic structures of diethylphenylphosphates	*(32)*
			O—O	0.77	For bond length of 1.33A.	*(81)*
	O (quinone ions)	1/3–1/2	C—O (quinone ions)	1	Frequencies of electron spin resonance absorption spectra of free-radical salts of quinhydrones	*(55)*
	O (quinone ions)	2/3	C—O (quinone ions)	1	Estimated from hyperfine structure of the electron spin resonance absorption spectra of free-radical salts of quinhydrones	*(55)*
	$\dot{O}$	1.2	C=O	1.5	MO treatment of semiquinone hyperfine splittings, with overlap neglected—essentially the same as found by Vincow and Fraenkel *(102)*	*(12)*
	$\dot{O}$	0.15	C=O	1.1	Reproduction of electron density distribution given by advanced MO calculations	*(16)*
	$\dot{O}$	1.5	C=O C—C (C of benzene ring to C of carboxyl group)	$2^{1/2}$ 0.894	$k_{C—C}$ from overlap integrals; used to calculate electronic state energies of benzaldehyde	*(40)*
	$\ddot{O}$ C (carboxyl)	1.8 0.2	C=O	1.4	Correlation with polarographic half-wave potentials and UV absorption spectra of ethyl esters of aromatic polycyclic carboxylic acids	*(42)*
	$\dot{O}$ (formyl) C (formyl)	2 0.2	C=O	$2^{1/2}$	Used to calculate the electronic structures of diethylphenylphosphates	*(32)*
	$\dot{O}$ $\dot{O}$	0.5, 1.25 1, 2	C=O C—O	$2^{1/2}$, $2^{1/2}$ $2^{1/2}$, $2^{1/2}$	Used to calculate bond lengths in benzoic acid	*(33)*
	C (carboxyl)	0.6, 0.6				
	C (adjacent to C=O)	0.36, 0.18				
	C (ortho to C=O)	0.22, 0.05				
	C (meta to C=O)	0.13, 0.02				
	C (para to C=O)	0.08, 0				
	$\dot{O}$	1	C=O	1	Charge densities calculated for maleimide systems	*(56)*
	$\dot{O}$	1.2	C=O	2	Recommended by Pullman	*(78)*
	$\dot{O}$	2	C=O	$2^{1/2}$	Reduction potentials of aromatic aldehydes and ketones	*(88)*
	$\dot{O}$	1	C=O	1	Recommended by Streitwieser	*(96)*
	$\dot{O}$	2	C=O	$2^{1/2}$	Indicated by Streitwieser as being frequently used but as appearing somewhat high	*(96)*
	$\dot{O}$	1.2	C=O	1.56	Chosen to give close agreement with spin densities of parasemiquinones	*(101)*
	$\dot{O}$	1.2	C=O	1.56	Spin density distributions of semiquinone anions as given by ESR spectra	*(102)*
	$\dot{O}$	1.2			Carbonyl vibration frequencies	*(7)* from *(78)*

Table I. Hückel Molecular Oribital Semiempirical Parameters (*Continued*)

Element		*h*	Bonding	*k*	Derivation and Application	Ref.
	Ȯ	1.2			Carbonyl vibration frequencies	*(9, 10)* from *(78)*
	Ȯ	4			Resonance energies	*(11)*
	Ȯ C (adjacent)	2 0.1			Half-wave potentials of unsaturated aromatic ketones, with hyperconjugation ignored	*(20)*
	Ȯ	≅1			Reproduction of experimental dipole moments	*(26)*
	Ȯ	2			Selection of *h* values to give π moments too high by a factor of 1.6	*(64)* from *(96)*
	Ȯ	1.2			Indicated by Pullman as determined by several authors from carbonyl vibration frequencies	*(78)*
	Ȯ	1.2			Carbonyl vibration frequencies	*(91)* from *(78)*
	Ȯ	0.50			Exploration of response surfaces for the determination of HMO parameters for phenol blue	*(93)*
	Ȯ	≅1			Indicated by Streitwieser as being supported by numerous authors as reproducing experimental dipole moments	*(96)*
	Ȯ	1.5			Used in HMO calculations on para-substituted fluorobenzoyls, which were then combined with F^{19} shielding results to test shielding theories; used with $h_F = 2$	*(99)*
	Ȯ	4			Resonance energies	*(105)*
			C=O	1.3	Lennard-Jones' relation	*(78)*
			C=O	1.4–2	Indicated by Streitwieser as being derived by several authors from assumed proportionality to the difference between single and double bond energies	*(96)*
			C⋯O	0.6	Ionization potential of furan	*(95)*
	O (from N—O)	≅0.8			Agreement with dipole moments of heterocyclic *N*-oxides	*(44)*
	O (from N—O)	1.2			Agreement with dipole moments	*(45)*
	O+	2.5			Recommended by Streitwieser	*(96)*
Phosphorus	Ö	2	P—O	0.6	Used to calculate the electronic structures of diethylphenylphosphates	*(32)*
	Ṗ Ȯ	−1 2	P=O	1	Used to calculate the electronic structures of diethylphenylphosphates	*(32)*
	OC_2H_5	2	P—OC_2H_5	0.6	Used to calculate the electronic structures of diethylphenylphosphates	*(32)*
	Ṗ S	−1 0.8	P=S	0.85	Used to calculate the electronic structures of diethylphenylphosphates; $h_{\dot{S}}$ uncertain, but adopted in accordance with the Pullmans' relation, $\Delta\alpha = \alpha_{\dot{O}} - \alpha_{\dot{S}} = 1.2$ *(77, 78)*	*(32)*
			C—P	0.96	For bond length of 1.68A.	*(81)*
Sulfur	S̈	1.5 2.0 1.5	C—S	1 1 0.8	Chosen as in the range commonly assumed of π electrons of heterocyclic systems, for [18] annulene trisulfide; π charges not too sensitive to parameter choice	*(23)*
	S̈	≅0	C—S	1	*h* from basis of equal electronegativities and similar ionization potentials of carbon and sulfur; *k* from the assumption that the exchange integral is a nearly constant fraction of the bond energy; applied to 1,4-dithiadiene and thiophene	*(43)*

S′	≅0	C—S′	≅0.8	Ionization potentials and resonance energies, applied to the Longuet-Higgins model of organic sulfur compounds	*(49)* from *(96)*
S′′	≅0	C—S′′	≅0.8		
		S′—S′′	≅1		
$\ddot{\mathrm{S}}$	0	$\mathrm{C}\overset{\cdots}{-}\mathrm{S}$	0.6	*h* set to zero on basis of similar electronegativities of carbon and sulfur; *k* from Lennard-Jones equation and bond length/bond energy relations	*(70)*
$\ddot{\mathrm{S}}$	0	$\mathrm{C}\overset{\cdots}{-}\mathrm{S}$	0.77	*k* from overlap integrals; used to calculate the electronic structure of thiazole	*(100)*
C (adjacent to both $\dot{\mathrm{N}}$ and $\ddot{\mathrm{S}}$)	0.1				
C (adjacent to $\ddot{\mathrm{S}}$ only)	0				
$\ddot{\mathrm{S}}$	1.1			Ionization energy of hydrogen sulfide	*(54)*
$\ddot{\mathrm{S}}$	0.8			Ionization energy of methyl mercaptan	*(54)*
$\ddot{\mathrm{S}}$	1.7			Chosen to give "best" fit to spectroscopic data and resonance energies	*(54)*
S	1			Endocyclic, not considering participation of *d* orbitals of sulfur	*(110)*
S	0			Endocyclic, considering participation of *d* orbitals of sulfur	*(110)*
		$\mathrm{C}-\ddot{\mathrm{S}}-$	0.6	Adopted by Pullman	*(78)*
		C=S	1.2	Adopted by Pullman	*(78)*
		C—S	0.93	For bond length of 1.68A.	*(81)*
		C—S	0.84	For bond length of 1.71A.	*(81)*
		C—S	0.7	Correlation with energies of N-V_1 transitions	*(110)*
S				Variation in sulfur integrals did not result in quantitative agreement with spin densities of the thioxanthone *S,S*-dioxide mononegative ion	*(101)*

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