N O T I C E

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I. Theory
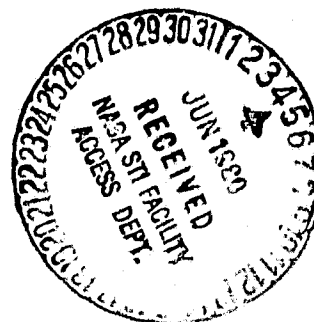
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ABSTRACT

Iterative Extended Hückel is modified by inclusion of explicit effective
internuclear and electronic interactions. The one-electron energies
are shown to obey a variational principle because of the form of the
effective electronic interactions. The modifications permit mimicking
aspects of valence bond theory with the additional feature that the
energies associated with valence bond-type structures are explicitly
calculated. In turn, a new hybrid molecular orbital-valence bond
scheme is introduced which incorporates variant total molecular elec-
tronic density distributions similar to the way that Iterative Extended
Hückel incorporates atoms. Nitrobenzene is used to illustrate the
approach.

1. Introduction

Iterative Extended Hückel (hereafter IEH) has been successfully applied to complex and diverse systems. These systems have ranged from porphyrins [1,2] to silica model sites [3]. IEH is one of the few semiempirical approaches which can inexpensively deal with large systems (e.g., greater than 40 atoms, 150 electrons). Moreover, most of the first 92 elements can be readily incorporated into an IEH program. As is true with any semiempirical method, there are inherent deficiencies in IEH [4,5]. Only gross comments can be made about geometries. For example, IEH does not explicitly treat nuclear-nuclear interaction terms. In fact, it does not incorporate either an effective nuclear-nuclear algorithm or an electronic-nuclear algorithm. IEH is an "atoms-in-molecule" approach and achieves a measure of sensitivity to the molecular environment through the charge self-consistency requirement. The self-consistent charge requirement does not yield a lower-bound variational energy for IEH, however. That is, the total electronic energy, which is a negative quantity, decreases in magnitude as charge self-consistency is achieved. Thus, an energy price is exacted in the IEH scheme by delocalizing electronic density. Useful modifications would correct the deficiencies mentioned above while retaining IEH's speed and versatility. It is the purpose of this note to report that such modifications (which also enhance sensitivity to the molecular environment) indeed are possible and can be incorporated with minimal disturbance to the desirable features of IEH. These modifications are made within the framework of the IEH "philosophy." That is, the structure of IEH is semiempirical, and all modifications are made within

that structure. The end product appears to be a much more versatile semiempirical program. It avoids or compensates for the pitfalls associated with standard IEH or CNDO, while successfully dealing with systems that IEH or CNDO cannot cope with. (This is detailed in the accompanying report.) It is still a semiempirical program, with concomitant limitations, that will be described in this note. We begin with a brief review of the relevant features of IEH.

2. Review of Standard IEH

IEH offers a prescription for the Hamiltonian matrix elements. The diagonal elements of the Hamiltonian matrix for the $\ell + 1$ iteration are given by

$$H^{(\ell+1)}_{k(i),k(i)} = (1 - |q_{i,\ell}|)E^0_{k(i)} + |q_{i,\ell}|E^{\pm}_{k(i)}. \qquad (2.1)$$

Here, $q_{i,\ell}$ is the charge on the ith atom from the ℓth iteration; $E^0_{k(i)}$, $E^{\pm}_{k(i)}$ are the valence orbital ionization energies of the kth orbital on the ith atomic center for the neutral $[E^0_{k(i)}]$ or singly charged $[E^{\pm}_{k(i)}]$ center. The proper $E^{\pm}_{k(i)}$ is determined by $q_{i,\ell}$. If $q_{i,\ell} < 0$, then $E^-_{k(i)}$ is chosen, for example. The prescription for the off-diagonal elements does vary [6], but the Wolfberg-Helmholz formula is representative, where

$$H^{(\ell+1)}_{k(i),n(j)} = \tfrac{1}{2}K\left(H^{(\ell+1)}_{k(i),k(i)} + H^{(\ell+1)}_{n(j),n(j)}\right) \cdot S_{k(i),n(j)}. \qquad (2.2)$$

Here, K is an interaction constant, usually taken to be greater than 1.75. In porphyrin work, it is set equal to 1.89 [1], for example. The

$H_{k(i),k(i)}^{(\ell+1)}$, $H_{n(j),n(j)}^{(\ell+1)}$ are the diagonal matrix elements for the $\underline{k}$th orbital on the $\underline{i}$th atom, and the $\underline{n}$th orbital on the $\underline{j}$th atom in the $\ell + 1$ iteration. The $S_{k(i),n(j)}$ are the integrated overlap between the $\underline{k}(i)$ and $\underline{n}(j)$ orbitals. The wavefunctions used to determine $S_{k(i),n(j)}$ are Slater-type orbitals optimized to agree with SCF overlap values, at least for bonding regions. Charge density is calculated using the Mulliken approximation where, after the $\underline{\ell}$th iteration, the charge

$$q_{i,\ell} = Z_i(\text{valence}) - \left(\sum_t \left\{ \sum_{k(i)} \eta_t \left[C_{t,k(i)}^{(\ell)} \right]^2 \right. \right.$$
$$\left. \left. + \tfrac{1}{2} \sum_{\substack{k(i),r(j) \\ i \neq j}} \eta_t C_{t,k(i)}^{(\ell)} C_{t,r(j)}^{(\ell)} S_{k(i),r(j)} \right\} \right). \tag{2.3}$$

The coefficients $C_{t,k(i)}^{(\ell)}$, for example, are the coefficients appearing in the t molecular orbital wavefunction, and they are associated with the $\underline{k}(i)$ orbitals in the $\underline{i}$th atom. Again, $S_{k(i),r(j)}$ are the integrated overlaps between the orbitals on the $\underline{i}$ and $\underline{j}$ atomic centers. The η_t are the occupation numbers of the molecular orbitals. The term

$$Z_i(\text{valence}) = Z_i - 2 \cdot \sum_{p=1}^{p(\text{valence})-1} p^2, \tag{2.4}$$

where Z_i is the nuclear charge on the $\underline{i}$th atom and the sum is over all shells below the valence shell. The one-electron molecular energies ε_t are assumed to contribute to the total energy,

$$E_{\text{total}} = \sum_t \eta_t \varepsilon_t. \tag{2.5}$$

3. The Modification

It has been argued using Extended Hückel (and by extension IEH) that nuclear-nuclear interactions are implicitly contained in E_{total} to some degree [4]. Certainly the degree is indeterminate. The state of affairs is amended by assuming that the electronic density found after the $\underline{\ell}$th iteration plays a role in determining explicit effective nuclear-nuclear interaction terms. The effective internuclear interaction between any two atomic centers is calculated by introducing the artifice that each center is surrounded by a non-conducting sphere whose radius equals one-half the distance between the centers. The Mulliken approximation is adopted along with the approximation that the probable electronic density within a sphere is determined by the radial portion of the atomic wavefunctions. The latter approximation insures invariance of the results to spacial orientation. Thus, if R_{ij} is the distance between the $\underline{i}$th and $\underline{j}$th atoms, the product of the screened nuclear charges (for the two atomic centers), after the $\underline{\ell}$th iteration, is given by

$$(Z_i Z_j)_{effective}^{(\ell)} = \left(Z_i(valence) - \sum_{k(i)} \int_0^{\frac{1}{2}R_{ij}} \phi_{k(i)}^2 r^2 dr \left\{ \sum_t \eta_t \left[C_{t,k(i)}^{(\ell)} \right]^2 \right. \right.$$

$$\left. + \frac{1}{2} \sum_{\substack{k(i),r(j) \\ i \neq j}} \eta_t C_{t,k(i)}^{(\ell)} C_{t,r(j)}^{(\ell)} S_{k(i),r(j)} \right\} \right)$$

$$\cdot \left(Z_j(valence) - \sum_{r(j)} \int_0^{\frac{1}{2}R_{ij}} \phi_{r(j)}^2 r^2 dr \left\{ \sum_t \eta_t \left[C_{t,r(j)}^{(\ell)} \right]^2 \right. \right.$$

$$\left. + \frac{1}{2} \sum_{\substack{k(i),r(j) \\ i \neq j}} \eta_t C_{t,k(i)}^{(\ell)} C_{t,r(j)}^{(\ell)} S_{k(i),r(j)} \right\} \right) . \quad (3.1)$$

The $\phi_{k(i)}$ and $\phi_{r(j)}$ are the radial portion of the STO functions adopted for the $\underline{k}(i)$ and $\underline{r}(j)$ atomic orbitals. As the distance between the two centers increases, the term

$$(Z_i Z_j)^{(\ell)}_{effective} \rightarrow q_{i,\ell} q_{j,\ell}, \quad R_{ij} \rightarrow \infty. \tag{3.2a}$$

That is, the expression in Eq. (3.1) approaches the product of the net charges on the $\underline{i}$th and $\underline{j}$th atoms after the $\underline{\ell}$th iteration at large distances. On the other hand, as the atoms are brought together,

$$(Z_i Z_j)^{(\ell)}_{effective} \rightarrow Z_i(\text{valence}) \; Z_j(\text{valence}), \quad R_{ij} \rightarrow 0. \tag{3.2b}$$

The effective nuclear-nuclear interaction term after the $\underline{\ell}$th iteration is given by

$$\sum_{i \neq j} (Z_i Z_j)^{(\ell)}_{effective}/R_{ij}, \tag{3.3}$$

in atomic units. Consequently,

$$E^{(\ell)}_{total} = \Sigma \eta_t \varepsilon_t^{(\ell)} + \Sigma (Z_i Z_j)^{(\ell)}_{effective}/R_{ij}. \tag{3.4}$$

The second type of modification attempts to address the problem of how an electron in an atomic orbital on a particular atomic center "experiences" its molecular environment. The valence orbital ionization energies (hereafter, VOIE) implicitly do account for one-center two-electron interactions to a large degree. Requiring charge self-consistency does result in the molecular environment impinging on an atomic center and, in turn, being affected by that center. However,

standard IEH does not explicitly treat multicenter electronic interactions. Such interactions are explicitly included in the modification scheme in an approximate fashion. Since the extent to which the VOIE and self-consistent charge requirement compensate for one-center and multicenter electronic interaction terms is uncertain, the modification will be sufficiently flexible that this very uncertainty can be used as a minimization condition. Consider an electron localized in an orbital on the ith atomic center, and assume the validity of the Mulliken approximation; an expression for the coulombic interaction between this electron and the electron density on the jth center then can be set equal to

$$\delta \varepsilon_{k(i),j}^{(\ell)} = a_{i,j} \cdot \sum_{n(j)} \rho_{n(j)}^{(\ell)} \int \phi_{k(i)}^2 r_{k(i),n(j)}^{-1} \phi_{n(j)}^2 d\tau. \tag{3.5}$$

Here, $a_{i,j}$ is a parameter dependent only upon the order and nature of the pair of elements involved in expression in Eq. (3.5), e.g., carbon, hydrogen. As implied, it is not assumed that $a_{j,i} = a_{i,j}$. The electronic density $\rho_{n(j)}^{(\ell)}$ refers to the electronic density assigned to the nth orbital on the jth atomic center after the ℓth iteration. All one-center terms are suppressed, since the VOIE are chosen to compensate for one-center terms. The total coulombic-type interaction of a localized electron in the kth orbital, ith atomic center in a molecular environment after the ℓth iteration, with reference to Eq. (3.5), is given by

$$\delta \varepsilon_{k(i)}^{(\ell)} = \sum_{j,j \neq 1} \delta \varepsilon_{k(i),j}^{(\ell)}. \tag{3.6}$$

In order to ensure rotational invariance, the ϕs appearing in the integral in Eq. (3.5) are restricted to the radial portion of the STO. That is, all coulombic interactions are treated as though occurring in a spherically symmetric environment. The $\delta\varepsilon_{k(i)}^{(\ell)}$ modifies the Hamiltonian matrix elements which involve the <u>k</u>th orbital on the <u>i</u>th center. With reference to Eq. (2.1), the element

$$H_{k(i),k(i)}^{(\ell+1)} = (1 - |q_{i,\ell}|)E_{k(i)}^0 + |q_{i,\ell}|E_{k(i)}^{\pm} + \delta\varepsilon_{k(i)}^{(\ell)}. \qquad (3.7)$$

Consequently, the off-diagonal elements $H_{k(i),n(j)}^{(\ell)} = H_{n(j),k(i)}^{(\ell)}$ also will be modified (following the prescription in Eq. (2.2)). It will be shown that, if $a_{i,j} \geq 0$ for all atomic types, the resulting set of molecular energies obey a variational principle.

In standard IEH, $H_{k(i),k(i)}^{(\ell+1)} < 0 \left[\delta\varepsilon_{k(i)}^{(\ell)} = 0\right]$, in general. The diagonal elements of the Hamiltonian matrix with $\delta\varepsilon_{k(i)} = 0$ will be denoted by $H_{k(i),k(i)}^{(\ell+1)}(0)$. When $a_{i,j} > 0$, then $\delta\varepsilon_{k(i)}^{(\ell)} \geq 0$ for any ℓ since the coulombic integrals are positive quantities as are the electronic densities. The equality holds only if the <u>i</u>th atom is infinitely distant from all other atomic centers. Therefore, for all cases of interest $\delta\varepsilon_{k(i)}^{(\ell)} > 0$. This term decreases the absolute magnitude of $H_{k(i),k(i)}^{(\ell+1)}$ with respect to that of $H_{k(i),k(i)}^{(\ell+1)}(0)$. In turn, the absolute magnitude of $H_{k(i),n(j)}^{(\ell+1)}$ also is decreased with respect to $H_{k(i),n(j)}^{(\ell+1)}(0)$. The assumption

$$H_{k(i),k(i)}^{(\ell+1)}(0) < 0$$

and the additional constraint that

$$0 < \delta\varepsilon_{k(i)}^{(\ell)} < |H_{k(i),k(i)}^{(\ell+1)}(0)|$$

for any $k(i)$, enables us to claim that when the mth eigenvalue of the Hamiltonian matrix $\underset{\sim}{H}^{(\ell+1)}(0)$, $\lambda_m^{(\ell+1)}(0) < 0$, then

$$\lambda_m^{(\ell+1)}(0) \leq \lambda_m^{(\ell+1)}, \tag{3.8a}$$

upon appeal to variational arguments [6,7]. Similarly, when $\lambda_m^{(\ell+1)}(0) > 0$,

$$\lambda_m^{(\ell+1)}(0) \geq \lambda_m^{(\ell+1)} \tag{3.8b}$$

from variational arguments [7; 2, Theorem 17]. Thus, viewing the Hamiltonian matrix as being parameterized by the set of $\{\delta\varepsilon_{k(i)}\}$, whose elements are positive and whose effect is to decrease the magnitude of the elements of the Hamiltonian matrix, yields the inequalities in Eqs. (3.8a,b). A brief overview concerning the interrelationship between the VOIE and the electronic interactions (basically coulombic in this scheme) might prove useful. The $\delta\varepsilon_{k(i)}$ decrease the VOIE (which is assumed to be a negative quantity). As a consequence, an electron will be held less tightly in that orbital on the ith atomic center. Formally, a smaller VOIE for the k(i) orbital can be shown to result in a decreased participation of k(i) in any particular bonding MO than would be the case if $\delta\varepsilon_{k(i)}$ were zero. In turn, the electronic density assigned to k(i) by the Mulliken approximation will be smaller and, hence, the charge on i larger. The electron density that must

be redistributed in order to conserve the total number of electrons will be redistributed among the remaining orbitals in the system. The additional electronic density will decrease the magnitudes of the VOIE of these orbitals, with reference to Eq. (2.1) and the following inequalities:

$$E_{k(i)}^{+} < E_{k(i)}^{0} < E_{k(i)}^{-}, \ E_{k(i)}^{0} < 0.$$

These inequalities are obeyed for any $\underline{k}(i)$. Consequently, the total molecular energy of the system is decreased in magnitude.

4. An Example of Imposed Charge Separation

Nitrobenzene was chosen as a test case for several reasons: (1) It is sufficiently complex that multicenter processes can be readily examined, yet it is an uncomplicated aromatic system. This simplicity is reflected by the fact that naive valence bond arguments correctly predict the attack site for electrophilic reaction, as an example. (2) It was of interest to explore what a blend of simple valence bond concepts with IEH would yield. All calculations were performed on the NASA-Ames CDC 7600. Firstly, the nitrogen electronic interaction terms were adjusted so that a stable charge of ca. +1 on the N was obtained when charge self-consistency was achieved. No other atomic center had explicit electronic interaction terms. This case was labelled NITRO in Fig. 1. The next case considered was inclusion of electronic interaction terms on the ortho carbons while maintaining a charge of ca. +1 on the nitrogen. It was found necessary to include both ortho carbons; asymmetric inclusion of electronic interaction terms resulted in

oscillation. Similarly, charge self-consistency could not be achieved for charges much greater than $+\frac{1}{2}$ on each of the ortho carbons. This case is labelled ORTHO in Fig. 1. Finally, the para position carbon was treated and charge self-consistency was achieved with net charges of ca. +1 on both the para carbon and nitrogen. These cases closely correspond to simple valence bond pictures. The ORTHO case basically represents the average of the valence bond structures where first one ortho carbon has a net charge of +1 and then the other ortho carbon has a net charge of +1. Table 1 lists all the eigenvalues for the four forms of nitrobenzene. In each case, the first 23 orbitals are filled. Comparison of the MO energies of the NITRO, ORTHO, and PARA entities with the corresponding MO energy for the NORMAL form shows that the inequalities in Eqs. (3.8a,b) are obeyed without exception, eigenvalue by eigenvalue. That is, in all cases

$$|\lambda_{i,NORMAL}| \geq |\lambda_{i,NITRO}|, \ |\lambda_{i,ORTHO}|, \ |\lambda_{i,PARA}|,$$

where $|\lambda_{i,F}|$ is the magnitude of the ith eigenvalue (MO) for the F form of nitrobenzene. This inequality can be systematically extended when the number of charge centers increases (all other factors such as charge magnitudes being equal). Thus, without exception

$$|\lambda_{i,NITRO}| \geq |\lambda_{i,ORTHO}|, \ |\lambda_{i,PARA}|.$$

The total energy of the various nitrobenzene forms are tabulated in Table 2. Comparison shows the massive energy debt incurred by imposing charge separation. All such structures (NITRO, ORTHO, PARA) are much less stable than normal nitrobenzene. Figure 1 presents a summary of

results. It is interesting that shifts of electronic density between ring and the NO_2 group are much smaller than shifts within the NO_2 or benzene. The distribution of electronic density for both ORTHO and PARA structures are in agreement with simple valence bond predictions (though the magnitudes are different from simple valence bond expectations). The major difference is that even with net charges of ca. +1 on both the nitrogen and ring, the net charges on the oxygens are in the neighborhood of $-\frac{1}{2}$ and not -1; the latter is the expected value from simple valence bond. The modification to IEH permits us to both mimic charge distributions and extract energy changes resulting from such distributions. The work also suggests that a hybrid MO-Valence Bond scheme is possible whereby the elements of the Hamiltonian matrix in this hybrid scheme are defined in the following fashion:

$$H_{F(a),F(b)} = \int \Psi_{F(a)} {}^H\Psi_{F(b)} d\tau = E_{F(a)} \delta_{F(a),F(b)} + \frac{1}{2}[1 - \delta_{F(a),F(b)}][E_{F(a)}$$

$$+ E_{F(b)}]K_{F(a),F(b)} S_{F(a),F(b)}, \qquad (4.1)$$

if the molecular wavefunctions for the structures NORMAL, NITRO, ORTHO, PARA take the form

$$\Psi_F = \prod_{i=1}^{23} \psi_{i,F} .$$

Here, $K_{F(a),F(b)}$ is a molecular interaction configuration constant, $E_{F(a)}$ and $E_{F(b)}$ are the respective energies of the molecular entities $F(a)$, $F(b)$.

The Kronecker delta

$$\delta_{F(a),F(b)} = 1, \quad F(a) = F(b),$$

$$= 0, \quad F(a) \neq F(b).$$

The overlap integral between the electronic density distributions represented by $F(a)$ and $F(b)$ for the nitrobenzene cases is given by

$$S_{F(a),F(b)} = \prod_{i=1}^{23} \left[\int \psi^*_{i,F(a)} \psi_{i,F(b)} d\tau \right]^2. \qquad (4.2)$$

When $F(a) = F(b)$,

$$H_{F(a),F(a)} = E_{F(a)}.$$

On the other hand, when $F(a) \neq F(b)$,

$$H_{F(a),F(b)} = \tfrac{1}{2} K_{F(a),F(b)} [E_{F(a)} + E_{F(b)}] S_{F(a),F(b)}.$$

Taking linear combinations of the $\Psi_{F(a)}$ as trial solutions leads to the requirement that

$$|\underset{\sim}{H} - E\underset{\sim}{S}| = 0. \qquad (4.3)$$

The elements of $\underset{\sim}{H}$, $H_{F(a),F(b)}$, are not configuration interaction terms in the usual sense where electronic correlation is obtained through mixing excited state with the ground state approximate wavefunctions. Here, structures which differ in charge distribution but are derived from the same set of atomic orbitals are allowed to mix. This roughly corresponds to a simple valence bond scheme. The full mixing of the

four density distributions, as depicted in Fig. 1, was not calculated.
Instead the simpler cases of (NORMAL, NITRO), (NORMAL, ORTHO), and
(NORMAL, PARA) have been treated with $K_{F(a),F(b)} = 1$. The Hamiltonian
matrix was transformed using a basis set which diagonalized the overlap
matrix; formally, the same procedure is used with IEH, except that here
the elements of the overlap matrix are not between two atomic centers,
but between two molecular electronic density distributions. For our
problem,

$$\underset{\sim}{H} - E\underset{\sim}{S} \rightarrow \underset{\sim\sim D}{US}^{-\frac{1}{2}}\underset{\sim}{U}^{\dagger}\underset{\sim\sim\sim}{HUS}_D^{-\frac{1}{2}}\underset{\sim}{U}^{\dagger} - E\underset{\sim}{1} , \tag{4.4}$$

where $\underset{\sim}{1}$ is the order 2 identity matrix and $\underset{\sim}{U}$ is an order 2 unitary
matrix

$$\underset{\sim}{U} = 2^{-\frac{1}{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \tag{4.5}$$

which obeys the relationship

$$\underset{\sim}{U}^{\dagger}\underset{\sim}{U} = \underset{\sim\sim}{UU}^{\dagger} = \underset{\sim}{1}. \tag{4.6}$$

The symbol $\underset{\sim D}{S}$ is the diagonalized overlap matrix. It is found that
the greater the number of centers of charge separation, the smaller the
overlap with the normal nitrobenzene configuration and correspondingly
smaller mixing with the ground state (normal nitrobenzene). In fact,
mixing ORTHO with NORMAL actually raises the final energy slightly (in
the seventh decimal place) with respect to the normal nitrobenzene ground
state energy. The results of this exercise are presented in Table 3.
It is noted, referring to Table 3, that the NITRO form is the most

important variant in that it mixes more with the NORMAL entity than either ORTHO or PARA. The IEH picture for the isolated nitrobenzene molecule, at least, appears to suffice.

5. Conclusion

Several modifications which permit internuclear interactions as well as electronic interactions to be accounted for explicitly have been introduced into conventional IEH. The electronic energies obey a variational principle as a result of the electronic interaction modification. The modified IEH has been applied to a simple, naive case where it was desired to impose charge separation and follow the effects. As a consequence, since certain gross features of valence bond theory could then be mimicked, a hybrid MO-Valence bond scheme was devised which employs total molecular electronic density distributions in a fashion similar to the way IEH incorporates atomic orbitals. This approach should be a useful tool for the organic chemist, since it is capable of quantitative evaluation of valence bond-type concepts, which still prove to be immensely valuable on a qualitative level. On the other hand, the modified IEH is a powerful tool for dealing with charge separation and for determining the effect of charge separation in reactions. This latter application will be the objective of the accompanying paper.

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8. Reference 2, Theorem 17

Table 1. The one-electron energies[a] for four variant total molecular electronic density distributions of nitrobenzene

MO	NORMAL[b]	NITRO[c]	ORTHO[d]	PARA[e]	
1	−37.17	−31.48	−30.32	−30.95	
2	−30.87	−29.29	−26.45	−27.39	F
3	−30.34	−26.45	−25.70	−26.08	I
4	−26.83	−25.66	−22.62	−24.39	L
5	−26.23	−25.43	−22.57	−22.74	L
6	−22.55	−20.11	−18.16	−18.83	E
7	−20.55	−20.06	−17.40	−18.45	D
8	−18.88	−17.28	−15.79	−16.13	M
9	−18.70	−16.88	−14.83	−15.34	O
10	−17.32	−14.94	−12.93	−13.63	L
11	−16.12	−14.78	−12.51	−13.60	E
12	−15.55	−14.58	−12.35	−13.51	C
13	−15.45	−14.12	−11.70	−12.76	U
14	−15.10	−13.11	−11.57	−11.70	L
15	−14.84	−12.98	−11.37	−11.48	A
16	−14.44	−12.48	−10.53	−11.36	R
17	−13.07	−12.44	−10.19	−10.70	O
18	−13.06	−11.42	−10.03	−10.64	R
19	−12.87	−11.41	−9.88	−10.16	B
20	−12.74	−10.53	−9.70	−10.15	I
21	−12.15	−9.02	−8.44	−8.72	T
22	−11.78	−8.82	−8.19	−8.52	A
23	−11.75	−8.76	−8.19	−8.46	L S

Table 1 — *Continued*

MO	NORMAL[b]	NITRO[c]	ORTHO[d]	PARA[e]	
24	−9.72	−7.66	−6.78	−7.02	
25	−7.16	−6.95	−5.39	−6.29	
26	−6.47	−5.70	−5.07	−4.86	U N F
27	−1.98	−1.89	−1.48	−1.62	I
28	+10.07	+9.00	+8.18	+8.47	L L E D
29	+10.40	+9.35	+8.51	+8.98	
30	+15.08	+13.10	+12.27	+12.38	M
31	+16.79	+15.10	+13.72	+13.92	O L
32	+20.66	+20.18	+17.91	+18.70	E C
33	+21.60	+21.18	+18.41	+20.10	U L
34	+26.04	+24.40	+20.38	+21.82	A R
35	+26.07	+24.63	+22.98	+22.02	
36	+33.44	+28.75	+26.00	+27.58	O R B
37	+45.01	+43.03	+37.27	+38.05	I T
38	+45.38	+43.71	+38.07	+40.50	A L
39	+62.15	+60.17	+52.45	+53.25	S
40	+62.57	+61.11	+53.22	+57.63	
41	+87.83	+85.62	+74.85	+78.47	

[a]In eV.

[b]Resulting electronic density distribution using conventional IEH
(see Fig. 1).

[c]Ca. +1 net charge maintained on the nitrogen (see Fig. 1).

[d]Ca. +1 net charge on nitrogen and ca. +½ net charge on both ortho car-
bons (see Fig. 1).

[e]Ca. +1 net charge on nitrogen and ca. +1 charge on para carbon (see
Fig. 1).

Table 2. Energies of four variant total molecular electronic density distributions of nitrobenzene

Type[a]	Total energy of the valence electrons (eV)	Total effective internuclear energies (eV)	Total effective energy (eV)
NORMAL	−856.8	+727.3	−129.5
NITRO	−764.1	+739.9	−24.2
ORTHO	−682.9	+741.3	+58.4
PARA	−711.3	+740.7	+29.4

[a]See Fig. 1.

Table 3. Overlap, coefficients, and energies for the interaction of several variant molecular electronic density distributions with NORMAL[a] nitrobenzene

(Type, NORMAL)	Overlap[b]	(C_{NORMAL}, C_{TYPE})[c]	Ground-state energy (eV)[d]
(NITRO, NORMAL)	4.72×10^{-2}	(1.0009, -0.0237)	-129.5775
(ORTHO, NORMAL)	6.31×10^{-4}	(1.0000, -0.0003)	-129.5028
(PARA, NORMAL)	3.26×10^{-3}	(1.0001, -0.0017)	-129.5281

[a]The electronic density of NORMAL nitrobenzene was obtained using conventional IEH (see Fig. 1).

[b]Overlap has been only approximately calculated. The overlap

$$\int \Psi^*_{TYPE} \Psi_{NORMAL} d\tau = \prod_{i=1}^{23} \left[\int \phi^*_{i,TYPE} \phi_{i,NORMAL} d\tau \right]^2,$$ where $\phi_{i,I}$ is the ith filled molecular orbital in an electronic configuration described by Ψ_I.

[c]The $\Psi_{\text{ground state}} = C_{NORMAL} \Psi_{NORMAL} + C_{TYPE} \Psi_{TYPE}$.

[d]The ground-state energy of NORMAL nitrobenzene $E_{NORMAL} = -129.5028$ eV.

FIGURE CAPTION

Fig. 1. The net charges and total overlap populations between neighboring atoms for four variants of the electronic density distribution for nitrobenzene. The structure labelled NORMAL was calculated with IEH. NITRO, ORTHO, and PARA used the electronic interaction modification to achieve a particular net charge on selected atoms, e.g., the nitrogen, ortho, and para carbons. The NITRO structure achieved charge self-consistency with the net charge shown on the nitrogen (0.97). ORTHO achieved charge self-consistency with the net charges shown on the nitrogen (0.91) and the ortho carbons (0.54). PARA achieved charge self-consistency with the net charges shown on the nitrogen (0.94) and the para carbon (0.81). The number in parentheses in the middle of a line on the left side of a structure is the total overlap population between the two atoms connected by that line. All other numbers (center and right) are the net charges on the appropriate atoms
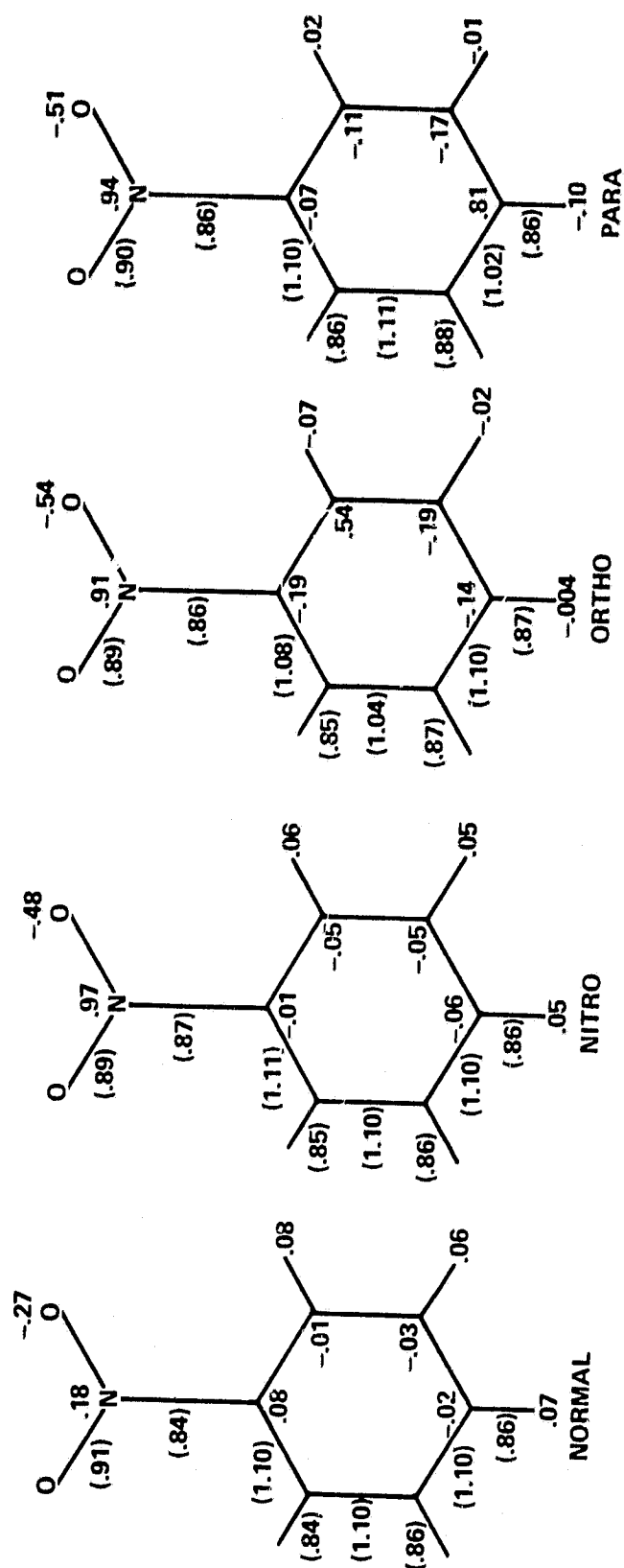
Fig. 1

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