

## PERTURBATION TREATMENT OF MOLECULAR GROUND STATE PROPERTIES

R. POLÁK

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Received October 3rd, 1973

---

A self-consistent perturbation procedure for calculating molecular ground state quantities is presented in which the zero-order wave function is built up of strictly localized orbitals. The method involves the construction of a fictitious unperturbed Hartree-Fock matrix, the solution of which is known in terms of localized orbitals and the pertinent perturbation. The general formalism uses a density matrix approach and is applied to the INDO semiempirical all-valence electrons SCF calculations of a few molecules in order to obtain information on the validity and limitations of the procedure.

---

In recent years considerable attention has been paid both to developing techniques capable of analyzing electronic wave functions from the standpoint of localizability of electron groups and to their applications to particular molecules and solids<sup>1</sup>. The emphasis has mostly been directed to the *a posteriori* analysis of various kinds of wave functions, and, as a result of these studies, there is no doubt that the canonical molecular orbitals have their equivalent counterpart represented by very well localized one-electron functions. Relatively less effort has been devoted to studying methods making explicit use of the localized and transferable property of these orbitals, particularly to numerical applications of such methods. Depending on the level of sophistication there are various ways to incorporate the presumption of electron localization into the theories. Within the semiempirical one-electron approaches, methods making a straight use of the strictly localized orbitals (SLO's) as describing the system of electrons<sup>2-7</sup> are the closest quantum chemical representation of the classical view of bonding, but, for certain purposes, they mean an oversimplification of the problem. Further, suitable applications of the idea of constructing the molecular wave function from molecular fragments have been successfully used in a number of theories and computations<sup>8-11</sup>. Also, in many-electron theories the idea of using localized orbitals to simplify perturbation and configuration interaction treatments has been many times advocated<sup>1,12-16</sup>.

In contrast to these theories we present a self-consistent perturbation approach in which we use a local orbital description of the system for calculating ground state properties<sup>1</sup> of molecules to comparable accuracy of Hartree-Fock calculations. Using the INDO Hamiltonian<sup>17</sup> we show numerical applications of the SC perturbation theory<sup>18-28</sup> to a number of molecules and discuss the results from the viewpoint of a comparison with the pertinent SCF solutions and transferability of SLO's between molecules containing identical atomic groupings.

### Self-Consistent Perturbation Theory

We consider a system of  $2n$  electrons described by a single-determinant wave function with doubly occupied MO's  $\psi_i$ , each of which is expressed as a linear combination of  $m$  orthonormal AO's,  $\chi = (\chi_1, \chi_2, \dots, \chi_m)$ ,

$$\psi_i = \chi c_i. \quad (1)$$

In Eq. (1) and in the following we are using the customary matrix notation (compare e.g.<sup>43-45</sup>). The corresponding energy expectation value  $E_0$  can be expressed in terms of the atomic representation<sup>12</sup>

$$E_0 = 2\text{Tr}\{\mathbf{h}\mathbf{r}_0\} + \text{Tr}\{\mathbf{g}(\mathbf{r}_0)\mathbf{r}_0\}, \quad (2)$$

where  $\mathbf{h}$  and  $\mathbf{g}(\mathbf{r}_0)$  refer to the one-electron part of the pertinent Hamiltonian and to the interaction energy of the electrons, respectively, and  $\mathbf{r}_0$  is the first-order density matrix,

$$\mathbf{r}_0 = \sum_{i=1}^n |\psi_i\rangle \langle \psi_i|. \quad (3)$$

Before proceeding further, in addition to  $\mathbf{r}_0$  projecting onto the manifold of occupied orbitals<sup>12,29</sup>, let us introduce its complement  $\mathbf{q}_0$ ,  $\mathbf{q}_0 = \mathbf{I} - \mathbf{r}_0$  and the projection matrices

$$\begin{aligned} \mathbf{r}_0^{(i)} &= |\psi_i\rangle \langle \psi_i|, \\ \mathbf{q}_0^{(k)} &= |\psi_k\rangle \langle \psi_k| \end{aligned} \quad (4)$$

associated with individual MO's, where the indices  $i$  and  $k$  refer to the occupied and virtual orbitals, respectively.

If the MO's are the solutions of the Hartree-Fock equation

$$(\mathbf{f}(\mathbf{r}_0) - \varepsilon)\mathbf{c} = \mathbf{0}, \quad (5)$$

where  $\mathbf{f}(\mathbf{r}_0) = \mathbf{h} + \mathbf{g}(\mathbf{r}_0)$ ,  $\varepsilon = \text{diag}(\varepsilon_1, \varepsilon_2, \dots, \varepsilon_m)$  and  $\mathbf{c} = (\mathbf{c}_1, \mathbf{c}_2, \dots, \mathbf{c}_m)$ ,  $E_0$  corresponds to the variationally optimized value. The solution of Eq. (5) can be obtained in such a way that, instead of seeking the roots of the pertinent secular determinant, we are looking for the singularities of the determinant of the matrix

$$\mathbf{G}_0(z) = (z\mathbf{I} - \mathbf{f}(\mathbf{r}_0))^{-1} \quad (6)$$

considered as a function of the complex variable<sup>30</sup>  $z$ . This kind of formulation permits a simple expression of the effect of single-particle perturbation upon the original

system in preserving self-consistency, since if  $\mathbf{f}(\mathbf{r}_0)$  changes to  $\mathbf{F}(\mathbf{r}) = \mathbf{f}(\mathbf{r}) + \mathbf{V}$ , the resolvent (or Green's function) of the perturbed system can be expressed by means of the Dyson equation<sup>30</sup>

$$\mathbf{G}(z) = (zI - \mathbf{F}(\mathbf{r}))^{-1} = \sum_{u=0}^{\infty} \mathbf{G}_0(z) (\mathbf{W}\mathbf{G}_0(z))^u, \quad (7)$$

where  $\mathbf{W} = \mathbf{V} + \mathbf{g}(\Delta\mathbf{r})$  by using the property<sup>31</sup> of  $\mathbf{g}(\mathbf{r})$ ,  $\mathbf{g}(\mathbf{r}_0 + \Delta\mathbf{r}) = \mathbf{g}(\mathbf{r}_0) + \mathbf{g}(\Delta\mathbf{r})$ . Since the perturbed first-order density matrix  $\mathbf{r}$  can be obtained as the sum of residues of the resolvent  $\mathbf{G}(z)$  inside the closed contour in the complex plane enclosing eigenvalues associated with occupied orbitals ("Coulson contour")<sup>32-34</sup>, it is possible to cast  $\mathbf{r}$  into the form of a series

$$\mathbf{r} = \mathbf{r}_0 + \mathbf{r}_1 + \mathbf{r}_2 + \dots \mathbf{r}_u \dots, \quad (8)$$

where

$$\mathbf{r}_u = (2\pi i)^{-1} \oint_C \mathbf{G}_0(\mathbf{W}\mathbf{G}_0)^u dz. \quad (9)$$

It was shown<sup>35</sup> that by using this resolvent operator formalism it is possible not only to rederive the basic formulae of the Hartree-Fock perturbation theory, but also to enlighten the relations between the SC perturbation theory and both the many-electron theory and the regular Hartree-Fock formalism. For instance, after integration of the expression (8) for  $u = 1$ , the first-order contribution becomes

$$\mathbf{r}_1 = \sum_r \sum_k (\varepsilon_i - \varepsilon_k)^{-1} (\mathbf{r}_0^i \mathbf{W} \mathbf{q}_0^k + \mathbf{q}_0^k \mathbf{W} \mathbf{r}_0^i). \quad (10)$$

Thus we get the first-order correction to the density matrix which is in full agreement with McWeeny's derivation<sup>19,21</sup> based on the projection operator method.

### *Perturbation Treatment for Localized Orbitals*

Suppose we have available a first-order density matrix  $\mathbf{r}_0$  which, e.g., we have constructed by means of orthonormal SLO's  $\boldsymbol{\eta}$ ,

$$\boldsymbol{\eta} = (\eta_1, \eta_2, \dots \eta_n) = \boldsymbol{\chi} \mathbf{C}, \quad (11)$$

representing bonds and lone pairs of the molecule under consideration. We are also given  $\mathbf{h}$  and  $\mathbf{g}(\mathbf{r}_0)$ ,  $\mathbf{F}(\mathbf{r}_0) = \mathbf{h} + \mathbf{g}(\mathbf{r}_0)$ , and in order to make use of the perturbation formalism described above, we have to set up  $\mathbf{f}(\mathbf{r}_0)$ , so that<sup>12</sup>

$$\mathbf{f}(\mathbf{r}_0) \mathbf{r}_0 = \mathbf{r}_0 \mathbf{f}(\mathbf{r}_0), \quad (12)$$

where

$$\mathbf{f}(\mathbf{r}_0) = \mathbf{F}(\mathbf{r}_0) - \mathbf{V}. \quad (13)$$

Thus, we have to decompose  $\mathbf{F}(\mathbf{r}_0)$  into a fictitious unperturbed Hartree-Fock matrix, the solution of which is known in terms of the first-order density matrix  $\mathbf{r}_0$ , and the perturbation  $\mathbf{V}$ . This may be achieved by the application of the projection operator method<sup>19,36</sup> on Eq. (12) which yields:

$$\begin{aligned} \mathbf{r}_0 \mathbf{F}(\mathbf{r}_0) \mathbf{r}_0 - \mathbf{r}_0 \mathbf{F}(\mathbf{r}_0) \mathbf{r}_0 &= \mathbf{r}_0 \mathbf{V} \mathbf{r}_0 - \mathbf{r}_0 \mathbf{V} \mathbf{r}_0, \\ \mathbf{r}_0 \mathbf{F}(\mathbf{r}_0) \mathbf{q}_0 &= \mathbf{r}_0 \mathbf{V} \mathbf{q}_0, \\ \mathbf{q}_0 \mathbf{F}(\mathbf{r}_0) \mathbf{r}_0 &= \mathbf{q}_0 \mathbf{V} \mathbf{r}_0, \\ \mathbf{q}_0 \mathbf{F}(\mathbf{r}_0) \mathbf{q}_0 - \mathbf{q}_0 \mathbf{F}(\mathbf{r}_0) \mathbf{q}_0 &= \mathbf{q}_0 \mathbf{V} \mathbf{q}_0 - \mathbf{q}_0 \mathbf{V} \mathbf{q}_0. \end{aligned} \quad (14)$$

We now observe that  $\mathbf{r}_0 \mathbf{V} \mathbf{r}_0$  and  $\mathbf{q}_0 \mathbf{V} \mathbf{q}_0$  are arbitrary and, therefore, we may put

$$\mathbf{V} = \mathbf{r}_0 \mathbf{F}(\mathbf{r}_0) \mathbf{q}_0 + \mathbf{q}_0 \mathbf{F}(\mathbf{r}_0) \mathbf{r}_0 \quad (15)$$

to satisfy Eqs (12) and (13). Generally, this kind of arbitrariness of dividing  $\mathbf{F}(\mathbf{r}_0)$  into two parts may be used for affecting the perturbation treatment in view of improving the convergence and complexity of the solution<sup>16,37</sup>. Particularly, using Eq. (15) we retain the symmetry of  $\mathbf{f}(\mathbf{r}_0)$  with reference to  $\mathbf{F}(\mathbf{r})$  or, in other words, the eigenvectors  $\mathbf{c}$  corresponding to  $\mathbf{f}(\mathbf{r}_0)$  are symmetry orbitals for the molecular symmetry group. The diagonalization of  $\mathbf{f}(\mathbf{r}_0)$  yields eigenvalues  $\epsilon_u$ ,  $u = 1, \dots, n$ , needed for the calculation of the perturbation terms of the kind (10).

It is note-worthy that the unitary transformation matrix relating the eigenfunctions  $\psi$  (which are expected to resemble considerably the exact MO's of  $\mathbf{F}(\mathbf{r})$ ) to the SLO's can be simply written as the product of two matrices,

$$\boldsymbol{\eta} = \boldsymbol{\psi}(\tilde{\mathbf{c}}\mathbf{C}), \quad (16)$$

where  $\tilde{\mathbf{c}}$  denotes the transpose of  $\mathbf{c}$ . Hence, we may easily construct a pseudopotential equation the solution of which are the SLO's originally introduced into the scheme. Consequently, it may be conjectured that by means of the procedure described above a useful first approximation to self-consistent pseudopotentials<sup>38-42</sup> in molecules leading to localized orbitals might be obtained.

### Numerical Applications

The procedure described above has been applied to the INDO Hamiltonian in its original version<sup>17</sup>. It is believed this will yield a proper insight into the features of

the suggested perturbation treatment, particularly with respect to the solution of Eq. (10) and the accuracy of the truncated perturbation expansion. Fortunately, within the INDO approximation the basis set of AO's is orthonormal, as it has been assumed in the theoretical consideration. Of course, non-orthogonal basis sets of AO's could be admitted on the same footing after their symmetrical orthogonalization.

As the starting point for the calculations we used the SLO's<sup>43</sup> defined as normalized one-centre functions  $\varphi_A$  and two-centre functions  $\eta_{AB} = q(\varphi_A + b\varphi_B)$  describing lone pairs and bonds, respectively. Capitals,  $\varphi$ 's and  $b$  denote the centres (atoms), hybrid orbitals (HO's) and the bond polarity parameter, respectively. Recently, there have been developed procedures for constructing both optimum hybrids and optimum bond orbitals at given hybrids, based on the maximization of the projection of localized bond orbitals onto the occupied SCF space<sup>44,45</sup>. From now on, if we refer to optimized quantities, optimization with respect to the above mentioned criterion of maximum projection will be meant. In order to test the convergence and the effectiveness of the perturbation procedure, various sets of SLO's have been used, differing in the closeness with which the SLO-approximation approaches the "exact" SCF solution. Thus, besides using optimized hybrids, calculations based on "directed" HO's<sup>46</sup> have been carried out. The "directed" HO's for second row elements have been defined in the following way: if  $q$  equivalent HO's on a given atom are to be established, at first, the  $q$  HO's of the form  $(q)^{-1/2}[(2s) + (q-1)^{1/2}(2p)]$  are constructed, where  $(2p)$  stands for a normalized linear combination of  $(2p)$  AO's representing the particular spatial orientation, either along the given bond or of the hypothetical lone pair. Since we require orthonormal orbitals, we define those orbitals as the final ones which are achieved through the successive Löwdin's symmetric orthogonalization. HO's defined in this way are close to the classical ones and can be easily constructed according to the geometrical arrangements in the molecule. Four possibilities of forming the SLO's have been considered:

- (a) optimized HO's, optimized SLO's SCF  $\pi$  MO's
- (b) directed HO's, optimized SLO's, SCF  $\pi$  MO's
- (c) directed HO's, fixed (transferable) SLO's, SCF  $\pi$  MO's
- (d) directed HO's, fixed (transferable) SLO's, localized  $\pi$  orbitals.

Let us add a few remarks to the numerical solution of Eq. (10). Bearing in mind the remark to Eq. (10), substituting for  $\mathbf{W}$ , and in view of Eq. (15) we may conveniently rewrite Eq. (10) in the form

$$\begin{aligned} \mathbf{r}_1 = & \sum_{i,k} \{(\varepsilon_i - \varepsilon_k)^{-1} [\mathbf{F}(\mathbf{r}_0)]_{ik} (\mathbf{c}_i \mathbf{c}_k^+ + \mathbf{c}_k \mathbf{c}_i^+)\} + \\ & + \sum_{i,k} \{(\varepsilon_i - \varepsilon_k)^{-1} [\mathbf{g}(\mathbf{r}_1)]_{ik} (\mathbf{c}_i \mathbf{c}_k^+ + \mathbf{c}_k \mathbf{c}_i^+)\}, \end{aligned} \quad (17)$$

TABLE I

Molecular Energies (mol. en., a.u.) and Gross Charges on the Hydrogen Atom (GC,  $10^{-4}$  units of the proton charge) Obtained by SCF Calculation and SC-Perturbation Treatments Based on Various Zero-Order Functions; Perturbation Energies Are Given Relative to the SCF Value

SCF "exact"	Type of calculation	Methane		Acetylene		Ethylene		Ethane	
		mol. en.	GCH	mol. en.	GCH	mol. en.	GCH	mol. en.	GCH
		-9.86091	-95	-14.83615	537	-16.54941	-3	-18.30372	-185
(a)	0. order	0.00566	-95	0.02267	543	0.05831	-3	0.05664	-188
	1. order	-0.00774	-94	-0.3088	541	-0.08228	-28	-0.07719	-195
	purif.	0	-95	0	535	0	3	0	-182
(b)	0. order	-	-	0.02835	591	0.06679	5	0.05905	-187
	1. order	-	-	-0.03948	572	-0.09402	-22	-0.08029	-195
	purif.	-	-	0	527	0	1	0	-182
(c)	0. order	0.00629	-198	0.02879	512	0.06685	0	0.05920	-198
	1. order	-0.00849	-94	-0.03987	573	-0.09407	-22	-0.08042	-195
	purif.	0	-95	0	527	0	1	0	-182
	fixed corr.	-0.00432	-99	-0.01947	622	-0.04564	63	-0.04103	-140
	purif.	0.00040	-99	0.00203	596	0.00474	68	0.00384	-136

where  $[A]_{ik} = [A]_{kl} = \mathbf{c}_i^+ \mathbf{A} \mathbf{c}_k$ , if  $\mathbf{A}$  is Hermitian ( $\mathbf{A} = \mathbf{A}^+$ ) and the  $\mathbf{c}_i$ 's are real. Thus,  $\mathbf{r}_1$  equals the sum of two matrices, the first being fixed and the second,  $\mathbf{r}_1$  - dependent. The solution of Eq. (17) has been obtained iteratively, starting by taking  $\mathbf{r}_1 = 0$  in the right-hand side of Eq. (17), as was suggested by Mc Weeny<sup>19</sup>. From numerical evidence it has been concluded that it is sufficient to impose the convergence criterion upon the matrix diagonal elements, since the off-diagonal corrections are smaller than the diagonal ones by the order of magnitude. Requiring the difference of two matrix elements of two successive iteration steps to be smaller than  $5 \cdot 10^{-5}$ , the average number of iteration steps has ranged from 6 to 8. Moreover, it has been found that the principal contribution to  $\mathbf{r}_1$  comes from the fixed part; however, the second one is not negligible.

The knowledge of the first-order perturbed density matrix suffices to determine the energy to the third order<sup>47</sup>, and, therefore, it might be conjectured that by limiting ourselves to computing  $\mathbf{r}_1$  we might obtain results of sufficient accuracy.

The perturbed density matrix including the first-order correction  $\mathbf{r}_1$  is idempotent

TABLE II

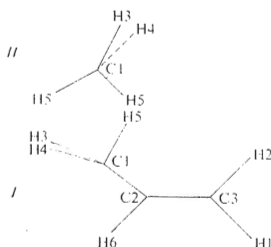
Molecular Energies (a.u.) Obtained by SCF Calculation and SC-Perturbation Treatments Based on Various Zero-Order Functions; Perturbation Energies Are Given Relative to the SCF Value

Type of calculation		Propylene		Butadiene	
		staggered	eclipsed	<i>trans</i>	<i>cis</i>
SCF	"exact"	-25.01295	-25.01082	-31.71463	-31.70845
(a)	0. order	0.12183	0.11951	0.13493	0.13904
	1. order	-0.16885	-0.16642	-0.18648	-0.19155
	purif.	0.00002	0.00003	0.00001	0.00003
(b)	0. order	0.13193	0.12969	0.15226	0.15699
	1. order	-0.18355	-0.18116	-0.21199	-0.21833
	purif.	0.00003	0.00003	0.00002	0.00003
(c)	0. order	0.13117	0.12891	0.15113	0.15583
	1. order	-0.18275	-0.18038	-0.21105	-0.21735
	purif.	0.00003	0.00002	0.00003	0.00004
(d)	0. order	0.13088	0.12863	0.19882	0.19979
	1. order	-0.18295	-0.18054	-0.28254	-0.28613
	purif.	0.00005	0.00003	0.00002	0.00004
	fixed corr.	-0.09082	-0.08855	-0.13739	-0.13580
	purif.	0.00887	0.00896	0.01403	0.01485

TABLE III

Atomic Gross Charges ( $10^{-4}$  units of the proton charge) and Dipole Moments (Debyes) for Propylenes Staggered and Eclipsed Obtained by SCF Calculation and SC-Perturbation Treatments Based on Two Kinds of Zero-Order Functions

Type of calculation	C1	C2	C3	H1	H2	H3	H4	H5	H6	Dipole moment
SCF "exact" staggered <sup>(I)</sup>	619	331	-138	-84	-68	-170	-170	-171	-149	0.2578
(a) 0. order	552	346	-56	-58	-54	-199	-199	-167	-163	0.0821
1. order	594	402	-90	-76	-71	-199	-199	-184	-177	0.1599
purif.	659	329	-211	-83	-60	-160	-160	-178	-136	0.3170
(d) 0. order	594	0	0	0	0	-198	-198	-198	0	0.0718
1. order	602	394	-93	-71	-71	-203	-203	-188	-166	0.1646
purif.	666	335	-206	-90	-66	-161	-161	-179	-137	0.3258
fixed corr.	544	124	-199	31	32	-171	-171	-157	-34	0.0792
purif.	585	106	-254	17	28	-150	-150	-155	-28	0.1434
SCF "exact" eclipsed <sup>(II)</sup>	619	334	-141	-77	-70	-148	-148	-215	-155	0.2053
(a) 0. order	552	352	-62	-53	-58	-180	-180	-204	-166	0.0927
1. order	591	405	-95	-70	-72	-183	-183	-213	-181	0.1247
purif.	658	331	-211	-75	-60	-139	-139	-220	-145	0.2523
(d) 0. order	594	0	0	0	0	-198	-198	-198	0	0.0718
1. order	597	397	-97	-66	-72	-187	-187	-216	-170	0.1294
purif.	665	338	-207	-82	-67	-140	-140	-221	-145	0.2624
fixed corr.	539	123	-200	34	32	-162	-162	-171	-34	0.0666
purif.	581	105	-251	21	28	-139	-139	-175	-30	0.1050





to first order. Therefore, it is both interesting and important to determine the extent to which this quasi-idempotency affects the calculated quantities. To define a strictly idempotent matrix  $\mathbf{r}'$  close to  $\mathbf{r} = \mathbf{r}_0 + \mathbf{r}_1$  it is sufficient to form a new set of  $m$  vectors diagonalizing  $\mathbf{r}$  and to use those  $n$  vectors for the construction of  $\mathbf{r}'$  whose associated eigenvalues are close to 1. We note, of course, that this approach resembles the kind of analysis applied to many-electron wave function from the viewpoint of natural orbitals<sup>29</sup>.

It should, however, be born in mind that Eq. (17) represents a nonlinear problem and that the difficulties with the iteration process of solving the regular SCF equations (5) are thus partially retained. The remedy for this situation is in decoupling Eq. (17), as it has been done within perturbation calculations on atomic structures<sup>27,28</sup>. We shall define the decoupled solution of Eq. (19) as that which equals the fixed part ( $\mathbf{r}_1$  - independent) of the right-hand side of Eq. (17):

## RESULTS AND DISCUSSION

The SC perturbation approach described in the previous section has been applied to a number of hydrocarbons and to molecules  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{NH}_3$  and  $\text{H}_2\text{CO}$  as listed in Tables I through V. The equilibrium geometries for the hydrocarbons were taken the same as in paper<sup>44</sup>. For the molecules  $\text{H}_2\text{O}$  and  $\text{H}_2\text{CO}$  we have used the data  $d(\text{O}-\text{H}) = 0.9584 \text{ \AA}$ ,  $\angle \text{HOH} = 104.45^\circ$  and  $d(\text{C}-\text{O}) = 1.22 \text{ \AA}$ ,  $d(\text{C}-\text{H}) = 1.08 \text{ \AA}$ ,  $\angle \text{HCH} = 120^\circ$ , respectively. The zeroth order, perturbed and purified perturbed first-order density matrices - corresponding to the coupled and event. decoupled (*i.e.* with fixed correction) solution - have been employed for the calculation of molecular ground state energies and dipole moments, and analyzed by presenting gross charges on atoms. For the sake of comparison, in all tables are also given values referring to the corresponding INDO SCF calculation which represents the exact solution of the problem to which the SC perturbation treatment is applied.

Our results for the selected group of hydrocarbons are displayed in Tables I-IV. Among the four versions of constructing the starting density matrix  $\mathbf{r}_0$ , as they have been introduced above, the first two ((a) and (b)) rely upon the knowledge of the SCF solution of the problem under consideration. The listed perturbation calculation results show an excellent agreement with the "exact" quantities, especially for the total molecular energies obtained by means of the purified density matrices. It is note-worthy that the purification process does not improve substantially the data related to the charge distribution in molecules.

On grounds of analyzing optimized SLO's of various C-H and C-C bonds we have found that the polarity parameter in the bond orbital  $q[(\text{C}) + b(\text{H})]$  can be well approximated by setting  $b$  equal to 1.02, 1.00 and 0.95 depending on whether the hybrid orbital (C) located on the carbon atom is of the type  $sp^3$ ,  $sp^2$  and  $sp$ , respectively, and that all C-C bonds in our investigated molecules can be described by

bond orbitals with<sup>46</sup>  $b = 1.0$ .  $\sigma$  orbitals determined in this way and  $\pi$  orbitals taken from the SCF calculation have been the starting orbitals for perturbation

TABLE IV

Atomic Gross Charges ( $10^{-4}$  units of the proton charge) and Dipole Moments (Debyes) for Butadienes *trans* and *cis* Obtained by SCF Calculation and SC-Perturbation Treatments Based on Two Kinds of Zero-Order Functions

Type of calculation	C1	C2	H1	H2	H3	Dipole moment
SCF "exact" <i>trans</i> <sup>(1)</sup>	-90	328	-85	-23	-130	0
(a) 0. order	-53	255	-57	-11	-134	0
1. order	-43	322	-87	-37	-155	0
purif.	-130	371	-92	-23	-126	0
(d) 0. order	0	0	0	0	0	0
1. order	-62	327	-78	-39	-149	0
purif.	-119	375	-99	-30	-127	0
fixed corr.	-219	184	24	48	-38	0
purif.	-240	221	9	47	-37	0
SCF "exact" <i>cis</i> <sup>(1)</sup>	-106	351	-90	8	-163	0.1616
(a) 0. order	-86	287	-65	22	-159	0.0706
1. order	-71	344	-93	-4	-175	0.1299
purif.	-136	384	-96	6	-158	0.2035
(d) 0. order	0	0	0	0	0	0
1. order	-82	337	-91	-6	-159	0.1673
purif.	-122	393	-108	1	-163	0.2107
fixed corr.	-223	176	12	67	-32	0.0919
purif.	-239	219	-3	65	-43	0.1188

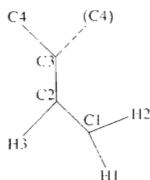


TABLE V  
Molecular Energies (mol. en., a.u.), Dipole Moments (dip. m., Debyes) and Gross Charges (GC,  $10^{-4}$  units of the proton charge) Obtained by SCF Calculation and SC-Perturbation Treatments Based on Two Kinds of Zero-Order Functions; Perturbation Energies Are Given Relative to the SCF Value

Type of calculation	SCF "exact"	(a)			(b)					
		0. order	1. order	purif.	0. order	1. order	purif.			
H <sub>2</sub> O	mol. en.	-19.01424	0.00037	-0.00060	0	0.04041	-0.08478	0.00005	-0.01408	0.00879
	dip. m.	2.1816	2.2139	2.1817	2.1816	2.3243	2.4196	2.1475	2.3800	2.3174
	GC O	-3340	-3341	-3341	-3340	-3718	-3615	-3201	-3941	-3841
HCN	mol. en.	-18.39993	0.02093	-0.03141	0.00004	0.04057	-0.07214	0.00018	-0.01953	0.00629
	dip. m.	2.4556	2.6349	2.5527	2.3962	2.8245	2.6890	2.3128	2.6383	2.5245
	GC C	905	967	885	819	1165	921	710	860	788
	GC N	-1399	-1531	-1435	-1299	-1770	-1513	-1168	-1498	-1387
NH <sub>3</sub>	mol. en.	-13.36252	0.00292	-0.00415	0	0.00908	-0.01545	0.00001	-0.00433	0.00143
	dip. m.	2.0148	2.1287	2.0148	2.0147	2.0061	2.0509	2.0111	2.0026	1.9936
	GC N	-2529	-2532	-2531	-2528	-2584	-2575	-2514	-2705	-2692
H <sub>2</sub> CO	mol. en.	-25.73678	0.06675	-0.12757	0.00225	0.10655	-0.21384	0.00442	-0.06248	0.01371
	dip. m.	1.9993	2.7909	2.2359	1.5403	3.0050	2.3268	1.3504	2.4506	2.0873
	GC O	-2381	-3293	-2605	-1595	-3571	-2699	-1305	-2661	-2149
	GC C	3285	3759	3314	2664	4044	3469	2463	2990	2648

calculations denoted by (c), the results of which practically coincide with those obtained by means of version (b).

Finally, version (d) of determining  $r_0$  has been chosen without any relationship to the SCF solution at all. In this treatment the sigma orbitals equal those used in version (c) and the pi orbitals are bond orbitals with  $b = 1.0$ , located at sites indicated by structural formulae. Of course, among all sample calculations this type of approximation exerts a salient influence on the zero order description of both butadiene isomers. The crudeness of the approximation manifests itself in the corresponding energy expectation values (Table II) and charge distributions (Table IV), the latter being uniform with respect to all atoms in both butadiene molecules. Carrying out the perturbation procedure up to first order we obtain again almost "exact" molecular energies and charge distributions which compare favourably with "exact" ones.

Such a good convergence behaviour of the perturbation calculations on hydrocarbons might raise the suspicion that it is due to the small polarity of these molecules. Therefore, analogous calculations have been performed for a few molecules with a pronounced redistribution of charge within the system relative to the atoms and a large dipole moment. Table V shows the molecular energies, dipole moments and charge distributions obtained in these calculations for water, hydrogen cyanide, ammonia and formaldehyde. Note that the deviations of the perturbation calculation results from the reference SCF calculation values are of the same order of magnitude as in the case of hydrocarbons with the exception of  $H_2CO$  for which the SLO description represents a poor zero-order approximation.

It is also note-worthy that even the decoupled solution of the first-order contribution (i.e. the fixed correction) to the density matrix, calculated for the less accurate zero-order functions, yields physical quantities of fairly good accuracy when compared with the coupled solution. Thus, the decoupled solution hands us approximate SCF physical quantities on a plate without making an iterative process.

## CONCLUSIONS

We have found that the self-consistent perturbation treatment of the electronic structure of molecules based on localized orbitals including first-order changes in the Fock-Dirac density matrix yields ground state expectation values of satisfactory accuracy when compared with reference SCF values and thus represents an alternative SCF solution of the given problem. Therefore in general, this approach might be of use for studying the convergence properties of the iteration solution of the regular SCF pseudo-eigenvalue problem.

It is also believed that the theoretical framework of the method developed in this paper allows for a simple study of pseudopotentials in molecules leading to localized orbitals.

*My thanks are due to Professor R. L. Flurry, jr, Professor W. D. Jones, and Dr M. Tomášek for reading the manuscript and some valuable suggestions.*

## REFERENCES

1. Weinstein H., Pauncz R., Cohen M.: *Advan. Atom. Mol. Phys.* 7, 97 (1971).
2. Brown R. D.: *J. Chem. Soc.* 1953, 2615.
3. Dewar M. J. S., Pettit R.: *J. Chem. Soc.* 1954, 1654.
4. Del Re G.: *J. Chem. Soc.* 1958, 4031.
5. Amos A. T., Musher J. I.: *J. Chem. Phys.* 49, 2158 (1968).
6. Daudel R.: *Comp. Rend.* 270, 929 (1970).
7. Herndon W. C.: *Chem. Phys. Letters* 10, 460 (1971).
8. Moffitt W.: *Proc. Roy. Soc. (London)* A210, 245 (1951).
9. Arai T.: *Rev. Mod. Phys.* 32, 370 (1960).
10. Christoffersen R. E., Maggiora G. M.: *Chem. Phys. Letters* 3, 419 (1969).
11. von Niessen W.: *J. Chem. Phys.* 55, 1948 (1971).
12. McWeeny R.: *Rev. Mod. Phys.* 32, 335 (1960).
13. Sinanoğlu O.: *J. Chem. Phys.* 37, 191 (1962).
14. Nesbet R. K.: *Advan. Chem. Phys.* 9, 321 (1965).
15. Diner S., Malrieu J. P., Claverie P.: *Theoret. Chim. Acta* 13, 1 (1969).
16. Amos A. T., Musher J. I.: *J. Chem. Phys.* 54, 2380 (1971).
17. Pople J. A., Beveridge D. L., Dobosh P. A.: *J. Chem. Phys.* 47, 2026 (1967).
18. Lefebvre R., Moser C. in the book: *Calcul des Fonctions d'Onde Moléculaire*, p. 109. Centre National de la Recherche Scientifique, Paris 1958.
19. McWeeny R.: *Phys. Rev.* 126, 1028 (1962).
20. Diercksen G., McWeeny R.: *J. Chem. Phys.* 44, 3554 (1966).
21. McWeeny R.: *Chem. Phys. Letters* 1, 567 (1968).
22. Sustmann R., Binsch G.: *Mol. Phys.* 20, 1 (1971).
23. Stevens R. M., Pitzer R. M., Lipscomb W. N.: *J. Chem. Phys.* 38, 550 (1963).
24. Amos A. T., Hall G. G.: *Theoret. Chim. Acta* 5, 148 (1966).
25. Cohen H. D., Roothaan C. C. J.: *J. Chem. Phys.* 43, S 34 (1965).
26. Musher J. I.: *J. Chem. Phys.* 46, 369 (1967).
27. Dalgarno A.: *Advan. Phys.* 11, 281 (1962).
28. Langhoff P. W., Karplus M., Hurst R. P.: *J. Chem. Phys.* 44, 505 (1966).
29. Löwdin P. O.: *Phys. Rev.* 97, 1474 (1955).
30. Ziman J. M.: *Elements of Advanced Quantum Theory*, Ch. 4. Cambridge University Press, 1969.
31. Simonetta M., Gianinetti E. in the book: *Molecular Orbitals in Chemistry, Physics and Biology*, p. 83. Academic Press, New York 1964.
32. Coulson C. A., Longuet-Higgins H. C.: *Proc. Roy. Soc. (London)* A191, 39 (1947).
33. Kato T.: *Progr. Theoret. Phys. (Kyoto)* 4, 514 (1949).
34. Messiah A.: *Quantum Mechanics*, Ch. 16. North-Holland, Amsterdam 1962
35. Polák R., Kvasnička V.: *Czechoslov. J. Phys., B* 23, 1298 (1973).
36. Feshbach H.: *Ann. Physik (New York)* 19, 287 (1962).
37. Epstein S. T.: *J. Chem. Phys.* 41, 1045 (1964).
38. Adams W. H.: *J. Chem. Phys.* 34, 89 (1961).
39. Gilbert T. L. in the book: *Molecular Orbitals in Chemistry, Physics and Biology*, p. 405. Academic Press, New York 1964.

40. Anderson P. W.: *Phys. Rev.* *181*, 25 (1969).
41. Kunz A. B.: *Phys. Stat. Solid.* *36*, 301 (1969).
42. Schlosser H.: *J. Chem. Phys.* *53*, 4035 (1970).
43. Polák R.: *Theoret. Chim. Acta* *14*, 163 (1969).
44. Polák R.: *Int. J. Quantum Chem.* *4*, 271 (1970).
45. Polák R.: *Int. J. Quantum Chem.* *6*, 1077 (1972).
46. Polák R.: *This Journal* *38*, 1450 (1973).
47. Hirschfelder J. O., Brown W. B., Epstein S. T.: *Advan. Quantum Chem.* *1*, 255 (1964).

Translated by P. Čársky.