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Commentationes

Optimum Parametrization of the Pople-Santry-Segal Method of Treating All Valence Electrons

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An optimised version of the simple all-valence-electron SCF MO method of Pople, Santry and Segal has been developed by deriving the basic core hamiltonian matrix elements $U_{\mu\mu}^{AA}$ for $2p$ and $1s$ orbitals empirically by a least-squares fitting of calculated to observed dipole moments. The calculated moments were found to be relatively insensitive to U_{2s2s}^{AA} and resonance integrals and so for the present the values suggested by Pople, Santry and Segal have been used for them. Optimum values for U_{2p2p}^{AA} and U_{1s1s}^{AA} are surprisingly close to the CNDO/2 values of these authors. Calculated dipole moments are sometimes sensitive to the assumed geometries and attention is drawn to several instances in which the idealised geometries assumed by Pople and Gordon lead to values notably different from those obtained by starting with the experimentally determined geometry. The present optimised scheme becomes less satisfactory for molecules in which large electron shifts occur or in which the atomic dipole is a dominant term.

Die Pople-Santry-Segal-Methode wurde modifiziert, indem die Rumpfintegrale $U_{\mu\mu}^{AA}$ für $1s$- und $2p$-Orbitale unter Verwendung der Fehlerquadratmethode an gemessenen Dipolmomenten angepaßt wurden; sie unterschieden sich nur wenig von den CNDO/2-Parametern. Die berechneten Dipolmomente sind ziemlich unempfindlich gegen Variationen von U_{2s2s}^{AA} und der Resonanzintegrale; hier wurden die Werte von Pople, Santry und Segal verwendet. Die berechneten Momente sind in einigen Fällen stark von der Geometrie abhängig und können sich für idealisierte und experimentelle Geometrien merklich unterscheiden. Bei Molekülen mit starker Elektronenverschiebung oder bei welchen die atomaren Dipole bedeutsam sind, ist unser Parametersatz nicht befriedigend.

Développement d'une version optimisée de la méthode des électrons de valence SCF MO de Pople-Santry-Segal par déduction empirique des éléments de matrice de coeur $U_{\mu\mu}^{AA}$ des orbitales $2p$ et $1s$ par ajustement quadratique des moments dipolaires calculés à ceux observés. Les moments calculés sont relativement insensibles à U_{2s2s}^{AA} et aux intégrales de résonance; les valeurs proposées par Pople Santry et Segal ont donc été utilisées dans ces cas. Les valeurs optimales de U_{2p2p}^{AA} et U_{1s1s}^{AA} sont étonnament voisines des valeurs CNDO/2 de ces auteurs. Les moments dipolaires calculés sont parfois sensibles aux géométries utilisées et l'on cite plusieurs cas où les valeurs obtenues à partir de géométries idéalisées et de géométries expérimentales sont notablement différentes. Ce schéma optimisé s'avère moins satisfaisant pour les molécules où de déplacement d'électrons importants se produisent ou bien dans lesquelles les dipôles atomiques sont des termes dominants.

Introduction

It is currently believed that an approximate molecular orbital treatment embracing all valence electrons, but treating inner shell electrons combined with nuclei as a fixed core, could provide a rational basis for discussion of various molecular properties. In order to make the calculations feasible for moderately large molecules some approximations in the LCAOSCF formalism are necessary.

Furthermore even an accurate solution of the Hartree-Fock equations does not appear to be adequate because some allowance for electron correlation seems necessary [1].

Some effort has therefore been expended [2—11] in developing SCF molecular orbital methods in which various basic integrals relating to atoms and pairs of atoms (or atomic orbitals and pairs of atomic orbitals) are evaluated empirically from appropriately chosen experimental data. In this way it is hoped that some acceptable allowance for correlation and other deficiencies will be attained. The arguments advanced to support the various empirical derivations of integrals involve, for example, an analysis of atomic spectroscopic data in terms of an approximate theory of atomic structure [2, 5, 11, 12]. In these circumstances it is not clear how reliable are such empirical integral values and how the final molecular orbital results may be hampered by inadequacies stemming from this source.

It therefore seems desirable to explore the effect of reversing this kind of procedure by proceeding as follows: Firstly we decide which basic integrals will be accepted as empirically adjustable; secondly we take *molecular* experimental data of the type that we might wish to interpret, and that can be related unambiguously to the total electronic wavefunction by one-electron operators[1], and proceed to find optimum values of the basic integrals by a least-squares fit to the molecular data.

The SCF MO Method

The LCAO form of the Hartree-Fock equations for molecular orbitals has been described by Roothaan [14]. Recently Pople, Segal and Santry have shown that these equations can be reduced so that they become manageable for molecules of a moderate size.

In summary the basic equations are

$$\boldsymbol{F}\boldsymbol{C} = \boldsymbol{C}\varepsilon \tag{1}$$

and

$$F^{\mathrm{AA}}_{\mu\mu} = U^{\mathrm{AA}}_{\mu\mu} + \left(P_{\mathrm{AA}} - \frac{1}{2} P_{\mu\mu}\right)\gamma_{\mathrm{A}} + \sum_{\mathrm{B}\neq\mathrm{A}} \left(P_{\mathrm{BB}}\gamma_{\mathrm{AB}} - X_{\mathrm{B}}\,{}_{\mathrm{B}}V^{\mathrm{AA}}\right) \tag{2}$$

$$F^{\mathrm{AA}}_{\mu\nu} = -\frac{1}{2} P_{\mu\nu}\gamma_{\mathrm{A}} \tag{3}$$

$$F^{\mathrm{AB}}_{\mu\nu} = \beta^{\mathrm{AB}}_{\mu\nu} - \frac{1}{2} P_{\mu\nu}\gamma_{\mathrm{AB}} \tag{4}$$

where A and B represent atomic sites;

μ and ν represent atomic orbitals;

$$U^{\mathrm{AA}}_{\mu\mu} = \left\langle \chi_\mu \middle| -\frac{1}{2}\hat{\nabla}^2 + X_{\mathrm{A}}\hat{V}_{\mathrm{A}} \middle| \chi_\mu \right\rangle, \tag{5}$$

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[1] One-electron operators are chosen in preference to two-electron operators because the expectation values of the former are less critically dependent on correlation effects [13].

which is the kinetic and potential energy of an electron in χ_μ experiencing the field of the atomic core of A;

$$P_{\mu\nu} = 2 \sum_{i}^{occ} C_{\mu i} C_{\nu i}\,; \tag{6}$$

$$P_{\mathrm{AA}} = \sum_{\mu \text{ on A}} P_{\mu\mu} \tag{7}$$

$$\gamma_{\mathrm{A}} = \left\langle nS^{\mathrm{A}}\, nS^{\mathrm{A}} \left| \frac{\hat{1}}{r_{12}} \right| nS^{\mathrm{A}}\, nS^{\mathrm{A}} \right\rangle, \tag{8}$$

where $n=1$ for H,

$n=2$ for Li, Be, B, C, N, O, F;

X_{A} is the core charge of A;

$$_{\mathrm{A}}V^{\mathrm{BB}} = \langle nS^{\mathrm{B}} | \hat{V}_{\mathrm{A}} | nS^{\mathrm{B}} \rangle, \tag{9}$$

where $\hat{V}_{\mathrm{A}}$ is the nuclear attraction operator for unit nuclear charge;

$$\beta_{\mu\nu}^{\mathrm{AB}} = 0.5\, S_{\mu\nu}(\beta_{\mathrm{A}}^{0} + \beta_{\mathrm{B}}^{0}) \tag{10}$$

where

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \tag{11}$$

and β_{A}^{0} and β_{B}^{0} are functions of atoms A and B only.

In the present study the $U_{\mu\mu}^{\mathrm{AA}}$'s have been treated as purely empirical parameters characteristic of A and χ_μ. Our intention has been primarily to explore the utility of the scheme proposed by Pople *et al.* though an evaluation of the $U_{\mu\mu}^{\mathrm{AA}}$'s derived from spectral data is discussed further in the Appendix.

Parametrization Scheme

The basic integrals to be derived were evaluated from a set of molecular dipole moments where these moments were calculated from the expressions[2]

$$\mu = \left(\sum_{g(=x,y,z)} \mu_g^2 \right)^{\frac{1}{2}} \tag{12}$$

$$\mu_g = \mu_g(q) + \mu_g(a) \tag{13}$$

$$\mu_g(q) = 2.5416 \sum_{\mathrm{A}} (X_{\mathrm{A}} - P_{\mathrm{AA}})\, g_{\mathrm{A}} \ \text{Debyes} \tag{14}$$

$$\begin{aligned} \mu_g(a) &= -\sum_{\mathrm{A}} P_{2s,2p_g}^{\mathrm{A}\,\mathrm{A}} \langle 2s^{\mathrm{A}} | g | 2p_g^{\mathrm{A}} \rangle \\ &= -14.674 \sum_{\mathrm{A}} P_{2s,2p_g}^{\mathrm{A}\,\mathrm{A}} / Z_\mu^{\mathrm{A}} \ \text{Debyes} \end{aligned} \tag{15}$$

For a starting point the $U_{\mu\mu}^{\mathrm{AA}}$'s and β_{A}'s of Pople, Segal and Santry were chosen and the differentials $(\delta\mu^x/\delta U_{\mu\mu}^{\mathrm{AA}})$ and $(\delta\mu^x/\delta\beta^{\mathrm{A}})$ were evaluated by finite differences for a series of molecules, x. It was then seen that the calculated dipole moments were insensitive to all but U_{1s1s}^{HH} and the U_{2p2p}^{AA}'s.

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[2] Since the Pople-Santry-Segal method [5] is based on the ZDO concept, the "homopolar dipole" terms, involving $\langle \chi^{\mathrm{A}} | g | \chi^{\mathrm{B}} \rangle$ are neglected.

A set of thirteen molecules was then chosen (for each of which the dipole moment and geometry have been derived by microwave spectroscopic studies) to represent a varied selection of bonding modes. From these a set of thirteen simultaneous equations of the form

$$\Delta\mu^{x} = \sum_{\mathrm{A=C,N,O,F}} \left\{ \left(\frac{\delta\mu^{x}}{\delta U^{\mathrm{AA}}_{2p2p}} \right) \Delta U^{\mathrm{AA}}_{2p2p} \right\} + \left(\frac{\delta\mu^{x}}{\delta U^{\mathrm{HH}}_{1s1s}} \right) \Delta U^{\mathrm{HH}}_{1s1s} \tag{16}$$

were obtained from which the unknowns $\Delta U^{\mathrm{HH}}_{1s1s}$ and $\Delta U^{\mathrm{AA}}_{2p2p}$, (A = C, N, O, F), were derived by a least-squares procedure. These new parameters were then used to recalculate the dipole moments of the initial set of molecules together with 23 other molecules whose dipole moments and geometries have been determined by microwave spectroscopy.

Table 1. *Values of* $-U^{\mathrm{AA}}_{2p2p}$ *and* $-U^{\mathrm{HH}}_{1s1s}$ *(eV)*

A	CNDO/1	CNDO/2	This Work
H	13.06	17.38	15.84
C	58.85	61.78	61.37
N	90.58	94.00	95.23
O	128.25	132.77	133.97
F	172.86	178.10	178.45

Table 1 shows the values of the $U_{\mu\mu}$'s obtained where they may be compared with those used in the CNDO/1 and CNDO/2 schemes. While it would be trivial to calculate the mean or standard deviations, we feel that the success of the method depends on every particular error as it is these which represent the confidence limits of the methods.

Table 2 shows the dipole moments calculated from the new parameters where they may be compared with those obtained from the CNDO/1 [6] and CNDO/2 [17] schemes and with the experimental data.

In general the results agree with experiment satisfactorily and are similar to those obtained from CNDO/2 which is expected because the $U^{\mathrm{AA}}_{\mu\mu}$'s are also similar. Table 2 lists two columns of results for CNDO/2; the first column, excluding the last five entries, were taken from Pople and Gordon's [7] paper where the molecular geometries were derived from a set of rules designed to cover a multitude of cases; the second column was computed using the experimental geometries. In some cases the discrepancy between the two is quite large. As an example of the care that must be taken in assuming molecular structures for use in such calculations, the molecule HNO_3,

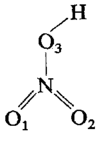

Table 2. *Values of calculated and experimental dipole moments (in Debyes)*

Molecule^a	CNDO/1	CNDO/2^b	CNDO/2^c	This Work	EXP
CO^d [1], [2]	1.29		0.96	0.50	0.13
H_2CO^d [3], [4]	1.27	1.98	1.90	2.19	2.34
H_2O^d [5], [6]	1.75	2.10	2.14	2.23	1.88
HCN^d [7]	2.08	2.48	2.47	2.83	2.99
HF^d [1], [8]	1.26	1.85	1.85	1.73	1.82
FCN^d [7]	1.59	1.55	1.70	2.09	2.17
F_2O^d [9]	0.06	0.21	0.14	0.15	0.30
Ketene^d [10]	0.60	1.30	1.23	1.69	1.41
Cyclopropene^d [11]	0.82		1.02	0.82	0.46
Formamide^d [12]	2.74	3.79	3.88	3.72	3.71
Diazirine^d [13]	0.90		1.22	1.75	1.59
CH_3F^d [15], [14]	1.16	1.66	1.72	1.60	1.86
$CH_2F_2{}^d$ [16]	1.38	1.90	1.95	1.86	1.96
CHF_3 [18], [17]	1.29	1.66	1.68	1.67	1.64
cis-CHF=CHF [19], [45]	1.91	2.83	2.77	2.58	2.42
HC≡CF [7]	0.51	1.04	0.94	0.90	0.73
$CF_3 \cdot CH_3$ [21], [20]	1.56	2.18	2.32	2.11	2.32
$CF_3 \cdot C{\equiv}CH$ [22]	1.47	2.48	2.71	2.33	2.36
$CH_2{=}CF_2$ [23], [45]	0.63	1.02	1.43	1.33	1.37
$CHF{=}CH_2$ [24]	0.97	1.51	1.58	1.42	1.43
HFCO [25], [26]	1.41	2.16	1.91	2.09	2.02
F_2CO [27]	0.74	1.42	0.86	1.16	0.95
O_3 [28]	1.00	1.26	1.18	1.23	0.53
HC≡C · CHO [29]	1.37	2.46	2.50	2.53	2.46
CH_3OH [30], [31]	1.66	1.94	1.98	2.07	1.69
HNO_3, [32]	2.26	2.24	3.03	2.85	2.16
HNCO [33]	1.79	1.88	2.08	2.16	1.59
ONF [34]	0.40		1.31	0.34	1.81
O_2NF [35]	1.74		1.78	1.92	0.47
HN_3 [36]	1.69	2.08	1.74	1.83	0.85
$CH_2{=}CH \cdot CN$ [37]	2.58		3.01	3.62	3.89
Furan [38]	0.19	0.71	0.71	0.70	0.66
Pyrrole [39], [40]	2.09	2.11	2.05	1.90	1.80
Pyridine [41], [42]	1.86	2.16	2.11	2.32	2.15
1,2,5-oxadiazole [43]	2.10	3.50	3.45	3.26	3.38
1,3,4-oxadiazole [44]	2.76	3.15	3.13	3.26	3.04

[a] The references against each molecule refer to the experimental dipole moments and geometries in that order. Where the geometry and dipole moment are quoted in one paper only a single reference occurs. The references are listed below.

[b] From [7] except for the last five entries which are from [24].

[c] Recalculated using experimental geometries.

[d] These molecules were used in the parametrization scheme.

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shows a variation of about 0.08 D per degree variation of the O_1NO_2 angle. The experimental value is 130° so that the "natural" assumption of 120° leads to an error of 0.8 D in the calculation.

Nevertheless some molecules, such as ONF, O_2NF, HN_3, and HNCO have dipole moments which are not well predicted by the CNDO scheme whereas other series of molecules, such as the heterocycles, fit in well. It seems that any molecule for which the atomic dipole, $\mu(a)$, comprises the major part of the resultant dipole moment or in which large electron shifts occur will have a large error in the predicted dipole moment.

In the case of ammonia, NH_3, a CNDO/1 calculation predicts

$$\mu(q) = 0.26\,\mathrm{D}$$
$$\mu(a) = 1.72\,\mathrm{D}$$
$$\mu_{\mathrm{TOTAL}} = 1.98\,\mathrm{D}$$

whereas

$$\mu_{\mathrm{EXP}} = 1.47\,\mathrm{D}$$

so that if the theory is to predict this moment correctly either the hydrogens must carry a negative charge or the atomic dipole must be drastically reduced. This atomic dipole is directly proportional to P_{2s2p}^{NN} which is not very sensitive to to parameter changes so that, unless the method of dipole moment calculations is changed, molecules such as ammonia cannot be treated properly in the present scheme.

Conclusions

The CNDO scheme may be used to predict the dipole moments of molecules containing H, C, N, O and F fairly accurately if the $U_{\mu\mu}$'s are carefully chosen and it seems that the $U_{\mu\mu}$'s used in the CNDO/2 scheme [17] are close to optimal in this sense. Such predictions, however, may be unsuccessful if; (a) large electron shifts occur, (b) the atomic dipole is a dominant factor in the total moment.

In view of the arguments of the Appendix, the discrepancy between the $U_{\mu\mu}$'s of the present scheme and those obtained from atomic spectra means that it is unlikely that energy calculations, especially those involving excited states, will prove fruitful unless some of the basic integral formulae are markedly revised.

We feel that a further improvement of the predictions of ground state properties can be made if the Löwdin transformation

$${}^{\lambda}C = {}^{\chi}S^{-\frac{1}{2}}\,{}^{\chi}C$$

is employed and the integrals solved in the non-orthogonal set, χ. A further reparametrization is then required and we are currently investigating this.

Appendix

${}^{\theta}U_{\mu\mu}^{\mathrm{AA}}$ *from Atomic Spectra*

If it is assumed that ${}^{\mathrm{A}}\theta_{\mu}$ is an orbital largely localized on nucleus A then ${}^{\theta}U_{\mu\mu}^{\mathrm{AA}}$ may be related to the approximate valence state ionization potential

$$-{}^{\theta}U_{\mu\mu}^{\mathrm{AA}} = \mathrm{A}^{(n-1)+},\, V_1 \rightarrow \mathrm{A}^{n+},\, V_0 \qquad (17)$$

where

$$n = X_{\mathrm{A}}$$

and V_i designates the valence state of the atomic ion. Since in all cases V_0 will be the ground state of the atomic core, we may write

$$-U_{\mu\mu}^{\mathrm{AA}} = -\mathrm{Pr.\,E}(G_1 \rightarrow V_1) + \mathrm{GSIP}(G_1 \rightarrow G_0) \qquad (18)$$

where G_i is the ground state of the core plus i valence electrons, Pr. E is the promotion energy and GSIP is the ground state ionization potential for the case with one valence electron.

Table 3. $-U_{\mu\mu}^{AA}$'s *(eV) for atomic ions from atomic spectral data*

A	Z_μ[a]	Y_A[b]	GSIP	Pr. E	VSIP	GSIP[c] (calc)	VSIP[d] (calc)
Li	1.3	1	5.39	1.85	3.54	5.39[e]	3.54
Be^{+}	2.3	2	18.21	3.96	14.25	18.25	14.33
B^{2+}	3.3	3	37.93	6.00	31.93	37.95	31.98
C^{3+}	4.3	4	64.49	8.00	56.49	64.49[e]	56.49
N^{4+}	5.3	5	97.89	9.99	87.90	97.88	87.86
O^{5+}	6.3	6	138.1	11.98	126.1	138.1	126.1
F^{6+}	7.3	7	185.2	13.98	171.2	185.2[e]	171.2

[a] Effective nuclear charge for the atomic ion derived from Slater's rules.
[b] Group Number.
[c] Calculated from $\mathrm{GSIP} = 3.422\, Z_\mu Y_A + 1.564\, Z_\mu - 1.091$.
[d] Calculated from $\mathrm{VSIP} = 3.431\, Z_\mu Y_A - 0.535\, Z_\mu - 0.222$.
[e] These values were used to determine the coefficients in c and d.

In Table 3 we have listed these quantities for the isoelectronic series Li to F^{6+}. Table 1 also shows that the GSIP and the VSIP are accurately represented by

$$-{}^{\theta}U_{\mu\mu}^{AA} = (a\, Y_A + b) Z_\mu + c \tag{19}$$

where Z_μ is the effective nuclear charge appropriate to the V_1 valence state derived by Slater's rules, and Y_A is the periodic group number of atom A. The ${}^{\theta}U_{\mu\mu}^{AA}$ that are appropriate to the uncharged atom may next be computed by substituting the requisite Z_μ values in (19). These values are listed in Table 4.

Pople Santry and Segal evaluated ${}^{\theta}U_{\mu\mu}^{AA}$ from atomic spectroscopic data by assuming that ${}^{A}\theta_\mu$ is independent of valence orbital occupation numbers for A or of the molecular environment in general. They derived the formula

$$U_{\mu\mu} = -I_\mu - (X_A - 1)\gamma_A \tag{20}$$

Values derived thus are listed in Table 4. It is evident that they rapidly deviate from values derived via (19). The discrepancy must mainly stem from the failure to recognize the variable electronegativity principle [15] that the orbital exponent of ${}^{A}\theta_\mu$ is a function of atom occupation numbers and hence I_μ and γ_A are likewise dependent on occupation numbers. The derivation of (20) implies constant values for these quantities, independent of occupation numbers.

Table 4. $-U_{\mu\mu}^{AA}$'s *for neutral atoms*

A	Z_μ[a]	Y_A	$U_{\mu\mu}^{AA}(2s)$[b]	$U_{\mu\mu}^{AA}(2p)$[b]	$U_{\mu\mu}^{AA}(2s)$[c]	$U_{\mu\mu}^{AA}(2p)$[c]
Li	1.3	1	5.39	3.54	5.39	3.54
Be	1.95	2	18.98	15.60	15.31	12.12
B	2.60	3	39.75	34.00	29.66	25.15
C	3.25	4	67.62	58.85	48.48	42.64
N	3.90	5	102.67	90.58	71.74	64.59
O	4.55	6	144.80	128.3	99.45	91.02
F	5.20	7	194.57	172.9	131.6	121.9

[a] Effective nuclear charge for the neutral atom derived from Slater's rules
[b] CNDO/1 values.
[c] Derived from the expression given below Table 3.

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