

Approximate Molecular Orbital Theory for Inorganic Molecules

II. Methods of Evaluating Basic Parameters

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A survey is made of possible procedures for evaluating the basic parameters of several molecular orbital methods previously set out in Part I. The importance of reliably evaluating the core-hamiltonian elements is emphasised. The most satisfactory procedure is to evaluate the matrix theoretically on a full overlap basis and then transform to a Löwdin basis for use in zero differential overlap MO methods.

The estimation of orbital exponents for Slater-type orbitals is given particular attention. The substantial advantage of using Burn's rules rather than Slater's rules is demonstrated and the VESCF approach, suitably adapted for all-valence-electron calculations, is proposed to allow for changes in the basis atomic orbitals caused by the intramolecular environment.

For two-electron integrals it is shown that values similar to those derived from Hartree-Fock atomic orbitals can be obtained by using a scaling scheme applied to values obtained theoretically using Slater type orbitals with Burns exponents.

The above scheme generates molecular Hartree-Fock matrix elements by essentially theoretical procedures. It is proposed as potentially the most satisfactory approximate molecular orbital theory for inorganic molecules. An alternative, semi-empirical scheme is suggested for further investigation. It uses the same theoretical procedure for the core hamiltonian but for two electron integrals it uses the empirical $(I - A)$ formula as the basis of a scaling procedure designed to allow indirectly for electron correlation and deviation from Hartree-Fock atomic orbitals.

Two new specific forms of CNDO approximation are described, fitting the above "theoretical" and "semi-empirical" categories. Also a particularly simple CNDO method – the CNDO-R method – is suggested as an alternative to Extended Hückel methods.

Ein Überblick über mögliche Verfahren zur Berechnung der grundlegenden Parameter verschiedener MO-Methoden aus Teil I wird gegeben. Die Wichtigkeit einer geeigneten Angabe der Rumpfwchselwirkungs-Elemente wird betont. Das befriedigendste Verfahren ist, die Matrix theoretisch mit einer vollen Überlappungsbasis zu berechnen und dann in eine Löwdin-Basis für die Verwendung in ZDO-MO-Methoden zu transformieren. Der Bestimmung der Orbital-Exponenten für Slater-Orbitale wird besondere Beachtung geschenkt. Der wesentliche Vorzug der Regeln von Burns vor den Regeln Slaters wird gezeigt. Für die VESCF-Näherung – angepaßt für Valenz-Rechnungen unter Einschluß aller Elektronen – wird vorgeschlagen, Änderungen in den grundlegenden atomaren Orbitalen zuzulassen, die durch die intramolekulare Umgebung verursacht werden. Für Zwei-Elektronen-Integrale wird gezeigt, daß Werte – ähnlich denen, die man aus Hartree-Fock-Atom-Orbitalen erhält – durch die Anwendung eines einfachen scaling-Verfahrens auf Werte, die mit Slater-Orbitalen mit Burns-Exponenten berechnet wurden, erzielt werden können.

Das oben genannte Verfahren erzeugt molekulare Hartree-Fock-Matrix-Elemente durch im wesentlichen theoretische Methoden. Es wird als die am meisten zufriedenstellende angenäherte

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Molekularorbitaltheorie für anorganische Moleküle vorgeschlagen. Ein anderes semi-empirisches Verfahren soll weiter untersucht werden. Es wendet dieselbe theoretische Methode für die Rumpfwchselwirkungs-Matrixelemente an, aber für die Zwei-Elektronen-Integrale benutzt es empirische $(I - A)$ -Formeln als Grundlage für ein scaling-Verfahren, durch das die Elektronenkorrelationen und Abweichungen von Hartree-Fock-Atom-Orbitalen berücksichtigt werden sollen.

Zwei neue spezifische Formen der CNDO-Näherung werden beschrieben, die in die oben genannten „theoretischen“ und „semiempirischen“ Kategorien passen. Ebenso wird eine besonders einfache CNDO-Methode – die CNDO-R-Methode – als Alternative zur erweiterten Hückel-Methode – vorgeschlagen.

Revue des différents procédés de détermination des paramètres de base pour plusieurs méthodes d'orbitales moléculaires précédemment envisagées dans la partie I. On insiste sur l'importance d'une évaluation convenable des éléments de l'hamiltonien de coeur. Le procédé le plus satisfaisant consiste à évaluer théoriquement cette matrice dans une base non orthogonale et à effectuer la transformation en base de Löwdin utilisable dans les méthodes d'orbitales moléculaires à recouvrement différentiel nul. La détermination des exposants dans les orbitales de Slater est considérée avec attention. L'avantage important que présentent les règles de Burns par rapport aux règles de Slater est démontré et l'on propose d'utiliser l'approche VESCF, convenablement adaptée aux calculs avec tous les électrons de valence, afin de tenir compte des modifications d'orbitales atomiques de base dues à l'environnement intramoléculaire. En ce qui concerne les intégrales biélectroniques des valeurs semblables à celles obtenues à partir des orbitales atomiques de Hartree-Fock peuvent être calculées à l'aide d'un schéma simple de réajustement appliqué aux valeurs théoriques données par les orbitales de Slater à exposants de Burns. Le procédé ci-dessus engendre les éléments de la matrice Hartree-Fock moléculaire par des voies essentiellement théoriques. On le propose comme la méthode approchée d'orbitales moléculaires la plus satisfaisante en principe pour les molécules inorganiques. On se propose d'étudier plus avant une autre méthode semi-empirique. Elle utilise le même procédé théorique pour le coeur mais pour les intégrales biélectroniques elle emploie la formule empirique $(I - A)$ comme base d'un procédé de réajustement destiné à rendre compte indirectement de la corrélation électronique et de l'écart à la base des orbitales atomiques de Hartree-Fock.

Deux nouvelles formes spécifiques de l'approximation CNDO sont décrites elles résultent de l'emploi des procédés "théorique" et "semi-empirique" ci-dessus. Une autre méthode CNDO particulièrement simple – la méthode CNDO-R – est proposée comme une alternative aux méthodes de Hückel étendues.

1. Introduction

In Part I [1] we discussed several categories of SCFMO treatments suitable for the study of inorganic systems. By considering several levels of approximation and simplification of the Hartree-Fock matrix elements, several alternative techniques present themselves for further testing as to their suitability.

In each case, having adopted some particular procedure for simplifying the formulae for matrix elements, we must decide upon procedures for evaluating the basic integrals that appear in these formulae. In calculations of the kind here discussed some or all of the basic integrals are almost always regarded as parameters that may be evaluated empirically or by judicious use of experimental data. The literature abounds with proposed procedures in near bewildering variety. In the present paper we survey some of the more popular empirical techniques to try to arrive at a consistent, reliable semi-empirical scheme. We also consider problems relating to the use of Slater-type orbitals in a method designed to reproduce results that would be obtained with Hartree-Fock AO's.

Calculations designed to test the methods that emerge from the analysis of Parts I and II will be presented in Part III.

2. Criteria for Parameter Choice

Since our aim is to establish methods that will be suitable for a variety of molecules we seek parameter schemes that are widely applicable, based generally on theoretical arguments and that correct as far as possible for the known inherent defects of the all-valence-electron molecular orbital approach. The criterion of wide applicability has a second connotation, namely that we hope to find parameter schemes that can be used for the calculation of a variety of molecular properties relating to both ground and excited electronic states. (It will probably continue to prove convenient for UV spectral calculations to be based on ground-state SCF molecular orbitals plus a configuration-interaction treatment of suitable size rather than a separate SCF treatment of each electronic state).

Given this, there is still scope for fundamentally different approaches in devising parameter schemes. In an empirical way, we could search for that set of parameters which gives the "best" values for a series of known experimental properties, thus using available experimental data to its maximum while regarding the theoretical implications of our choice as secondary. This approach is well-suited to the simpler all-valence method, the CNDO method, but becomes much more difficult as the method becomes more complex simply because the number of unknown parameters increases dramatically.

Therefore we attempt to develop schemes having a strong theoretical basis. This does not, however, preclude the use of experimental data when a theoretical justification can be made for such use. Hence two main ideas are followed:

To search for parameter schemes largely independent of experimental data, leading to a "theoretical scheme with Hartree-Fock and electron correlation corrections".

To search for parameter schemes in which experimental data are used as much as possible, provided that a theoretical understanding has been established, leading to "semi-empirical parameter schemes".

As has been established in the π -electron-only MO theory for organic molecules, there is scope in parameter choice for the correction of inherent deficiencies in the method being used. The main deficiencies of the theory developed in Part I are fairly clear. One is the inherent deficiency of the LCAOMO approximation, that changes in the nature of the atomic orbitals upon molecule formation are not allowed for. The variable electronegativity SCF (VESCf) approach of Brown and Heffernan [2, 3] is suggested as a way of partially correcting for this error. A second is the deviation of our approximate methods from the true Hartree-Fock solution, the deviation depending vitally upon the choice of basic atomic orbitals. Slater-type atomic orbitals have the advantage of flexibility and ease of calculation, and it is suggested that a suitable choice of orbital exponent coupled with a Hartree-Fock scaling scheme for theoretical integrals partially overcomes the Hartree-Fock deviation problem. The problem of electron correlation remains to be considered.

It should be remembered that we are not taking advantage here of the full flexibility offered by the CNDO method; for this the reader is referred to the work of Pople, Santry and Segal, [4, 5], and of Brown and Burden [6].

Also, in our search for generality, we are not taking advantage of the possibility of correlating parameters with *ab initio* calculations, as in the work of Pople,

Santry and Segal, since such calculations are rare for molecules containing some of the larger atoms we wish to consider. Similarly, although π -electron-only MO theory provides a wealth of information on parameter choice, much of this work can only be generalized to molecules containing first row atoms. Our hope on the other hand is to provide a basis for consistent and comparative calculations for molecules containing atoms of any row of the Periodic Table.

3. All-Valence-Electron Methods

In Part I, we distinguished between full overlap all-valence-electron methods, that obey the secular equation:

$$FC = SC\epsilon \quad (1)$$

and zero differential overlap methods, in which the basic atomic orbitals are made orthogonal by Löwdin's method [7] so that the secular equation becomes:

$${}^{\lambda}F{}^{\lambda}C = {}^{\lambda}C\epsilon. \quad (2)$$

The Ruedenberg and Mulliken methods come under the former heading, while the NDDO, MCZDO¹ and CNDO come under the latter, and are grouped in order of increasing approximation and hence decreasing complexity.

After the full overlap or ZDO approximations detailed in Part I have been invoked, the integrals that have to be specifically evaluated are the kinetic energy integrals $\langle \mu | \hat{T}(1) | \nu \rangle$, nuclear attraction integrals of the one-centre ($\langle \mu_A | \hat{V}_A(1) | \nu_A \rangle$), two-centre ($\langle \mu_A | \hat{V}_B(1) | \nu_A \rangle$ and $\langle \mu_A | \hat{V}_B(1) | \lambda_B \rangle$) and three centre ($\langle \mu_A | \hat{V}_C(1) | \lambda_B \rangle$) types, together with one centre [$\langle \mu_A \nu_A | \lambda_A \sigma_A \rangle$] and two-centre [$\langle \mu_A \nu_A | \lambda_B \sigma_B \rangle$] electron repulsion integrals.

There are available theoretical means, that are quite general, for obtaining all of these integrals, opening the way for completely non-empirical calculations if desired. The method of evaluation depends on the type of basis atomic orbitals chosen. For Gaussian basis atomic orbitals, the formulae set out by Harris [8] may be used. While such a choice presents certain advantages, particularly in the rapidity of integral evaluation, most approximate MO methods to date have

¹ The Fock Hamiltonian matrix F has elements composed of one-electron (H) and two-electron (G) parts:

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \quad (3)$$

with

$$H_{\mu\nu} = \langle \mu | \hat{T}(1) | \nu \rangle + \sum_A X_A \langle \mu | \hat{V}_A(1) | \nu \rangle, \quad (4)$$

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\sigma | \lambda\nu)]. \quad (5)$$

$H_{\mu\nu}$ is an element of the so-called "core Hamiltonian matrix", and consists of kinetic energy integrals $\langle \mu | \hat{T}(1) | \nu \rangle$ and nuclear attraction integrals $\langle \mu | \hat{V}_A(1) | \nu \rangle$. X_A is the "core charge" on centre A, that is, the charge remaining on A after the valence electrons have been removed. Sometimes $H_{\mu\mu}$ is referred to as the "Coulomb integral", α_{μ} , $H_{\mu\nu}$ ($\mu \neq \nu$) as the "resonance integral" $\beta_{\mu\nu}$ and we use the identities:

$$H_{\mu\mu} \equiv \alpha_{\mu}, \quad (6)$$

$$H_{\mu\nu} \equiv \beta_{\mu\nu}. \quad (7)$$

used Slater-type orbitals (STO's) or Hartree-Fock atomic orbitals, the latter having been expressed as linear combinations of appropriate STO's by Clementi [9]. For the present, we choose to investigate the applicability of STO's, and employ the C-functions method of integral evaluation of Roothaan and co-workers [10] as refined by Klimenko and Dyatkina [11]. The method is applicable to quantum shells greater than $n=2$. Three-centre nuclear attraction integrals present some problems here, and are found approximately as detailed in the next section. For one-centre integrals, the tables of Zauli [12] are sometimes convenient. Other integral evaluation methods have been reviewed by Magnusson [13] and by Harris and Michels [14].

Hence a theoretical evaluation of all necessary integrals is possible. We now need to consider whether there is any advantage in using experimental data, and how best we can introduce refinements to the parameter choice in order to partially correct for methodological deficiencies. To do this we first consider various ways of calculating core Hamiltonian elements, then empirical approximations to repulsion integrals, and finally corrections to the parameter schemes for the change of atomic orbitals with intramolecular environment, and for the Hartree-Fock deviation.

4. The Core Hamiltonian

Already, the *S*-expansion technique of the previous paper has indicated the importance to be attached to the elements of the core Hamiltonian, α_μ , $\beta_{\mu\nu}^{AA}$ and $\beta_{\mu\lambda}^{AB}$. Results of molecular orbital calculations, described in later papers, further confirm this conclusion and show that relatively small changes in the basic integrals of these elements cause fairly large changes in calculated results, and this arises because such small changes are magnified by the large core charges arising in all-valence-electron calculations. Therefore three different ways of treating the core Hamiltonian have been closely examined.

4.1. Full Overlap Basis Core Hamiltonian.

In this method the core Hamiltonian elements are calculated in a full overlap basis theoretically except that the Goepfert-Mayer-Sklar approximation (see below) is used for the one centre part of α_μ . The resulting core Hamiltonian matrix is either used directly in the full overlap (Mulliken and Ruedenberg) methods, or is transformed to a Löwdin basis for use with the repulsion integral approximations of the differential overlap methods, via the transformation:

$${}^\lambda H = S^{-\frac{1}{2}} H S^{-\frac{1}{2}}. \quad (8)$$

The elements of *H* are given by Eq. (4). The Goepfert-Mayer-Sklar approximation takes the form:

$$\hat{T}(1) + X_A \hat{V}_A(1) | \chi_\mu^A \rangle = -I_\mu(X_A) | \chi_\mu^A \rangle \quad (9)$$

where $I_\mu(X_A)$ is an appropriate valence state ionization potential for the removal of an electron in orbital χ_μ in the field of the nucleus and inner shell electrons

of atom A only. Then also,

$$\langle \lambda_B | \hat{T}(1) + X_A \hat{V}_A(1) | \mu_A \rangle = -I_\mu(X_A) \langle \lambda_B | \mu_A \rangle = -S_{\mu\lambda} I_\mu(X_A). \quad (10)$$

The core elements now are:

$$\alpha_\mu = -I_\mu(X_A) + \sum_{B \neq A} X_B \langle \mu | \hat{V}_B(1) | \mu \rangle, \quad (11)$$

$$\beta_{\mu\nu}^{AA} = \sum_{B \neq A} X_B \langle \mu | \hat{V}_B(1) | \nu \rangle, \quad (12)$$

$$\begin{aligned} \beta_{\mu\lambda}^{AB} &= \frac{1}{2} [\langle \mu | \hat{T}(1) + X_A \hat{V}_A(1) | \lambda \rangle + \langle \mu | \hat{T}(1) + X_B \hat{V}_B(1) | \lambda \rangle \\ &\quad + X_A \langle \mu | \hat{V}_A(1) | \lambda \rangle + X_B \langle \mu | \hat{V}_B(1) | \lambda \rangle] + \sum_{C \neq A, B} X_C \langle \mu | \hat{V}_C(1) | \lambda \rangle \\ &= \frac{1}{2} [-S_{\mu\lambda} I_\mu - S_{\mu\lambda} I_\lambda + X_A \langle \mu | \hat{V}_A(1) | \lambda \rangle + X_B \langle \mu | \hat{V}_B(1) | \lambda \rangle] \\ &\quad + \sum_{C \neq A, B} X_C \langle \mu | \hat{V}_C(1) | \lambda \rangle. \end{aligned} \quad (13)$$

The three-centre integrals $\langle \mu_A | \hat{V}_C(1) | \lambda_B \rangle$ present some calculational problems, and are therefore approximated using the Ruedenberg approximation in the NDDO, MCZDO and Ruedenberg methods, or the Mulliken approximation in the CNDO or Mulliken methods.

Then respectively either

$$\langle \mu_A | \hat{V}_C(1) | \lambda_B \rangle = \frac{1}{2} \left[\sum_\nu^A S_{\nu\lambda} \langle \mu | \hat{V}_C(1) | \nu \rangle + \sum_\sigma^B S_{\mu\sigma} \langle \sigma | \hat{V}_C(1) | \lambda \rangle \right] \quad (14)$$

or

$$\langle \mu_A | \hat{V}_C(1) | \lambda_B \rangle = \frac{S_{\mu\lambda}}{2} [V_C^{AA} + V_C^{BB}] \quad (15)$$

where V_C^{AA} and V_C^{BB} are the average nuclear attraction integrals required for rotational invariance of the Mulliken approximation.

The other integrals $\langle \mu_A | \hat{V}_A(1) | \lambda_B \rangle$ and $\langle \mu_A | \hat{V}_B(1) | \lambda_B \rangle$ may also be found in either of these ways, or may be theoretically evaluated. If the Mulliken approximation is used, a particularly simple expression for $\beta_{\mu\lambda}^{AB}$ suitable for the Mulliken or CNDO methods, results:

$$\begin{aligned} \beta_{\mu\lambda}^{AB} &= \frac{1}{2} \left[-S_{\mu\lambda} I_\mu - S_{\mu\lambda} I_\lambda + \frac{S_{\mu\lambda}}{2} (X_A V_A^{AA} + X_A V_A^{BB} + X_B V_B^{BB} + X_B V_B^{AA}) \right] \\ &\quad + \frac{S_{\mu\lambda}}{2} \sum_{C \neq A, B} [X_C V_C^{AA} + X_C V_C^{BB}] \\ &= \frac{S_{\mu\lambda}}{2} \left[-I_\mu + \sum_{D \neq A} X_D V_D^{AA} - I_\lambda + \sum_{E \neq B} X_E V_E^{AB} \right. \\ &\quad \left. + \frac{1}{2} (X_A V_A^{AA} - X_A V_A^{BB} + X_B V_B^{BB} - X_B V_B^{AA}) \right] \\ &= \frac{S_{\mu\lambda}}{2} [\alpha_\mu + \alpha_\nu + \frac{1}{2} \{ X_A (V_A^{AA} - V_A^{BB}) + X_B (V_B^{BB} - V_B^{AA}) \}] \end{aligned} \quad (16)$$

with

$$\alpha_\mu = -I_\mu + \sum_{B \neq A} X_B V_B^{AA} \quad (17)$$

and

$$\beta_{\mu\nu}^{\text{AA}} = 0. \quad (18)$$

The strong influence of the core charges on the magnitude of the core elements is illustrated in these equations.

4.2. Löwdin Basis Core Hamiltonian

In previous work (Pariser and Parr [15], Fischer-Hjalmars [16], Ohno [17]), the expression suggested for ${}^\lambda\beta_{\mu\lambda}^{\text{AB}}$ in a Löwdin basis is:

$${}^\lambda\beta_{\mu\lambda}^{\text{AB}} = \beta_{\mu\lambda} - \frac{S_{\mu\lambda}}{2}(\alpha_\mu + \alpha_\lambda). \quad (19)$$

From the S -expansion technique (Part I) it can be seen that this corresponds to the assumption that terms $\beta_{\mu\lambda}S_{\mu\lambda}$ may be neglected to the first order in overlap. If this is the case, core elements suitable for the CNDO method may be calculated directly in a Löwdin basis as follows (from Eq. (40)–(42) of Part I):

$${}^\lambda\alpha_\mu = \alpha_\mu + O(S^2), \quad (20)$$

$${}^\lambda\beta_{\mu\nu}^{\text{AA}} = 0, \quad (21)$$

$${}^\lambda\beta_{\mu\lambda}^{\text{AB}} = \frac{S_{\mu\lambda}}{4} [X_{\text{A}}(V_{\text{A}}^{\text{AA}} - V_{\text{A}}^{\text{BB}}) + X_{\text{B}}(V_{\text{B}}^{\text{BB}} - V_{\text{B}}^{\text{AA}})] + O(S^2) \quad (22)$$

using also Eq. (16) and (21).

Thus we obtain simple expressions, particularly easy to use in practice. However comparative calculations on the sulphate anion described in Part III show that the approximations made here are too drastic for quantitative results, although the qualitative interpretations placed on these results are in agreement with more accurate methods. The reason is that the terms in βS neglected here are substantial owing to the high core charges, and therefore ${}^\lambda\alpha_\mu$ as obtained here is too large in magnitude while ${}^\lambda\beta_{\mu\lambda}^{\text{AB}}$ is smaller than a theoretical $\beta_{\mu\lambda}^{\text{AB}}$ transformed to the Löwdin basis in Sect. 4.1. A more accurate alternative is provided by Eq. (47)–(49) of Part I.

4.3. Semi-Empirical Core Hamiltonian

In the sense that empirical valence state ionization potentials are used in α_μ , methods (1) and (2) are already semi-empirical. The semi-empirical core Hamiltonian, however, allows the resonance integral $\beta_{\mu\lambda}^{\text{AB}}$ to be obtained in an empirical way, by making it proportional to the amount of overlap of the orbitals χ_μ and χ_λ , and to the core charges on atoms A and B.

$$\beta_{\mu\lambda}^{\text{AB}} = -K_{\text{AB}}S_{\mu\lambda} \frac{(X_{\text{A}} + X_{\text{B}})}{2}. \quad (23)$$

K_{AB} being a constant of proportionality dependent only on the atoms A and B and not upon the particular orbitals involved, a condition necessary for rotational invariance [4]. At this stage the spectroscopically determined β vs. R expression

for benzene [18] may be used to find K_{AB} :

$$K_{AB} = \frac{|\beta_{CC}(R_{AB})|}{|S_{CC}(R_{AB})|} \quad (24)$$

the values for the carbon-carbon quantities β_{CC} and S_{CC} being found at the distance R_{AB} , and the core charges X_C being +1.

Calculations using this semi-empirical resonance integral, when compared with those using the theoretical method (Sect. 4.1), give the interesting result that those resonance integrals involving p -orbitals are of roughly the same value in the two cases, while those involving s -orbitals are quite different, the semi-empirical values being lower. β_{CC} and S_{CC} , having been evaluated for carbon $2p$ -orbitals, apparently can only be used to standardize for p -orbitals of other atoms. Some justification for the form of equation (25), including the dependence on the core charges, follows from a consideration of approximations for nuclear attraction integrals presented below. It should be noted that Ruedenberg [19] suggests that rather than equation (23), a proportionality to $S(1-S)$ may be more appropriate.

4.4. Approximate Nuclear Attraction Integrals

Approximate means for the calculation of nuclear attraction integrals have also been examined, and may be suitable for simplifying even further the CNDO and Mulliken methods. Following the Pariser-Parr approach of π -electron theory [15], these integrals may be expressed as a sum of neutral atom and electron repulsion integral parts:

$$X_B \hat{V}_B(1) = \hat{V}_{B^0}(1) - \sum_{\lambda}^{B, \text{ valence}} n_{\lambda} [\hat{J}_{\lambda}(1) - \frac{1}{2} \hat{K}_{\lambda}(1)] \quad (25)$$

where $\hat{V}_{B^0}(1)$ is the operator for the interaction of electron 1 with neutral atom B, and the sum is over all of the valence electrons on B, with n_{λ} the occupation number of χ_{λ} in the neutral atom. Then,

$$\begin{aligned} X_B \langle \mu_A | \hat{V}_B(1) | \mu_A \rangle &= \langle \mu_A | \hat{V}_{B^0} | \mu_A \rangle - \sum_{\lambda}^{B, \text{ valence}} n_{\lambda} [(\mu\mu | \lambda\lambda) - \frac{1}{2}(\mu\lambda | \lambda\mu)] \\ &= \langle \mu_A | \hat{V}_{B^0} | \mu_A \rangle - \sum_{\lambda}^{B, \text{ valence}} n_{\lambda} (\mu\mu | \lambda\lambda) \end{aligned} \quad (26)$$

since $(\mu\lambda | \lambda\mu)$ is neglected in the ZDO approximation. In π -electron theory the so-called neutral atom penetration integrals $\langle \mu_A | \hat{V}_{B^0} | \mu_A \rangle$ are small (usually less than 1 eV) and are often neglected. Such an assumption gives a simple CNDO formula:

$$\begin{aligned} X_B V_B^{AA} &= - \sum_{\lambda}^{B, \text{ valence}} n_{\lambda} \gamma_{AB} \\ &= - X_B \gamma_{AB}. \end{aligned} \quad (27)$$

That is

$$V_B^{AA} = - \gamma_{AB} = V_A^{BB}. \quad (28)$$

Calculated values of neutral atom penetration integrals, however, range up to 4 eV in the sulphur-oxygen case, and so this approximation is a poor one when high core charges are present. Its effect on results obtained is discussed in Part III.

When the point charge approximation of Pople [20] is applied, the very simple result:

$$V_A^{BB} = V_B^{AA} = -\gamma_{AB} = -\frac{14.4}{R_{AB}} \text{ eV} \quad (29)$$

with R_{AB} in Å, follows. Taking another approximation of this nature, that of Ohno [17]:

$$X_A \langle \mu_A | \hat{V}_A | \lambda_B \rangle = -2S_{\mu\lambda} X_A \frac{14.4}{R_{AB}} \quad (30)$$

in which it is assumed that the charge distribution $\chi_\mu^A(1)\chi_\lambda^B(1)$ may be represented by a point at the midpoint of the bond, $(R_{AB})/2$, the "Ohno β " [17] is derived from Eq. (19):

$$\lambda\beta_{\mu\lambda}^{AB} = \frac{S_{\mu\lambda}}{2} (X_A + X_B) \left[\frac{2 \times 14.4}{R_{AB}} + \gamma_{AB} \right]. \quad (31)$$

Now from Eq. (29) for γ_{AB} :

$$\lambda\beta_{\mu\lambda}^{AB} = -\frac{S_{\mu\lambda}}{2} (X_A + X_B) \frac{14.4}{R_{AB}}, \quad (32)$$

giving a resonance integral formula suitable for use in the Extended Hückel method (to be discussed in a separate publication) and in a simplified CNDO method, the "CNDO R -method" to be set out in Sect. 8 of this paper. The dependence on $S_{\mu\lambda}$ and $\frac{1}{2}(X_A + X_B)$ provides justification for the semi-empirical resonance integral of Eq. (25).

Calculations using the Ohno beta itself, Eq. (31), give values for spectral transition energies that are too high, showing that the magnitude of the beta value is too great. This conclusion is borne out by a comparison with the transformed theoretical resonance integrals of Sect. 5.1. Hence we are in agreement with Ohno [17] and Pilar [21] who conclude that scaling of the Ohno beta is necessary, although there is no evidence from this work that the scaling factor is constant at 0.85 as these two authors have suggested.

The arguments of this section apply to the case where not all of the valence electrons on a particular atom are included in the calculation, if the core Hamiltonian elements, Eq. (6), are replaced by:

$$H_{\mu\nu} = \langle \mu | \hat{T}(1) | \nu \rangle + \sum_A \left\{ X_A \langle \mu | \hat{V}_A(1) | \nu \rangle + \sum_{\sigma}^{A, \text{ valence not included}} n_{\sigma} [(\mu\nu | \sigma\sigma) - \frac{1}{2} (\mu\sigma | \sigma\nu)] \right\} \quad (33)$$

the second sum being over those valence electrons not included in the calculations. Then nuclear attraction integrals of the general type $X_B \langle \mu_A | \hat{V}_B | \nu_A \rangle$ are replaced in the formulae for α and β by:

$$X_B \langle \mu_A | \hat{V}_B | \nu_A \rangle + \sum_{\lambda}^{B, \text{ valence not included}} n_{\lambda} (\mu\nu | \lambda\lambda) \quad (34)$$

The development of reliable methods for calculating the resonance integral has been a major concern of this work. Other formulae have been examined

and found wanting from either the point of view of generality or from the point of view of lack of a theoretical basis. Thus the Pople-Santry-Segal formula [4], in which the resonance integral constant K_{AB} or Eq. (23) is calibrated against *ab initio* work, is not applicable to second row elements or transition metals, where *ab initio* calculations are in short supply. Similarly the Fischer-Hjalmar formula [16] falls down when experimental spectroscopic data are unavailable. On the other hand, the Wolfsberg-Helmholtz expression [22],

$$\beta_{\mu\lambda} = K \frac{S_{\mu\lambda}}{2} (\alpha_{\mu} + \alpha_{\lambda}) \quad (35)$$

and variations of this, do not have the correct behaviour with respect to a change in the origin of the energy scale unless K is unity [23], while satisfactory results are obtained in most cases only when values of K greater than unity are employed. A comparison of Eq. (35) with the theoretically derived β of Eq. (16) shows that important terms are missing from this Wolfsberg-Helmholtz β . Similar arguments on theoretical grounds apply to expressions used by Dewar and Klopman [24], to the variation of β as the inverse sixth power of the bond length [25], and to the variation of β with bond order [26].

Evidence is presented in Part III to show that as well as being the most appropriate from a theoretical viewpoint, the full overlap calculation of core elements (Sect. 4.1) is able to give the best agreement with experimental electronic spectra of the methods considered. The calculation of the electronic spectrum appears as a most sensitive test of the values of these elements.

5. Empirical and Approximate Electron Repulsion Integrals

Another major issue for all-valence-electron calculations concerns the values to be used for electron repulsion integrals. Theoretical values calculated using Slater-type atomic orbitals are known from experience with π -electron calculations to be too large in magnitude. A common practice has therefore been to use empirical data to obtain monocentric Coulomb repulsion integrals, while the corresponding two-centre integrals are often found by approximate means which relate them to the monocentric integrals. Can these methods be extended to all-valence calculations?

We consider first of all empirical estimates of one centre repulsion integrals. The most important formula here is that of Pariser [27], which follows a consideration of the energy difference ΔE of the reaction:



ΔE may on the one hand be identified with the repulsion between the two electrons in $C\bar{\cdot}$, and on the other with the difference between the ionization potential $C \cdot \rightarrow C^+$ and the electron affinity $C \cdot \rightarrow C\bar{\cdot}$.

$$\Delta E = (\mu\mu|\mu\mu)_{\text{exp}} = I - A \quad (37)$$

This "experimental" repulsion integral ought now to be compared with the theoretical value for $C\bar{\cdot}$, as pointed out by Brown [28] and by Sinanoğlu and

Orloff [29]. If STO's are used to find the theoretical value, then the discrepancy between the two is mainly due to the use of STO's rather than true Hartree-Fock atomic orbitals, and secondly to electron correlation (Fischer-Hjalmars [16], Sinanoğlu and Orloff [29]). Thus $(\mu\mu|\mu\mu)_{\text{exp}}$ contains Hartree-Fock and electron correlation corrections, the work of Ref. [16] and [29] providing the theoretical justification for its use (see however Part IV).

There are three possibilities for the use of the Pariser ($I - A$) formula in obtaining monocentric repulsion integrals:

i) Empirical monocentric repulsion integrals, found by using the ($I - A$) formula for the Coulomb repulsion integrals; empirical Slater-Condon parameters for the exchange repulsion integrals.

ii) Semi-empirical monocentric repulsion integrals, in which Coulomb repulsion integrals are found as in (i), but used with theoretical values of exchange repulsion integrals.

iii) Monocentric repulsion integrals, obtained by using the ($I - A$) formula in conjunction with theoretical integral values – to obtain a scaling factor which is then applied to the theoretical values of all monocentric repulsion integrals.

All monocentric repulsion integrals may be expressed theoretically as linear combinations of the Slater-Condon parameters F and G [30], numerical values of which can be calculated from observed atomic spectra [31, 32]. Fischer-Hjalmars [16] has therefore suggested combining these theoretical expressions with the experimental data to give empirical repulsion integrals. Difficulties arise with Coulomb repulsion integrals because of complications in obtaining the Slater-Condon parameters F_0 needed for their evaluation [31, 32]. However, the parameters needed for exchange repulsion integrals have been tabulated by Hinze and Jaffé [31] for many atoms, and the theoretical expressions for all monocentric integrals in terms of these parameters and for real orbitals are given in the Appendix.

The semi-empirical evaluation of repulsion integrals, (ii), has not been used in practice in this work, but the idea that theoretical values of exchange repulsion integrals need no correction receives support in the discussion of Hartree-Fock integrals and electron correlation in Sect. 7 and in a later paper of the series.

When the approach, (iii), is used, certain questions become important. In particular, is the ratio of empirical to theoretical Coulomb repulsion integrals constant for different orbitals on the same atom, and for different atoms in the same row of the Periodic Table? Tables 1 to 4 show that this is the case when Burns's orbital exponents [33] are used in the theoretical calculation of the integrals, rather than exponents calculated by the simple Slater rules [34]. Burns's rules for orbital exponents have been derived by a comparison of Slater-type orbital wave functions with Hartree-Fock wave functions, and differ from Slater's rules in distinguishing between s - and p -orbitals in the same quantum shell, in using only integral n -quantum numbers, and in allowing for the screening effect of electrons in orbitals outside the one being considered. The important difference for this work is thus, for orbitals of the same quantum shell and ζ the orbital exponent:

Slater rules: $\zeta_s = \zeta_p$,

Burns rules: $\zeta_s > \zeta_p$ in general.

Table 1. *Coulomb repulsion integrals for first row elements. – Empirical and theoretical values (eV)*

Element	Empirical		Theoretical Burns		Theoretical Slater	
	γ_{ss}	γ_{pp}	γ_{ss}	γ_{pp}	γ_{ss}	γ_{pp}
Li	4.57	2.98	3.95	3.46	4.70	5.06
Be	—	5.35	7.17	6.92	7.91	8.52
B	9.21	8.10	10.38	9.59	11.12	11.98
C	11.10	10.93	13.59	13.05	14.33	15.44
N	12.87	13.10	16.80	15.71	17.55	18.90
O	17.63	15.27	20.02	19.17	20.76	22.36
F	13.87	17.36	23.23	22.63	23.97	25.83

Table 2. *Coulomb repulsion integrals for second row elements. – Empirical and theoretical values (eV)*

Element	Empirical		Theoretical Burns		Theoretical Slater	
	γ_{ss}	γ_{pp}	γ_{ss}	γ_{pp}	γ_{ss}	γ_{pp}
Na	4.67	2.95	5.38	3.17	4.33	4.70
Mg	6.15	4.46	6.91	4.44	5.85	6.35
Al	7.35	5.10	8.43	6.09	7.38	8.00
Si	10.37	6.37	9.95	7.74	8.90	9.65
P	11.72	9.31	11.47	9.01	10.42	11.30
S	8.54	10.01	12.99	10.66	11.94	12.95
Cl	9.57	11.30	14.52	12.31	13.46	14.60

Table 3. *Empirical Coulomb repulsion integrals for charged species: sulphur and chlorine (eV)*

Species	Sulphur integral		Chlorine integral	
	γ_{ss}	γ_{pp}	γ_{ss}	γ_{pp}
A ²⁺	13.17	11.02		14.76
A ³⁺	14.42	13.69	13.09	12.38
A ⁴⁺	15.05	24.67	16.43	15.48
A ⁵⁺			16.74	16.70

In Tables 1 and 2 empirical values of Coulomb repulsion integrals determined from the $(I - A)$ formula and using the neutral atom valence state ionization potentials and electron affinities of Hinze and Jaffé [35] are compared with the corresponding theoretical integrals calculated for the negative ion with both Slater and Burns exponents.

An important difference emerges from the theoretical results:

Slater $\gamma_{ss} < \gamma_{pp}$,

Burns $\gamma_{ss} > \gamma_{pp}$,

relationships which would lead to different *s*- and *p*-orbital occupation numbers in actual calculations. Allowing for experimental error in the electron affinities, the Burns result is paralleled by the empirical integrals. In order to test this conclusion in the case of sulphur and chlorine, where the tendency is not observed, empirical integrals have been evaluated for charged species of these elements from the ionization potential data of Moore's tables [36] and the valence state formulae of Moffitt [37]. Table 3 lists the results obtained, showing that the

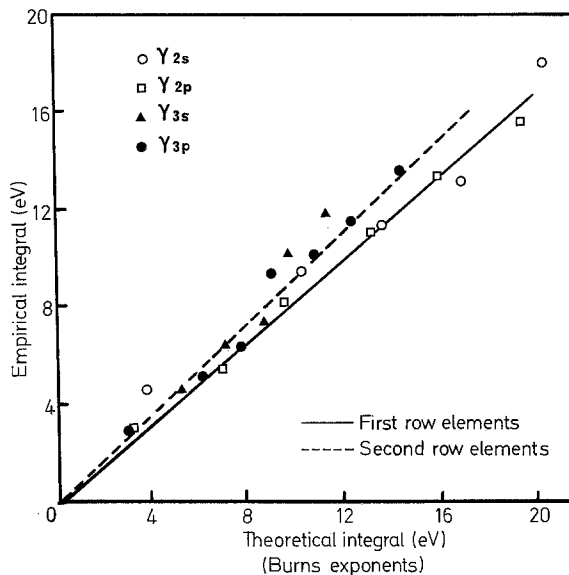


Fig. 1. Comparison of empirically evaluated $(I - A)$ one-centre coulomb-repulsion integrals with values obtained by direct integration using Slater orbitals and exponents given by Burns's rules

Burns exponents tendency is maintained except in the case of S^{4+} and pointing to a possible error in the neutral atom empirical data for sulphur and chlorine in Table 2.

When the neutral atom empirical data are plotted against the theoretical Burns integrals, a linear graph is obtained, Fig. 1, again allowing for the discrepancies in the cases of F, S and Cl. Hence there is support for the argument of using the relation:

$$\gamma^E = k\gamma^T \quad (38)$$

where γ^E and γ^T are the appropriate empirical and theoretical Coulomb repulsion integrals while k is a constant, the scaling factor, independent of the particular atom along any row of the Periodic Table. Further, Fig. 1 together with Table 4 shows that when Burns exponents are used, it is reasonable to make k independent of the particular orbital, s or p , concerned, although this is not the case for Slater exponent integrals.

The scaling factors listed in Table 4 are averages of the ratio of the empirical to theoretical repulsion integrals taken over first row (γ_{2s} and γ_{2p}) and second row (γ_{3s} and γ_{3p}) elements respectively. There is excellent agreement between the separate s - and p -orbital average scaling factors in each case when Burns exponents are used to calculate theoretical integrals. The scaling factor is independent of orbital type for orbitals having the same quantum number. For Slater exponents this agreement is not reached, and a separate scaling factor for s - and p -orbitals in the one quantum shell is required.

Therefore, if $\gamma_{\mu\nu}$ is the value of a particular monocentric Coulomb repulsion integral to be used in a calculation while $\gamma_{\mu\nu}^T$ is its theoretical value calculated

Table 4. Average neutral atom repulsion integral scaling factors for first and second row atoms

Integral	Scaling factor Slater integrals	Overall average Slater factor	Scaling factor Burns integrals	Overall average Burns factor
$\gamma_{1s}(\text{H})$	1.16	1.16	1.26	1.26
γ_{2s}	0.753	0.715	0.790	0.792
γ_{2p}	0.677		0.794	
γ_{3s}	1.082	0.920	0.939	0.942
γ_{3p}	0.758		0.945	

using Burns's exponents, we have:

$$\gamma_{uv} = k\gamma_{uv}^T \quad (39)$$

where

$$k_A = 0.792 \quad \text{for a first row atom A,}$$

$$k_A = 0.942 \quad \text{for a second row atom A.}$$

The question of the scaling of monocentric exchange integrals is left for the moment.

Many approximate methods for two centre Coulomb repulsion integrals have been formulated. Nishimoto and Mataga [38] and Roos [29] base their formulae on the conditions:

$$\begin{aligned} (\mu_A \mu_A | \lambda_B \lambda_B) &= 0 \quad \text{at } R_{AB} = \infty, \\ (\mu_A \mu_A | \lambda_B \lambda_B) &= \frac{1}{2} [(\mu\mu | \mu\mu) + (\lambda\lambda | \lambda\lambda)] \quad \text{at } R_{AB} = 0. \end{aligned} \quad (40)$$

Because it is difficult to apply these and other methods such as the point charge method of Pople [20], the uniformly charged sphere model of Parr [40], the multipole formulation of Parr [41], and the fourth-degree polynomial in R_{AB} of Fischer-Hjalmar [16] to the other two centre integrals required, $(\mu_A \nu_A | \lambda_B \sigma_B)$, direct theoretical evaluation has been adopted in this work.

Nevertheless, as the case of benzene has illustrated [42], these two-centre integrals, too, will be overestimated by theoretical means. Brown and Peel [43] have developed a means of scaling these integrals based upon the condition (40) for the scaling factors, and with the added condition that the shape of the theoretical repulsion integral versus bond length curve is maintained after scaling. The formula:

$$\Delta\gamma_{\mu\lambda}^{AB} = \frac{1}{2} (\Delta\gamma_{\mu\mu} + \Delta\gamma_{\lambda\lambda}) e^{-kR_{AB}^2} \quad (41)$$

where $\Delta\gamma = \gamma^T - \gamma$ and k is a constant ($k = 0.5702 \text{ \AA}^{-2}$) evaluated so that the expression fits the corresponding $\Delta\gamma$ values for the theoretical and spectroscopically determined repulsion integrals for benzene quoted in Ref. [42]. The formula (41) has been used in this work for χ_μ and χ_λ the valence s -orbitals on the corresponding atoms and the scaling factor

$$k_{AB} = \frac{(\gamma_{ss}^{AB})^T - \Delta\gamma_{ss}^{AB}}{(\gamma_{ss}^{AB})^T} \quad (42)$$

has been used to scale other two-centre repulsion integrals.

Let us now turn to the possibilities for a completely theoretical treatment of electron repulsion integrals, examining the influence of the choice of basis atomic orbitals on their evaluation, and asking whether a correction scheme may be devised which corrects for the deviation of any chosen set from the basis of true Hartree-Fock atomic orbitals.

6. Approximate Methods and the Hartree-Fock Solution

Part of the correction necessary to theoretical values of electron repulsion integrals in past work has been attributed by some authors [16, 29] to the deviation of the Slater type atomic orbitals used from true Hartree-Fock atomic orbitals. In particular, Orloff and Sinanoğlu [29] have shown that much better agreement is obtained between the theoretical and empirical ($I - A$) Coulomb repulsion integral for carbon $p\pi$ -orbitals simply by calculating the former with Hartree-Fock atomic orbitals. Their investigation opens the possibility of giving a theoretical basis to the repulsion integral corrections already discussed in the previous section.

The advantage of Slater-type atomic orbitals are the comparative ease of computation of theoretical integrals, savings in computer time and space, and the use of the VESCF method by means of the simple dependence of STO integrals on effective nuclear charge Z_μ (see next section). Improvements to STO's are possible in the choice of orbital exponent and in the scaling of theoretical integrals calculated with the chosen exponents.

Inadequacies in the simple Slater rules [30] for the calculation of orbital exponents have been suspected for some time. A number of other ways for calculating exponents are now available [33, 44–47]. If our concern is with obtaining approximate Hartree-Fock values for integrals, the set of rules, already discussed, devised by Burns [33] by comparison of STO and Hartree-Fock moment integrals appears to be most promising. The rules of Clementi and Raimondi [46, 47], determined for atomic energy minimization are similarly promising, although more complex, and differ from the Slater's rules in a similar way to the Burn's rules (see Sect. 5).

Again when theoretical monocentric Coulomb repulsion integrals for s - and p -orbitals calculated using Slater's and Burns's rules are compared with Hartree-Fock values in Table 5, the tendency discussed in Sect. 6 is observed. The γ_{ss} are greater than the γ_{pp} in the Hartree-Fock and Burns cases, while the reverse relationship occurs for Slater exponents.

In the case of manganese, where integrals have been calculated using the approximate Hartree-Fock atomic orbitals of Richardson, Nieuwport, Powell, and Edgell [48, 49], there is quite a large deviation of the Slater integral involving d -orbitals from the Burns and Hartree-Fock values. Later calculations, especially those in which the role of d -orbitals in molecules containing second row atoms is investigated, show that this is an important and general deficiency in Slater exponents themselves. Note, however the encouraging agreement between the Burns and Hartree-Fock values.

The ratio HF/Burns values vary rather erratically, although not differing greatly from 1.0. The charge on the oxygen atom has a considerable influence,

Table 5. Comparison of theoretical monocentric repulsion integrals (eV)

Element	Integral	Slater exponents	Burns exponents	Hartree-Fock AO's ^a	Ratio HF/Burns
O ⁻¹	γ_{ss}	20.7582	20.0169	21.0381	1.0510
	γ_{pp}	22.3653	19.1703	18.9100	0.9864
O ⁰	γ_{ss}	22.4881	21.7467	21.7114	0.9984
	$\gamma_{p\bar{p}}$	21.6176	18.7669	19.8061	1.0554
	γ_{pp}	24.2291	21.0341	22.0007	1.0460
O ⁺¹	γ_{ss}		23.4766	22.6981	0.9668
	γ_{pp}		22.8979	24.9105	1.0879
Mn ⁰	γ_{ss}	5.6404	7.9266	7.3025 ^b	0.9213
	γ_{pp}	6.1403	5.3610	4.7028 ^b	0.8772
	γ_{dd}	14.0451	22.0704	19.1419 ^b	0.8673

^a Hartree-Fock atomic orbitals of Clementi, Ref. [9].

^b Approximate Hartree-Fock atomic orbitals of Richardson, Nieuwpoort, Powell and Edgell [48, 49] used, and integrals calculated by B. H. James.

Table 6. Neutral atom Hartree-Fock correction factors for monocentric integrals

Integral	O	S	Cl	Mn
Nuclear attraction $\langle \mu_A \hat{V}_A \mu_A \rangle$	1.1503	1.1992	1.2024	1.0388
Repulsion $\gamma_{\mu\mu}^{\Lambda\Lambda}$	0.9984	1.0350	1.0315	0.9197

and so does the type of orbital. Closest agreement is attained for neutral oxygen. The results for manganese show close agreement between the p -orbital and d -orbital ratios. In order to check this trend, a further integral $\gamma_{p\bar{p}}$ for neutral oxygen was calculated, and also the fourteen unique Coulomb repulsion integrals involving s -, p - and d -orbitals for manganese. The $\gamma_{p\bar{p}}$ ratio (1.055) for neutral oxygen was in agreement with the γ_{pp} ratio, while the other manganese integrals agreed with the γ_{pp} and γ_{dd} values listed in Table 5, giving an average ratio of 0.885 ± 0.02 .

Two courses of action seem open to us here. Either we may use different scaling factors for integrals involving s -orbitals, and for integrals involving p - and d -orbitals, or we may assume that little error is introduced by using an average scaling factor for each atom and each pair of atoms. The latter would only be possible if the atomic charges do not differ greatly from zero. First we investigate the extent of scaling required for the various types of integral involved in the calculations at various bond lengths, assuming neutral atoms. Table 6 contains some sample results.

In most cases, the difference between the Hartree-Fock and Burns value is very small, especially for two-centre integrals. Except in the case of manganese, only monocentric and overlap integrals require scaling. Monocentric nuclear attraction integrals are about 20% too low in value when Burns's exponents are used. This problem is avoided, however, when empirical valence state ionization potentials are used in actual calculations. The Hartree-Fock correction for

overlap integrals has a relatively large effect on calculated electronic spectra, because of the consequent change in the magnitude of the resonance integrals β . Differences in oxygen-oxygen overlap integrals increase with increasing distance between the oxygen atoms. These differences are small in absolute terms (changing from a Burns value of 0.0164 to a Hartree-Fock value of 0.0232 in the sulphate anion), but, as will be shown in a later paper, cause a marked alteration in calculated transition energies.

It seems therefore that the taking of an average scaling factor introduces little error and for a general integral I we may write:

$$(I_{\mu\lambda}^{AB})^{\text{HF}} = (k_I^{AB})^{\text{HF}} (I_{\mu\lambda}^{AB})^{\text{Burns}} \quad (43)$$

where the average Hartree-Fock correction factor $(k_I^{AB})^{\text{HF}}$ depends only on the type of integral I and the atoms A and B, but not upon the orbitals μ and λ involved. $(k_I^{AB})^{\text{HF}}$ appears to differ from unity only for one centre repulsion integrals and overlap integrals in most cases, and then a suitable average value may be found by calculating k for the two integrals, I_{ss} and I_{pp} . Hence when Burns's rules for orbital exponents are used the balance between s -, p - and d -orbitals on the one centre given by full Hartree-Fock atomic orbitals is maintained. In addition theoretical integrals are closer to their Hartree-Fock values, and may be scaled where necessary from the data of Tables 5 and 6. The postulate of an average correction factor for all integrals of the same type on the same atom or between the same pair of atoms applies, provided the atomic charge does not differ greatly from neutrality. With their simplicity as well, the advantages of Burns's rules are obvious, and with the Hartree-Fock correction factors, they seem to make a reasonable allowance for the deviation of basis STO's from full Hartree-Fock atomic orbitals. An alternative possibility presently under examination is the use of Gaussian basis atomic orbitals.

7. The VESCF Method and Intramolecular Environment

The Variable Electronegativity Self Consistent Field (VESCF) procedure of Brown and Heffernan [2, 3] is particularly suitable for all valence electron calculations, because it allows the important parameters to vary as the number of electrons associated with each atom in the molecule changes. That is, the effect of the intramolecular environment on the form of the basis atomic orbitals is taken into account, but a simple alternative is sought to the laborious procedure of optimizing orbital exponents by the variational technique².

In principle all parameters in the calculation are made dependent upon the effective nuclear charges Z_μ for orbitals χ_μ and a simple rule is adopted for calculating Z_μ :

$$Z_\mu = Z_\mu^{\text{inner}} - (n_\mu - 1)\sigma_{\mu\mu} - \sum_{\nu}^A n_\nu\sigma_{\mu\nu} \quad (44)$$

² The basic procedure designated VE is to avoid the great labour of direct optimisation of atomic orbitals via the variation theorem by using empirical rules devised, for example, by studies of individual atoms and ions. For Slater type orbitals the exponent rules of Slater or Burns are regarded as crude indications and lead to approximate expressions such as (52) for the effect of the molecular environment on basic integrals. However, more elaborate calculations would justify the seeking of more elaborate and reliable empirical rules.

where the orbital χ_μ is centred on atom A, Z_μ^{inner} is the effective nuclear charge of the nucleus and inner-shell electrons for an electron in orbital χ_μ , $\sigma_{\mu\nu}$ are the shielding constants from Burns's or Slater's rules, being the amount by which an electron in orbital χ_ν shields the electron χ_μ from the nucleus, n_ν are the occupation numbers given by

$$n_\nu = P_{\nu\nu}, \quad \text{Löwdin basis} \quad (45)$$

$$n_\nu = P_{\nu\nu} + \sum_{B \neq A} \sum_{\lambda}^B P_{\nu\lambda} S_{\nu\lambda}, \quad \text{full overlap basis.} \quad (46)$$

Because of the dependence of the n_ν on the bond order matrix, new values of Z_μ are calculated within the SCF procedure as each new set of molecular orbital eigenvectors is produced. Then new values of the parameters are generated from the new values of Z_μ for the next iteration.

In practice the full VESCF procedure is too time-consuming for the more complex calculations and larger molecules required here. Fortunately only the monocentric integrals are greatly dependent on Z_μ within the range of Z_μ values to be expected in a calculation. Consequently only these integrals are expressed as functions of the effective nuclear charges in the version of the VESCF method used in this work. Theoretically, the following relationships are obtained:

$$\langle \mu_A | \hat{T}(1) | \mu_A \rangle = k_T Z_\mu^2, \quad (47)$$

$$\langle \mu_A | \hat{V}_A(1) | \mu_A \rangle = \frac{27.21}{n^2} Z_\mu \text{ (eV)}, \quad (48)$$

$$\begin{aligned} \langle \mu_A \mu_A | v_A v_A \rangle &= k_C Z_\mu \quad \text{when } Z_\mu = Z_\nu \\ &= f(\zeta_\mu, \zeta_\nu) \quad \text{otherwise,} \end{aligned} \quad (49)$$

$$\begin{aligned} \langle \mu_A v_A | v_A \mu_A \rangle &= k_E Z_\mu \quad \text{when } Z_\mu = Z_\nu \\ &= q(\zeta_\mu, \zeta_\nu) \quad \text{otherwise.} \end{aligned} \quad (50)$$

Here n is the principal quantum number, the constants k_T , k_C and k_E and the functions f and q are available from Zauli's tables [12], and the orbital exponents ζ_μ , ζ_ν are given by:

$$\zeta_\mu = \frac{Z_\mu}{n}. \quad (51)$$

The other monocentric parameter is the valence-state ionization potential appearing in the Coulomb integral expression (11). In normal VESCF procedure this is obtained as a quadratic in Z_μ :

$$I_\mu = a Z_\mu^2 + b Z_\mu + c \quad (52)$$

where a , b and c are determined from atomic spectral data, and the formula is to be compared with the theoretical expression from Eqs. (8) and (47–50):

$$\begin{aligned} I_\mu &= \langle \mu | \hat{T}(1) + N_A \hat{V}_A(1) + \sum_v^{\text{inner shells}} n_\nu (\hat{J}_\nu(1) - \frac{1}{2} \hat{K}_\nu(1)) | \mu \rangle \\ &= k_T Z_\mu^2 + N_A \frac{27.21}{n^2} Z_\mu + \sum_v^{\text{inner shells}} n_\nu [f_d(Z_\mu Z_\nu) - \frac{1}{2} g(Z_\mu Z_\nu)] \end{aligned} \quad (53)$$

providing some justification for the form of Eq. (52) since the n_ν and Z_ν are constant under the inner shells-valence separability conditions.

The empirical constants a , b , and c are determined from atomic spectroscopic data for an isoelectronic series of ions including the reference ion A. In such cases an extra variable, the core charge, is introduced. If a direct proportionality of valence state ionization potential to core charge is assumed, then core charges may be equalized along the series via a scaling procedure:

$$I_{\mu}^B(X_A) = \frac{X_A}{X_B} I_{\mu}^B(X_B) \quad (54)$$

where $I_{\mu}^B(X_A)$ is now the valence state ionization potential for atom B if B has the same core charge as the reference atom A.

In all-valence-electron calculations, small deviations in Z_{μ} make large differences to Hamiltonian elements, even more so than in the π -electron-only calculations for which the VESCF method was originally designed. The reason is the high core charges involved in the core Hamiltonian, which cause small changes in the basic integrals to be magnified. Consequently the importance of using the VESCF method is increased.

On the other hand the method is not without its disadvantages. The scaling procedure (54) appears to need refinement and has led Julg [50] to develop a linear variation in Z_{μ} equation for the valence state ionization potential. Also if the Z_{μ} values vary outside a small range, two-centre integrals need to be adjusted, a problem easily resolved in, say, the CNDO method, but much more difficult in methods as complex as the NDDO method.

8. Special Consideration of the CNDO Method

Only an average Coulomb repulsion integral and an average nuclear attraction integral is required for each atom A (γ_A , V_A^{AA} respectively) and pair of atoms A and B (γ_{AB} and V_A^{BB}) in the CNDO and Mulliken methods. Calculations show that the way in which these averages are found has a large effect on the final results. When theoretical values of integrals, based on Burns's values of orbital exponents, are considered, the original proposal of Pople, Santry, and Segal, that integrals involving the appropriate valence shell s-orbitals are suitable averages, is seen to be less satisfactory. Especially for the calculation of electronic spectra, it is better to use actual weighted averages (see Part III and the examples in Ref. [51–52]):

$$I_{AB} = \left(\sum_{\mu}^A \sum_{\lambda}^B I_{\mu\lambda} \right) / n_A n_B \quad (55)$$

where I represents a general integral for which an average is required, the sums are over the valence orbitals of the respective atoms included in the calculation, and n_A and n_B are the numbers of such orbitals. In the "theoretical CNDO method" all integrals I take their respective theoretical values and core elements in the full overlap basis are formed from Eq. (16), (17), and (18). The Hartree-Fock scaling procedure is invoked.

There are numerous possibilities for "semi-empirical CNDO methods", mostly depending on the choice of repulsion integrals, since on both theoretical and practical grounds Eq. (16)–(18) represent the most reliable way of obtaining

the core Hamiltonian matrix. Thus the $(I - A)$ formula supplies all the necessary one-centre Coulomb repulsion integrals. Two-centre Coulomb repulsion integrals may be related to the one-centre ones via the uniformly charged sphere approximation [40], or the Nishimoto-Mataga formula [38], or the Roos formula [39]. The uniformly charged sphere approximation has the advantage of being a simple representation of the orthogonalized atomic orbitals which form the basis of the zero differential overlap methods. According to the arguments of Sect. 6, Hartree-Fock and electron correlation corrections to repulsion integrals are indirectly allowed for in any of the above ways.

Finally a simple CNDO method, the "CNDO R-method", may be suggested as an alternative to Extended Hückel methods. It has the advantage of being as simple to use as these methods, promising more reliable results of a semi-quantitative nature. Its name stems from the requisition of the dependence of two-centre integrals on the bond length R . In the point charge approximation with the neglect of neutral atom penetration integrals, Eq. (28) and (29), and using the reduced "Ohno β " of equation (32), we have:

$$F_{\mu\mu} = -I_{\mu} + (P_{AA} - \frac{1}{2}P_{\mu\mu})\gamma_A + \sum_{B \neq A} (P_{BB} - X_B) \frac{14.4}{R_{AB}}, \quad (56)$$

$$\begin{aligned} F_{\mu\nu}^{AB} &= -k \frac{S_{\mu\nu}}{2} (X_A + X_B) \frac{14.4}{R_{AB}} - \frac{1}{2}P_{\mu\nu} \frac{14.4}{R_{AB}} \\ &= -\frac{1}{2} \frac{14.4}{R_{AB}} [k(X_A + X_B) S_{\mu\nu} + P_{\mu\nu}]. \end{aligned} \quad (57)$$

Here k (0.8–0.9) is a scaling factor for the resonance integral. The only unknowns are the one-centre repulsion integrals γ_A . These are easily found from the $(I - A)$ formula, or from the tables of Sichel and Whitehead [53] for first and second row atoms. The "CNDO R-method" is suggested merely as a simple, easy-to-use alternative to Extended Hückel calculations. The information it can give would be little more than the information obtained in Extended Hückel work.

9. Conclusions

In our attempt to devise parameter choice schemes of general applicability and having a sound theoretical basis, a number of important points have emerged:

a) In zero differential overlap methods, the calculation of the full-overlap-basis core Hamiltonian matrix, followed by a transformation to the Löwdin basis for use with zero differential overlap repulsion integral approximations is a feasible course of action as well as having the soundest theoretical basis.

b) A "theoretical parameter scheme" is possible and practicable in a basis of Slater-type atomic orbitals. The scheme then depends upon making adequate Hartree-Fock and electron correlation corrections. By using Burns's rules for orbital exponents together with an average Hartree-Fock scaling factor for those integrals that need further correction, the difference between STO's and Hartree-Fock AO's is minimized. In a following paper of the series it will be shown how electron correlation may be allowed for in this scheme.

c) "Semi-empirical parameter schemes" are also possible, and depend on the use of the $(I - A)$ formula and Slater-Condon parameters. Via the $(I - A)$ formula,

an empirical scaling scheme for theoretical integrals may be developed for repulsion integrals. Presumably Hartree-Fock and electron correlation corrections are then adequately taken into account in an indirect way.

d) The VESCF approach, as well as being able to cope with the high core charges of all valence electron calculations, allows for the effect of intra-molecular environment on the basis atomic orbitals. It may be used in conjunction with either "theoretical" or "semi-empirical" parameter schemes.

e) Special features of the "theoretical" and "semi-empirical" CNDO methods have been discussed, and the simple "CNDO R-method" suggested as an alternative to Extended Hückel methods for rapid calculations giving a limited amount of information.

Appendix

Theoretical Expressions for Monocentric Repulsion Integrals in Terms of Slater-Condon Parameters

The Slater-Condon parameters are defined and discussed in Ref. [12] and [30], and in textbooks on atomic spectroscopy. Any monocentric repulsion integral in principle may be calculated from these F and G parameters:

$$J_{\mu\nu} = (\mu\mu|\nu\nu) = \sum_k a^k(l^\mu, m_l^\mu, l^\nu, m_l^\nu) D_k F_k(n^\mu l^\mu, n^\nu l^\nu),$$

$$K_{\mu\nu} = (\mu\nu|\nu\mu) = \delta(m_s^\mu, m_s^\nu) \sum_k b^k(l^\mu, m_l^\mu, l^\nu, m_l^\nu) D_k G_k(n^\mu l^\mu, n^\nu l^\nu).$$

The appropriate combinations of F and G parameters for integrals involving complex orbitals are easily found from the data in Ref. [30]. Here we list the corresponding expressions for real orbitals. The F and G parameters may be calculated theoretically or evaluated empirically from spectroscopic data, and in the latter case find most use for calculating monocentric exchange integrals.

Slater-Condon Parameters Expressions for Monocentric Coulomb and Exchange Repulsion Integrals

Orbitals Involved		Coulomb Repulsion Int.	Exchange Repulsion Int.
μ	ν		
s	s	F_0^{ss}	
s	p	F_0^{sp}	G_1^{sp}
p	p	$F_0^{pp} + 4F_2^{pp}$	—
p	\bar{p}	$F_0^{pp} - 2F_2^{pp}$	$3F_2^{pp}$
s	d	F_0^{sd}	G_2^{sd}
p_z	d_{z^2}	$F_0^{pd} + 4F_2^{pd}$	$2G_1^{pd} + 27G_3^{pd}$
p_z	d_{xz}	$F_0^{pd} + 2F_2^{pd}$	$3G_1^{pd} + 24G_3^{pd}$
p_x	d_{z^2}	$F_0^{pd} - 2F_2^{pd}$	$G_1^{pd} + 18G_3^{pd}$
p_z	$d_{x^2-y^2}$	$F_0^{pd} - 4F_2^{pd}$	$15G_3^{pd}$
d	d	$F_0^{dd} + 4F_2^{dd} + 36F_4^{dd}$	—
d_{xy}	$d_{x^2-y^2}$	$F_0^{dd} + 4F_2^{dd} - 34F_4^{dd}$	$35F_4^{dd}$
d_{z^2}	d_{xz}	$F_0^{dd} + 2F_2^{dd} - 24F_4^{dd}$	$F_2^{dd} + 30F_4^{dd}$
d_{xz}	d_{yz}	$F_0^{dd} - 2F_2^{dd} - 4F_4^{dd}$	$3F_2^{dd} + 20F_4^{dd}$
d_{z^2}	d_{xy}	$F_0^{dd} - 4F_2^{dd} + 6F_4^{dd}$	$4F_2^{dd} + 15F_4^{dd}$

Relationships that hold for integrals not listed here are:

(a) Involving p - and d -orbitals.

$$\begin{aligned} \text{(i)} \quad & J(p_z, d_{xz}) = J(p_z, d_{yz}) = J(p_x, d_{xz}) = J(p_x, d_{xy}) \\ & = J(p_y, d_{yz}) = J(p_y, d_{xy}) = J(p_x, d_{x^2-y^2}) = J(p_y, d_{x^2-y^2}) \end{aligned}$$

$$\text{(ii)} \quad J(p_x, d_{z^2}) = J(p_y, d_{z^2})$$

$$\text{(iii)} \quad J(p_z, d_{x^2-y^2}) = J(p_z, d_{xy}) = J(p_x, d_{yz}) = J(p_y, d_{xz})$$

(iv) Similarly for the exchange integrals, K .

(b) Involving d -orbitals only.

$$\text{(i)} \quad J(d_{z^2}, d_{xz}) = J(d_{z^2}, d_{yz})$$

$$\text{(ii)} \quad J(d_{xz}, d_{yz}) = J(d_{xz}, d_{xy}) = J(d_{xz}, d_{x^2-y^2}) = J(d_{yz}, d_{xy}) = J(d_{yz}, d_{x^2-y^2})$$

$$\text{(iii)} \quad J(d_{z^2}, d_{xy}) = J(d_{z^2}, d_{x^2-y^2})$$

(iv) Similarly for the exchange integrals K .

These formulas are useful:

(i) in deriving theoretical expressions for all of the integrals in terms of their orbital exponents. Only a limited number of F and G parameters need be derived theoretically to obtain the wide range of repulsion integrals listed here;

(ii) in obtaining empirical exchange and, in some cases, Coulomb-repulsion integrals;

(iii) in deriving simple relationships between the integrals involving different orbitals of the same set, which can then act as a test of values of integrals being used, especially where these have been found semi-empirically.

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