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Self Consistent Field Molecular Orbital Calculation for Pyrrole

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The electronic structure and spectrum of pyrrole have been studied using the semiempirical LCAO SCF MO method. With configuration interaction included, low excited singlet states are calculated to occur at 5.98 ev, 6,74 ev, 7,33 ev, and 8,20 ev, in good agreement with the experimental values of about 5.88 ev, 6.77 ev, and 7,21 ev. The dipole moment of the molecule is calculated to 1.84 D, to be compared with the experimental value 1.80 D. Tables of core-attraction integrals for combinations of carbon and nitrogen atoms are presented.

Elektronenstruktur und -spektrum des Pyrrols wurden nach der halbempirischen LCAO SCF MO-Methode untersucht. Unter Einschluß der Konfigurationenwechselwirkung wurden niedrigliegende angeregte Singulettniveaus bei 5,98, 6,74, 7,33 und 8,20 eV (über dem Grundzustand) errechnet, in guter Übereinstimmung mit den experimentellen Werten von etwa 5,88, 6,77 und 7,21 eV. Das Dipolmoment des Moleküls ergibt sich zu 1,84 D, bei einem experimentellen Wert von 1,80 D. Tabellen von (sphärischen) Rumpf-Elektron-Integralen für alle vier Kombinationen von *C* und *N* werden angegeben.

La structure et le spectre électroniques du pyrrole ont été étudiés à l'aide de la méthode sémiempirique LCAO SCF MO. L'interaction de configurations inclue, le calcul donne des états excités à 5,98, 6,74, 7,33 et 8,20 eV (au-dessus de l'état fondamental), en bon accord avec les valeurs expérimentales de 5,88, 6,77 et 7,21 eV. Le moment dipolaire calculé de la molécule est 1,84 D, l'expérience donnant 1,80 D. Des tables d'intégrales d'attraction entre un coeur sphérique et un électron d'un autre atome sont données pour les quatre combinaisons d'atomes *C* et *N*.

I. Introduction

In this communication we present a self-consistent field molecular orbital calculation for pyrrole. For the same molecule similar extensive calculations have previously been reported by **Brown** and **Heffernan** [*3*]. The positions of the first and third excited singlet states were given quite correctly by these authors. However, the second excited singlet state was predicted to be at considerably lower energy than is observed. This situation is quite similar to what has been observed in calculations on benzene [*12*] and heterocycles containing pyridine nitrogen [*9*], i. e. nitrogen atoms which contribute only one electron to the conjugated system, in contradistinction to pyrrole nitrogen which contributes two electrons. For hydrocarbons and pyridine heterocycles the difficulty of predicting correctly the position of the second excited singlet state has been overcome by using smaller values of the two electron integrals $(\mu\mu \mid \nu\nu)$ than was suggested by **Pariser** and **Parr** [*12*] (See e. g. the discussion by **Brown** and **Heffernan** [*4*].) In particular, the formula suggested by **Mataga** and **Nishimoto** [*8*] for the $(\mu\mu \mid \nu\nu)$ integrals seems very adequate.

The position of the second excited singlet state of pyrrole, as predicted by the present calculation, is in good agreement with the experimental value. The improvement was obtained partly by adopting MATAGA and NISHIMOTO's formula for the $(\mu\mu \mid \nu\nu)$ integrals, partly by evaluating the core-attraction integrals theoretically. Tables of such integrals were prepared for further use.

II. Formulation of the method

The computational scheme for the LCAO SCF MO method is described by ROOTHAAN [*15*]. This scheme was followed in the present work with the additional simplification which results from the approximation of zero differential overlap. Only the π-electrons were considered explicitely. The expression for the π-electron Hamiltonian is then

$$\hat{\boldsymbol{H}} = \sum_{i=1}^{2n} \hat{\boldsymbol{H}}_{\text{core}}(i) + \frac{1}{2} \sum_{i \neq j=1}^{2n} (e^2/r_{ij}) \tag{1}$$

$2n$ being the number of π-electrons, which equals 6 in the present case. The following matrix elements then occur, φ_μ denoting the μ.th 2 p_z atomic orbital:

$$\alpha_\mu = \int \varphi_\mu(1)\ \hat{\boldsymbol{H}}_{\text{core}}(1)\ \varphi_\mu(1)\ d\tau_1 \tag{2}$$

$$\beta_{\mu\nu} = \int \varphi_\mu(1)\ \hat{\boldsymbol{H}}_{\text{core}}(1)\ \varphi_\nu(1)\ d\tau_1 \tag{3}$$

$$(\mu\mu \mid \nu\nu) = \int\int \varphi_\mu(1)\, \varphi_\nu(2) \frac{e^2}{r_{12}} \varphi_\mu(1)\, \varphi_\nu(2)\ d\tau_1\ d\tau_2 \tag{4}$$

When the operator $\hat{\boldsymbol{H}}_{\text{core}}$ is broken down into a kinetic contribution and contributions from the atomic cores, as originally proposed by GOEPPERT-MAYER and SKLAR [*5*], we obtain for integrals of the α_μ-type:

$$\alpha_\mu = -I_\mu + \sum_{\nu \neq \mu} (\mu \mid \boldsymbol{V}_\nu \mid \mu) - \sum_{\lambda} (\lambda : \mu\mu) \tag{5}$$

The term $-I_\mu$ represents the kinetic energy of an electron in orbital φ_μ plus its energy in the field from the μ'th atomic core. $(\mu \mid \boldsymbol{V}_\nu \mid \mu)$ designates the energy of the same electron in the field of the ν'th atomic core of the conjugated system. Finally $(\lambda : \mu\mu)$ is the usual penetration integral [*13*], the summation extending over neutral atoms of the molecule, i. e. hydrogen atoms in the present case.

The integral $(\mu \mid \boldsymbol{V}_\nu \mid \mu)$ may be written

$$(\mu \mid \boldsymbol{V}_\nu \mid \mu) = -V(\nu : \mu\mu) - (\nu\nu \mid \mu\mu) \tag{6}$$

where $-V(\nu : \mu\mu)$ represents the energy of an electron in orbital φ_μ, which arises from the interaction with a spherical symmetric charge distribution around atom ν (see appendix).

In the present calculation the summation over λ in eq. (5) was neglected, since it gives almost identical contributions to each α_μ and thus has almost no influence either on the form of the molecular orbitals or on excitation energies. With this simplification and considering eq. (6), eq. (5) may be written

$$\alpha_\mu = -\left\{ I_\mu + \sum_{\nu \neq \mu} [V(\nu : \mu\mu) + (\nu\nu \mid \mu\mu)] \right\} \tag{7}$$

If m denotes the total number of atomic orbitals and $2n$ is the number of π-electrons, then the solution of Roothaan's equations results in n doubly occupied orbitals and m-n "virtual" orbitals which may be used for constructing excited state wavefunctions. The procedure to be followed as well as the expressions for the matrix elements between excited configurations have been given elsewhere [*8*, *9*]. The singlet configurational wavefunction in which one electron is excited from an occupied molecular orbital ψ_i to a virtual orbital ψ_k will be written ${}^1\Phi_{i\to k}$, while the notation ${}^3\Phi_{i\to k}$ will be used for the corresponding triplet function. Oscillator strengths were calculated according to the expression given by MULLIKEN and RIEKE [*10*].

III. Semiempirical evaluation of the integrals

For reasons which have been discussed by PARISER and PARR [*12*] the integrals set up in section II should be assigned values by semiempirical methods. In molecules containing doubly charged core atoms, like pyrrole nitrogen, this assignment is quite difficult to perform in a proper way. In our opinion the most consistent assignment is the one suggested by BROWN and HEFFERNAN [*2*, *3*] which has therefore been followed in the present work. In this "variable electronegativity method" formulae depending on the π-electron density are set up for the various integrals. The first self consistent field calculation is performed with integrals derived from a presupposed charge distribution. If the charge distribution resulting from this calculation is different from the one presupposed the whole calculation is repeated with new values for the integrals. This procedure is continued until a self consistent charge distribution is arrived at.

Let the π-electron density at atom μ be denoted $P_{\mu\mu}$. The effective charge Z_μ is then given by [*2*]

$$Z_\mu = N_\mu - 1.35 - 0.35\,(3 + P_{\mu\mu}) \tag{8}$$

where N_μ is the charge of the μ'th nucleus. Integrals are derived from the Z_μ-values in the following way:

The integrals I_μ should be identified with the ionization potentials for the processes

$$\begin{aligned} C\,(sp^3,\,V_4) &\rightarrow C^+\,(sp^2,\,V_3) + e^- \\ N^+\,(sp^3,\,V_4) &\rightarrow N^{++}\,(sp^2,\,V_3) + e^-. \end{aligned} \tag{9}$$

These ionization potentials are derived from the interpolation formulae [*3*]

$$\begin{aligned} I_C &= 0.3605\,Z_\mu^2 + 9.0923\,Z_\mu - 21.818 \text{ ev} \\ I_{N^+} &= 0.4510\,Z_\mu^2 + 11.3625\,Z_\mu - 27.267 \text{ ev}. \end{aligned} \tag{10}$$

Integrals of the type $(\mu\mu\,|\,\mu\mu)$ should according to PARISER and PARR be determined as the difference between an ionization potential and an electron affinity. This difference is sufficiently well reproduced by PAOLINI's formula [*11*]

$$(\mu\mu\,|\,\mu\mu) = 3.29_4\,Z_\mu. \tag{11}$$

The bicentric integrals $(\mu\mu\,|\,\nu\nu)$ were in the present work determined from the formula of MATAGA and NISHIMOTO [*8*]

$$(\mu\mu\,|\,\nu\nu) = \frac{e^2}{a_{\mu\nu} + r_{\mu\nu}} \tag{12}$$

where $\dfrac{e^2}{a_{\mu\nu}} = \dfrac{1}{2}\,[(\mu\mu\,|\,\mu\mu) + (\nu\nu\,|\,\nu\nu)]$ and $r_{\mu\nu}$ is the interatomic distance. It may be appropriate to mention that the formula (12) fulfills the proper limiting conditions laid down by Pariser and Parr in their semiempirical discussion, only the interpolation method is different.

Integrals of the types $V\ (\nu : \mu\mu)$ and $\beta_{\mu\nu}$ were not varied. The integrals $V\ (\nu : \mu\mu)$ were evaluated theoretically and their values taken from the tables in the appendix. The integrals $\beta_{\mu\nu}$ were only taken into consideration for nearest neighbours and were determined from Pariser and Parr's formula

$$\beta_{\mu\nu} = -6442 \exp\left(-5.6864\, r_{\mu\nu}\right) \text{ ev} \qquad (13)$$

not only for β_{CC}, but also for β_{CN}. This gives $\beta_{CN} = -2.49$ ev, close to the value used by Brown and Heffernan [3], i. e. — 2.45 ev. All interatomic distances were taken from the determinations of Bak et al. [1].

IV. Results and discussion

In Tab. 1 we represent the self consistent molecular orbitals and the one electron energies resulting from our calculation. The molecular orbitals are classified according to their transformation properties in the point group C_{2v}.

Table 1

Symmetry	Energy (ev)	SCF MO s
b_2	— 19.284	$\psi_1 = 0.7004\, \varphi_1 + 0.4398\, (\varphi_2 + \varphi_5) + 0.2475\, (\varphi_3 + \varphi_4)$
a_2	— 14.776	$\psi_2 = 0.6117\, (\varphi_2 - \varphi_5) + 0.3547\, (\varphi_3 - \varphi_4)$
b_2	— 14.494	$\psi_3 = 0.5614\, \varphi_1 - 0.1254\, (\varphi_2 + \varphi_5) - 0.5716\, (\varphi_3 + \varphi_4)$
b_2	— 4.668	$\psi_4 = 0.4407\, \varphi_1 - 0.5393\, (\varphi_2 + \varphi_5) + 0.3348\, (\varphi_3 + \varphi_4)$
a_2	— 3.529	$\psi_5 = 0.3547\, (\varphi_2 - \varphi_5) - 0.6117\, (\varphi_3 - \varphi_4)$

The excited state wave functions, their energies above the ground state, and the oscillator strengths are given in Tab. 2.

No triplet states are known experimentally, while three singlet states are known [7], corresponding to excitation energies about 5.88 ev, 6.77 ev, and 7.21 ev.

Table 2

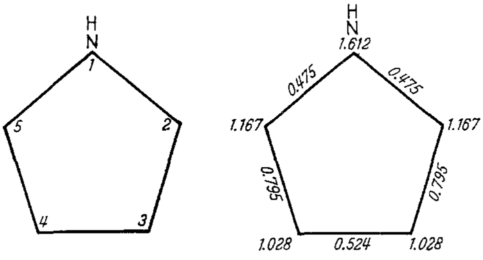
Symmetry	Energy (ev)	Oscillator strength	State functions
A_1	5.985	0.135	$0.4613\, {}^1\Phi_{2\to5} - 0.8872\, {}^1\Phi_{3\to4}$
B_1	6.735	0.255	$0.9732\, {}^1\Phi_{2\to4} + 0.2301\, {}^1\Phi_{3\to5}$
B_1	7.326	0.347	$0.2301\, {}^1\Phi_{2\to4} - 0.9732\, {}^1\Phi_{3\to5}$
A_1	8.201	0.979	$0.8872\, {}^1\Phi_{2\to5} + 0.4613\, {}^1\Phi_{3\to4}$
B_1	3.286		$0.8318\, {}^3\Phi_{2\to4} + 0.5551\, {}^3\Phi_{3\to5}$
A_1	3.700		$0.3999\, {}^3\Phi_{2\to5} + 0.9166\, {}^3\Phi_{3\to4}$
B_1	5.245		$0.5551\, {}^3\Phi_{2\to4} - 0.8318\, {}^3\Phi_{3\to5}$
A_1	5.380		$0.9166\, {}^3\Phi_{2\to5} - 0.3999\, {}^3\Phi_{3\to4}$

We then make the assignments A_1, B_1, B_1. Brown and Heffernan in their work proposed the assignment B_1, A_1, B_1. However, the two lowest excited states, as determined by these authors, were only slightly separated. Our calculation of oscillator strengths is in accordance with the fact [7] that the first transition is known to be less intense that the second and the third transitions.

From the results given in Tab. 1 π-electron density and bond orders were calculated, and the results are given in Fig. 1. The calculation definitely shows, in agreement with experiment, that the carbon atoms 2 and 5 are the most sensitive to electrophilic attack.

From the calculated π-electron density the dipole moment of the molecule was calculated to 1.84 D. The experimental value is 1.80 D [*16*]. Hence, according to the present calculation, the dipole moment may be accounted for without considering polarization of the σ-bonds. We may thus conclude that the σ-contribution to the total dipole moment is small. A recent paper by HAMANO and HAMEKA [*6*] suggests that the π-contribution should be as small as 1.21 D, the rest being σ-contribution. This result was arrived at through a consideration of the σ-electrons only. However, polarization of the σ-bonds depends on the π-electron density as well, and we think that the value arrived at through our much more detailed calculations is at least not more defective than HAMANO and HAMEKA's value.

According to Koopman's theorem the ionization potential should be equal to the orbital energy, with opposite sign, corresponding to the highest occupied orbital. This value is 14.49 ev, while the experimental value for the ionization potential is 8.90 ev [*14*]. Thus our value is too high. This is due to our treatment of the core-attraction integrals. If, as it is often done, penetration integrals between atoms of the conjugated system are neglected, better values for the ionization potential may often be arrived at. A calculation which neglected such integrals was carried out, giving an ionization potential equal to 10.14 ev, which is quite satisfactory. However, the first and the second excited states were now only slightly separated, and furthermore the atoms 3 and 4 turned out to be slightly more negative than the atoms 2 and 5.



a b

Fig. 1. a) Numbering of atoms, b) Calculated π-electron density and bond orders

Ionization potentials are dependent on the absolute values of the α_μ-integrals, while only the relative values of these integrals affect other properties of the molecule. Thus a calculation which gives an ionization potential of the right magnitude should not be considered to be superior for that reason if, on the other hand, it neglects certain terms in the expression for the α_μ-integrals, on which the ionization potential is highly dependent.

Appendix

The following tables (A—D) give the core-attraction integrals $V(a:bb)$ introduced in eq. (6), as a function of interatomic distance R in Å. The integrals are in atomic units (1 a. u. = 27.21 ev).

The quantity $-V(a:bb)$ is the electrostatic energy of an electron in the $2\,p_\pi$-orbital φ_b centered at b in the spherical symmetric field V_a arising from a charge distribution around the center a. This charge distribution is made up of the atomic nucleus at a, two 1s-electrons which were drawn into the nucleus in the calculation, and 4 electrons in $2\,s$, $2\,p_x$, $2\,p_y$ and $2\,p_z$ respectively. The actual form of V_a is

Tables of Core Attraction Integrals $V(a:bb)$

Table A. *a* carbon, *b* carbon

R	Integral	R	Integral	R	Integral
1.30	4.4021 10^{-2}	1.35	3.6747 10^{-2}	1.40	3.0595 10^{-2}
1.45	2.5409 10^{-2}	1.50	2.1052 10^{-2}	1.55	1.7402 10^{-2}
1.60	1.4352 10^{-2}	1.65	1.1812 10^{-2}	1.70	9.7020 10^{-3}
1.75	7.9529 10^{-3}	1.80	6.5067 10^{-3}	1.85	5.3137 10^{-3}
1.90	4.3318 10^{-3}	1.95	3.5252 10^{-3}	2.00	2.8641 10^{-3}
2.05	2.3232 10^{-3}	2.10	1.8816 10^{-3}	2.15	1.5216 10^{-3}
2.20	1.2287 10^{-3}	2.25	9.9081 10^{-4}	2.30	7.9787 10^{-4}
2.35	6.4166 10^{-4}	2.40	5.1537 10^{-4}	2.45	4.1342 10^{-4}
2.50	3.3123 10^{-4}	2.55	2.6507 10^{-4}	2.60	2.1189 10^{-4}
2.65	1.6919 10^{-4}	2.70	1.3494 10^{-4}	2.75	1.0752 10^{-4}
2.80	8.5581 10^{-5}	2.85	6.8051 10^{-5}	2.90	5.4060 10^{-5}
2.95	4.2904 10^{-5}	3.00	3.4020 10^{-5}	3.05	2.6951 10^{-5}
3.10	2.1332 10^{-5}	3.15	1.6870 10^{-5}	3.20	1.3331 10^{-5}
3.25	1.0525 10^{-5}	3.30	8.3036 10^{-6}	3.35	6.5458 10^{-6}

Table B. *a* nitrogen, *b* nitrogen

R	Integral	R	Integral	R	Integral
1.30	3.9925 10^{-1}	1.35	3.8300 10^{-1}	1.40	3.6824 10^{-1}
1.45	3.5479 10^{-1}	1.50	3.4246 10^{-1}	1.55	3.3111 10^{-1}
1.60	3.2061 10^{-1}	1.65	3.1087 10^{-1}	1.70	3.0178 10^{-1}
1.75	2.9329 10^{-1}	1.80	2.8531 10^{-1}	1.85	2.7780 10^{-1}
1.90	2.7071 10^{-1}	1.95	2.6400 10^{-1}	2.00	2.5763 10^{-1}
2.05	2.5158 10^{-1}	2.10	2.4582 10^{-1}	2.15	2.4032 10^{-1}
2.20	2.3507 10^{-1}	2.25	2.3004 10^{-1}	2.30	2.2523 10^{-1}
2.35	2.2062 10^{-1}	2.40	2.1619 10^{-1}	2.45	2.1194 10^{-1}
2.50	2.0785 10^{-1}	2.55	2.0391 10^{-1}	2.60	2.0012 10^{-1}
2.65	1.9646 10^{-1}	2.70	1.9294 10^{-1}	2.75	1.8954 10^{-1}
2.80	1.8625 10^{-1}	2.85	1.8307 10^{-1}	2.90	1.8000 10^{-1}
2.95	1.7703 10^{-1}	3.00	1.7416 10^{-1}	3.05	1.7138 10^{-1}
3.10	1.6868 10^{-1}	3.15	1.6606 10^{-1}	3.20	1.6353 10^{-1}
3.25	1.6107 10^{-1}	3.30	1.5868 10^{-1}	3.35	1.5636 10^{-1}

Table C. *a* carbon, *b* nitrogen

R	Integral	R	Integral	R	Integral
1.30	4.3941 10^{-2}	1.35	3.6028 10^{-2}	1.40	2.9465 10^{-2}
1.45	2.4038 10^{-2}	1.50	1.9564 10^{-2}	1.55	1.5887 10^{-2}
1.60	1.2873 10^{-2}	1.65	1.0409 10^{-2}	1.70	8.3992 10^{-3}
1.75	6.7646 10^{-3}	1.80	5.4379 10^{-3}	1.85	4.3635 10^{-3}
1.90	3.4953 10^{-3}	1.95	2.7952 10^{-3}	2.00	2.2317 10^{-3}
2.05	1.7790 10^{-3}	2.10	1.4160 10^{-3}	2.15	1.1254 10^{-3}
2.20	8.9324 10^{-4}	2.25	7.0797 10^{-4}	2.30	5.6039 10^{-4}
2.35	4.4301 10^{-4}	2.40	3.4978 10^{-4}	2.45	2.7584 10^{-4}
2.50	2.1728 10^{-4}	2.55	1.7096 10^{-4}	2.60	1.3436 10^{-4}
2.65	1.0549 10^{-4}	2.70	8.2735 10^{-5}	2.75	6.4825 10^{-5}
2.80	5.0742 10^{-5}	2.85	3.9681 10^{-5}	2.90	3.1003 10^{-5}
2.95	2.4201 10^{-5}	3.00	1.8875 10^{-5}	3.05	1.4709 10^{-5}
3.10	1.1453 10^{-5}	3.15	8.9103 10^{-6}	3.20	6.9269 10^{-6}
3.25	5.3810 10^{-6}	3.30	4.1769 10^{-6}	3.35	3.2400 10^{-6}

Table D. *a* nitrogen, *b* carbon

R	Integral	R	Integral	R	Integral
1.30	$3.8853\ 10^{-1}$	1.35	$3.7361\ 10^{-1}$	1.40	$3.5994\ 10^{-1}$
1.45	$3.4737\ 10^{-1}$	1.50	$3.3577\ 10^{-1}$	1.55	$3.2503\ 10^{-1}$
1.60	$3.1505\ 10^{-1}$	1.65	$3.0575\ 10^{-1}$	1.70	$2.9706\ 10^{-1}$
1.75	$2.8890\ 10^{-1}$	1.80	$2.8122\ 10^{-1}$	1.85	$2.7399\ 10^{-1}$
1.90	$2.6714\ 10^{-1}$	1.95	$2.6066\ 10^{-1}$	2.00	$2.5450\ 10^{-1}$
2.05	$2.4863\ 10^{-1}$	2.10	$2.4305\ 10^{-1}$	2.15	$2.3772\ 10^{-1}$
2.20	$2.3262\ 10^{-1}$	2.25	$2.2774\ 10^{-1}$	2.30	$2.2306\ 10^{-1}$
2.35	$2.1857\ 10^{-1}$	2.40	$2.1425\ 10^{-1}$	2.45	$2.1011\ 10^{-1}$
2.50	$2.0612\ 10^{-1}$	2.55	$2.0228\ 10^{-1}$	2.60	$1.9857\ 10^{-1}$
2.65	$1.9500\ 10^{-1}$	2.70	$1.9155\ 10^{-1}$	2.75	$1.8822\ 10^{-1}$
2.80	$1.8500\ 10^{-1}$	2.85	$1.8189\ 10^{-1}$	2.90	$1.7888\ 10^{-1}$
2.95	$1.7596\ 10^{-1}$	3.00	$1.7314\ 10^{-1}$	3.05	$1.7040\ 10^{-1}$
3.10	$1.6775\ 10^{-1}$	3.15	$1.6518\ 10^{-1}$	3.20	$1.6268\ 10^{-1}$
3.25	$1.6026\ 10^{-1}$	3.30	$1.5791\ 10^{-1}$	3.35	$1.5562\ 10^{-1}$

$$V_a = \frac{\delta_a}{r_a} + \frac{\zeta_a}{2} e^{-2\zeta_a r_a}\left[\frac{16}{2\zeta_a r_a} + 12 + 4\,(2\zeta_a r_a) + (2\zeta_a r_a)^2\right]$$

where δ_a is equal to 1 if the atom at *a* is nitrogen and equal to 0 when it is carbon. ζ_a is the orbital exponent occuring in the analytical form of the 2 *p*- and 2 *s*-orbitals, $\zeta_C = 1.59$, $\zeta_N = 1.92$. r_a is the distance from the center *a*.

Since the charge of the electron is negative, $V(a{:}bb)$ is *a* positive quantity.

In the case where atom *a* is carbon the integral $V(a{:}bb)$ is identical with the penetration integral $(a{:}bb)$ as defined by PARR and CRAWFORD [13]. When *a* is nitrogen the integrals are different.

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