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Penetration in the CNDO Theory

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An explicit form for the penetration integrals in CNDO theory is developed and tested on first row diatomic molecules. It is shown that the non-penetration integral theory CNDO/BW is more satisfactory for predicting bond lengths and equilibrium energies because it gives an unstable $^3\Sigma_u^+$ for H_2, whereas introduction of the penetration integrals makes this state stable.

INTRODUCTION

The CNDO theory should include penetration effects to be used in chemisorption studies. An explicit form for the penetration integrals is derived and incorporated into the CNDO theory.

THEORY

The CNDO Roothaan equations for a closed shell system are[1]

$$\sum_{l=1}^{n} F_{kl}\, C_{li} = E_i\, C_{ki} \qquad (k, i = 1, \ldots N) \tag{1}$$

where F_{kl}, the Fock matrix elements, are

$$F_{kk} = H_{kk} - (1/2)\, P_{kk}\, (kk \mid kk) + \sum_{r} P_{rr}\, (kk \mid rr) \tag{2}$$

and

$$F_{kl} = H_{kl} - (1/2)\, P_{kl}\, (kk \mid ll) \qquad k \neq l \tag{3}$$

The P_{ii} are the elements of the population matrices. To preserve invariance to orthogonal transformations among atomic orbitals on the same atom, the Coulomb integrals[2], are assigned a common value γ_{AB} for all φ_k and φ_r on atoms A and B, respectively

$$\gamma_{AB} = (kk \mid rr) \tag{4}$$

The diagonal core Hamiltonian matrix elements, H_{kk}, are

$$H_{kk} = \int \varphi_k^* (1) (-{}^1\!/_2\, \nabla^2 - V_A)\, \varphi_k (1)\, d\tau_1 - \sum_{B \neq A} \varphi_k^* (1)\, V_B\, \varphi_k (1)\, d\tau_1 = U_{kk} - \sum_{B \neq A} V_{AB} \tag{5}$$

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and represent the kinetic and potential energies of an electron in the k^{th} orbital of an atom A with the field about A and with the core of atom B. The off-diagonal terms are

$$H_{kl} = U_{kl} - \sum_{B \neq A} \int \varphi_k^* (1) V_B \varphi_l (1) d\tau_1 \quad (6)$$

where φ_k is on A and φ_l on B. In CNDO the H_{kl} elements are approximated by

$$H_{kl} = -\beta_{AB} S_{kl} \quad (7)$$

where β_{AB} is an empirical parameter and S_{kl} is the overlap matrix

$$S_{kl} = \int \varphi_k^* (1) \varphi_l (1) d\tau_1 \quad (8)$$

Using the population matrices, equation (1) becomes

$$F_{kk} = U_{kk} + (P_{AA} - \tfrac{1}{2} P_{kk}) \gamma_{AA} + \sum_{B \neq A} (P_{BB} \gamma_{AB} - V_{AB}) \quad (9)$$

and

$$F_{kl} = -\beta_{AB} S_{kl} - \tfrac{1}{2} P_{kl} \gamma_{AB} \qquad k \neq l \quad (10)$$

where

$$P_{AA} = \sum_{k}^{A} P_{kk} \quad (11)$$

Equation (9) can be rewritten as

$$F_{kk} = U_{kk} + (P_{AA} - \tfrac{1}{2} P_{kk}) \gamma_{AB} + \sum_{B \neq A} (P_{BB} - Z_B) \gamma_{AB} + \sum_{B \neq A} (Z_B \gamma_{AB} - V_{AB}) \quad (12)$$

where $\sum_{B \neq A} (Z_B \gamma_{AB} - V_{AB})$ is the penetration term which describes the interaction of an electron on atom A with the core of atom B[3]. The parameter γ_{AB} has the following well known constraints:

$$\begin{aligned} \lim \gamma_{AB} &= \sqrt{\gamma_{AA}^* \gamma_{BB}^*}\,; \; R_{AB} \to 0 \\ \lim \gamma_{AB} &= 0\,; \; R_{AB} \to \infty \\ \lim \gamma_{AB} &= \frac{V_{AB}}{Z_B}\,; \; \gamma_{ii} \to \infty \end{aligned} \quad (13)$$

where R_{AB} is the interatomic distance and γ_{ii}^* is the average electronic repulsion between electrons in orbitals located on atom i. The penetration is set equal to zero (*i. e.* $V_{AB} = Z_B \gamma_{AB}$) in CNDO/2 in order to correctly describe the $^3\Sigma_u^+$ state of H_2[4]. The new theory, CNDO/VZ, attempts to re-introduce the penetration term by using new forms for γ_{AB} and V_{AB}, γ_{AB} (VZ) and V_{AB} (VZ); VZ denotes the interaction between atom A of potential V with atom B of nuclear charge Z. γ_{AB} (VZ) is in the form of the damped Mataga-Nishimoto Coulomb integral[5]:

$$\gamma_{AB}(VZ) = \frac{(1 - e^{-\lambda R_{AB} \gamma_{AA}^*})(1 - e^{-\lambda R_{AB} \gamma_{BB}^*})}{R_{AB}} + \sqrt{\gamma_{AA}^* \gamma_{BB}^*}\, e^{-\lambda R_{AB} \gamma_{BB}^*} \quad (14)$$

λ is a constant and all other terms have been defined. γ_{AB} (VZ) obeys the same limit conditions as γ_{AB}. V_{AB} (VZ) is given by

$$V_{AB}(VZ) = \frac{Z_B (1 - e^{-\lambda R_{AB} \gamma_{AA}^*})}{R_{AB}} \quad (15)$$

with constraints[5]:

$$\lim V_{AB} = \lambda Z_B \gamma_{AB} ; \; R_{BA} \rightarrow 0$$
$$\lim V_{AB} = 0 ; \; R_{AB} \rightarrow \infty \qquad (16)$$
$$\lim V_{AB} = \frac{Z_B}{R_{AB}} ; \; \gamma_{ii}^{*} \rightarrow \infty$$

RESULTS AND DISCUSSION

The CNDO program used is similar to CNDO/2 with the addition of the CNDO/VZ parameters, equations (14) and (15)[6]. The atomic parameters, γ_{ii}, are evaluated from Hinze and Jaffe valence state data[7]. The interatomic repulsion parameter, N_{AB}, of CNDO/2 is omitted since this interaction is contained within the CNDO/VZ equations.

TABLE I

Empirical Parameters λ and β_{AB} used in CNDO/VZ Method

Molecule	λ	β_{AB}
H_2	2.240	0.149
Li_2	1.10	0.403
N_2	2.40	0.311
O_2	5.00	0.341
BH	1.60	0.158
^-OH	3.01	0.607
FH	2.12	0.390
ClH	1.64	0.285

TABLE II

Comparison of the Calculated Bond Distances and Binding Energies as Obtained by CNDO/VZ Method with CNDO/BW Results and Experimental Findings

	Internuclear Distance/Å			Binding Energy/eV		
Molecule	Calculated	CNDO/BW	Exptl.	Calculated	CNDO/BW	Exptl.
H_2	0.740	0.741	0.741	4.752	4.751	4.751
Li_2	2.492	2.672	2.672	4.279	1.050	1.050
N_2	1.035	1.098	1.098	9.904	9.903	9.903
O_2	1.199	1.207	1.2074	5.232	5.213	5.213
BH	1.262	1.212	1.233	3.578	4.493	3.577
^-OH	0.972	0.952	0.971	4.635	5.025	4.628
FH	0.972	0.917	0.917	6.110	6.110	6.110
ClH	1.261	1.275	1.275	4.612	4.615	4.615

The λ and β_{AB} parameter pairs of CNDO/VZ were generated to match experimentally obtained binding energies and bond lengths (Table I). CNDO/VZ gives bond lentghs and binding energies for diatomics H_2, N_2, O_2, ^-OH, FH and ClH which are in good agreement with experiment and CNDO/BW[8]; Li_2 is the exception in its binding energy (Table II). However, CNDO/VZ predicts a stable $^3\Sigma_u^+$ state of H_2 (Figure 1).

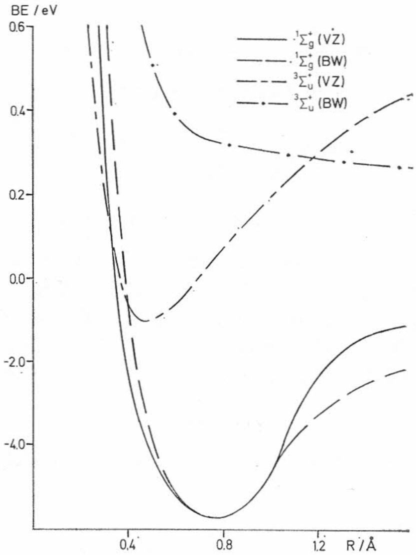

Figure 1: Binding Energies (BE) as a function of the internuclear distance (R) for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H_2 using CNDO/VZ and CNDO/BW.

The CNDO/BW parametrization of the CNDO theory, which successfully predicts experimental bond lengths and binding energies for a variety of systems, uses the Ohno[9] form of γ_{AB}

$$\gamma_{AB} = (R_{AB}^2 + a^2)^{-1/2} \quad (17)$$

where

$$a = 2\,(\gamma_{AB}^* + \gamma_{BB}^*)^{-1/2} \quad (18)$$

with constraints

$$\lim \gamma_{AB} = \frac{\gamma_{AA}^* + \gamma_{BB}^*}{2}; \; R_{AB} \to 0$$

$$\lim \gamma_{AB} = 0; \; R_{AB} \to \infty \quad (19)$$

$$\lim \gamma_{AB} = \frac{1}{R_{AB}}; \; \gamma_{ii}^* \to \infty$$

It was therefore decided to see the effect of constraining γ_{AB} (VZ) and V_{AB} (VZ) to the CNDO/BW limits. This also gave a stable $^3\Sigma_u^+$ state of H_2, and no other change in results.

CONCLUSION

The attempt to include penetration integrals in the CNDO theory is unsuccessful. The damped Mataga-Nishimoto form[5] of γ_{AB} (VZ) and V_{AB} (VZ) do not properly describe the $^3\Sigma_u^+$ state of H_2: it appears a fundamental error in the form and not due to the limit conditions.

CDNO/BW correctly describes the $^3\Sigma_u^+$ state of H_2 as well as the properties of most first row diatomics and a variety of larger systems using the

$V_{AB} = Z_B \gamma_{AB}$ approximation. Although theoretically unjustified this is numerically a good approximation because the additional parametrization of CNDO/BW of the core repulsion energy N_{AB}, compensates for the error from neglecting the penetration integrals.

Recent Li[10,11] cluster calculations using CNDO/BW describe effects for which the penetration term should be important. This suggests that future cluster studies as well as chemisorption[12] studies may be undertaken using CNDO/BW.

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SAŽETAK

O integralima penetracije u CNDO metodi

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Razmatran je problem uključivanja penetracijskih integrala, koji opisuju interakciju elektrona jednog atoma s košticom drugog atoma, u semiempirijsku CNDO shemu. Pokazano je da se to ne može uraditi na zadovoljavajući način, jer tada tripletno stanje $^3\Sigma_u^+$ molekule H_2 postaje stabilno. S druge strane, CNDO/BW shema opisuje stanja dvoatomskih molekula na korektan način, iako su penetracijski integrali zanemareni. To se može objasniti empirijskom parametrizacijom ostalih integrala, koja ublažava nedostatak tih integrala.