

A NEW SEMI-EMPIRICAL APPROXIMATION IN MOLECULAR ORBITAL THEORY

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A semi-empirical approximation in molecular orbital theory is proposed and a few properties of diatomic homonuclear molecules are calculated using this approximation. The results are compared with those of Cusachs for homonuclear diatomic molecules.

1. Introduction

Mulliken [1] was the first to initiate the semi-empirical approximation in molecular orbital theory in which the exchange integral was assumed to be proportional to the overlap. Following his suggestion various authors have put forth approximations for the exchange integral. Of these, seven approximations assume the linear-or-up-to-quadratic terms in the proportionality of the overlap for the exchange integral. For a diatomic molecule AB a few of the approximations are as follows:

$$H_{AB} = KS \left(\frac{H_{AA} + H_{BB}}{2} \right); \quad \text{Wolfsberg-Helmholtz, [2]} \quad (1)$$

$$= KS(H_{AA}H_{BB})^{1/2}; \quad \text{Ballhausen-Gray, [3]} \quad (2)$$

$$= \frac{1}{2} S(K - |S|) (H_{AA} + H_{BB}); \quad \text{Cusachs, [4]} \quad (3)$$

$$= \frac{1}{2} [K + H_{AA} + H_{BB}]S; \quad \text{Berthier, [5]} \quad (4)$$

$$= K \frac{H_{AA}H_{BB}}{\frac{1}{2}(H_{AA} + H_{BB})}; \quad \text{Yeranos. [6]} \quad (5)$$

In these approximations, H_{AB} stands for the exchange integral whereas K is a splitting factor, S is the overlap function, H_{AA} and H_{BB} are diagonal integrals referring to the two nuclei A and B respectively.

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Looking at these approximations, it is easy to write a general approximation out of which these emerge as special cases. Thus we write for H_{AB}

$$H_{AB} = K \cdot \text{Mean}(H_{AA}, H_{BB})f(S) \quad (6)$$

with $f(S) = a_1S + a_2S^2$, a_1 and a_2 being dimensionless constants. When we give a_1 , a_2 different values we recover the approximations (1) to (5) given above and other approximations can also be cast in this general form. Thus we have with

$$a_1 = 1, \quad a_2 = 0, \quad \text{Mean}(H_{AA}, H_{BB}) = A.M(H_{AA}, H_{BB});$$

$$a_1 = 1, \quad a_2 = 0, \quad \text{Mean}(H_{AA}, H_{BB}) = G.M(H_{AA}, H_{BB});$$

$$a_1 = 1, \quad a_2 = -\frac{1}{2}, \quad \text{Mean}(H_{AA}, H_{BB}) = A.M(H_{AA}, H_{BB});$$

$$a_1 = 1, \quad a_2 = 0, \quad \text{Mean}(H_{AA}, H_{BB}) = H.M(H_{AA}, H_{BB});$$

as the approximations proposed by Wolfsberg [2], Ballhausen-Gray [3], Cusachs [4] and Yeranov [6] respectively. Further, for homonuclear diatomic molecules, $H_{AA} = H_{BB}$ and $A.M.(H_{AA}, H_{BB}) = G.M(H_{AA}, H_{BB}) = H.M(H_{AA}, H_{BB}) = H_{AA}$. Thus for homonuclear diatomic molecules our approximation for H_{AB} reduces to

$$H_{AB} = K \cdot H_{AA}(a_1S + a_2S^2). \quad (7)$$

But, for such molecules, $K = 2$. So

$$H_{AB} = 2H_{AA}(a_1S + a_2S^2). \quad (8)$$

We therefore adopt the above approximation for homonuclear diatomic molecules. In the next section we show how we find the values of the constants a_1 and a_2 . For H_2 molecule the method is essentially self-consistent.

2. The values for a_1 and a_2

Recently Cooper *et al.* [7] have utilized Cusachs' approximation to work out the energy of the first spectral transition (Δ), ionization potential ($I. P.$), and dissociation energy (D_e) of various homonuclear diatomic molecules. They have shown that for H_2 and Cu_2 molecules the Cusachs approximation fits in well with observed values. They also observed a special feature of Cusachs' approximation, namely, that the potential energy *versus* overlap (S) has a minimum which, however, is not the case with various other approximations. Thus once one is able to determine the value of S which yields a minimum in the $V(R)$ *versus* S function then with the help of this value, (S), the Δ , $I. P.$ and D_e values of homonuclear diatomic molecules can be easily calculated. Thus for H_2 molecules, with Cusachs' approximation, $V(R)$ has a minimum at $S = 0.414$ and Δ , $I. P.$ and D_e are $0.586 H_{AA}$, $1.172 H_{AA}$ and $0.343 H_{AA}$ respectively. Thus if one knows the values of H_{AA}

then it is easy to know the values of Δ , $I.P.$ and D_e respectively. Cooper *et al.* also point out that the force constant is given by the formula

$$k_e = \frac{-4H_{AA}}{1+S} \left(\frac{\partial S}{\partial R} \right) R_e^2,$$

and utilizing the relation between k_e and ω_e^2 : $\omega_e^2 = \frac{k}{0.0089} \times$ (reduced mass of the molecule) [8]; value of ω_e has been found to be $\omega_e = 3720 \text{ cm}^{-1}$. However Cooper *et al.*'s derivation of k_e is incorrect dimensionally and the expression for k_e should read

$$k_e = \frac{-4H_{AA}}{1+S} \left(\frac{\partial S}{\partial R} \right)^2.$$

Now, we assume our approximation for H_2 molecules is $H_{AB} = 2H_{AA}(a_1S + a_2S^2)$, and we look for a value of S which will yield a minimum in $V(R)$ versus S . It is found that, with the above value of H_{AB} , potential energy has a minimum at

$$S = -1 + (1 - \beta)^{1/2} \quad (9)$$

where

$$\beta = \left(\frac{2a_1 - 1}{2a_2} \right).$$

However, when we put $a_1 = 1$, $a_2 = -\frac{1}{2}$ we recover the Cusachs case of a minimum at $S = 0.414$. With the above minimum value (9) of S , we work out Δ , $I.P.$ and D_e as follows:

$$I.P. = 2a_2H_{AA}[\beta - 2 + 2(1 - \beta)^{1/2}] + H_{AA}; \quad (10)$$

$$\Delta = 4a_2H_{AA} \frac{[\beta - 2 + 2(1 - \beta)^{1/2}]}{2 - (1 - \beta)^{1/2}}, \quad (11)$$

and

$$D_e = -4a_2H_{AA}[\beta - 2 + 2(1 - \beta)^{1/2}] \quad (12)$$

where in D_e (12) we have given the correct sign (-) on the R. H. S. unlike in the earlier work [7]. As a check, with $a_1 = 1$, $a_2 = \frac{1}{2}$ we get the same values as are obtained with the Cusachs approximation [7].

Now our plan is to determine a_1 and a_2 self-consistently. In other words, if we look at equations (10) and (11) and if we know $I.P./H_{AA}$ and Δ/H_{AA} , we see that they are nothing but a set of simultaneous equations between two unknowns a_1 and a_2 , and thus we will get a unique set of values for a_1 and a_2 . This is the main feature of our approximation. Now if we define

$$A = \frac{1}{2} \left| \frac{I.P.}{H_{AA}} \right| - \frac{1}{2} \quad \text{and} \quad B = \frac{1}{4} \left| \frac{\Delta}{H_{AA}} \right|,$$

then from equations (10) and (11) we have

$$\frac{A}{B} = 2 - (1 - \beta)^{1/2}. \quad (13)$$

A and B are known as for $I. P.$ and Δ . We use the experimentally observed values [7] and H_{AA} is given by Cooper *et al.* [7]. Thus β is known. Knowing β , we solve the equations for a_1 and a_2 and we find that $a_1 = 0.7633$, $a_2 = 0.1444$.

TABLE I

Comparison of calculated and experimental values for H_2

	Present Approx.	Cusachs' Approx. [7]	Experimental [9]
D_e	3.64 eV	4.69 eV	4.75 eV, 4.47 eV
$I.P.$	15.42 eV	15.95 eV	15.42 eV
Δ	11.4 eV	7.98 eV	11.4 eV
ω_e	3772 cm^{-1}	3720 cm^{-1}	4390 cm^{-1}

TABLE II

Comparison of calculated and experimental values for S -interacting systems

	D_e (eV)	$I.P.$ (eV)	Δ (eV)	Remarks
H_2^+	2.35	15.95	7.98	Cusachs
	1.82	15.42	11.4	Present
	2.79	16.25	...	Exp.
He_2^+	1.78	23.02	14.5	Cusachs
	1.80	22.15	20.7	Present
	2.7	27.3	...	Exp.
Li_2	1.83	6.24	3.1	Cusachs
	1.43	6.05	4.46	Present
	1.03	4.91	1.75	Exp.
Li_2^+	0.91	6.24	3.41	Cusachs
	0.72	6.05	4.46	Present
	1.03	4.91	...	Exp.
Na_2	1.70	5.80	2.96	Cusachs
	1.44	5.50	4.14	Present
	0.73	4.87	1.81	Exp.
K_2	1.37	4.69	2.34	Cusachs
	1.07	4.53	3.35	Present
	0.32	4.09	1.44	Exp.

Note: For Cusachs and experimental (Exp.) values in Tables, see [7].

3. The new approximation and the results obtained with it

Our new approximation for homonuclear diatomic molecules reads

$$H_{AB} = K(0.7633S - 0.1444S^2)H_{AA} \quad (14)$$

as compared with Cusachs' expression $H_{AB} = K(S - 0.5S^2)H_{AA}$, with $K = 2$. With our approximation we calculate the value of D_e and ω_e^2 .

$$k_e = \frac{8a_2H_{AA}}{1+S} \left(\frac{\partial S}{\partial R} \right)^2, \text{ wherein } \frac{\partial S}{\partial R} \text{ is to be evaluated at } S = -1 + (1-\beta)^{1/2} = 0.6807,$$

in the present case, whereas for Cusachs' case it was at $S = 0.414$. Accordingly, we present in Table I a comparison of $I. P.$, Δ , D_e , as obtained with our approximation, compared with Cusachs' and experimental ones. Thus we see that with our approximation we get better values of Δ and $I. P.$ as compared with Cusachs' values. However, our value of D_e is low. Now, using our approximation we calculate Δ , $I. P.$ and D_e for a few other S -interacting systems and these are presented in Table II along with values from Cusachs' approximation.

Conclusion

(1) We have suggested a semi-empirical approximation in molecular orbital theory which is akin in spirit to the approximation of Cusachs, who has assumed up-to-quadratic dependence of the overlap for the approximation of off-diagonal matrix elements. This novel feature of the approximation is based on Rundenberg's [10] result that the two-center kinetic-energy integral depends on the square of the overlap. We see (Table I) that for H_2 molecules D_e is not well reproduced. Further, our approximation has been tested for a few homonuclear diatomic molecules (Table II). The results have a fluctuating character, as in some cases we have a slightly better result than Cusachs and in other cases much worse.

(2) We have not yet done calculations for homonuclear diatomic molecules involving two p -orbitals or two d -orbitals, say, for Cu_2 , Ag_2 , Au_2 , Zn_2 , which we hope to do at a later date.

(3) Although we have suggested the approximation for homonuclear diatomic molecules, it is easy to extend it to the general case using

$$H_{AB} = K(0.7633S - 0.1444S^2) \left(\frac{H_{AA} + H_{BB}}{2} \right). \quad (15)$$

It will be worthwhile to test this suggestion for heteronuclear molecules.

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