

Molecular Model Potentials: Combination of Atomic Boxes

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A new Combination of Atomic Boxes (CAB) molecular orbital model is introduced, having the following characteristics:

- 1) Atomic model potentials are one-dimensional potential boxes of finite depth U_A and of length L_A , the box-parameters being chosen to give valence electron ionization energies.
- 2) Explicit molecular model potentials are constructed by combining all the model potentials of the atoms in the molecule.
- 3) A minimum computational effort leads to rigorous solutions of the resulting Schroedinger equation.

The model is tested on a large variety of π -electron systems containing atoms of four rows of the periodic system. Branched and cyclic molecules are also treated. The comparison of the calculated first and higher ionization and first excitation energies with the observed data gives the mean deviations 0.540 eV and 0.388 eV resp.

The common physical basis of the CAB and the model-pseudopotential methods is discussed. The constant potential within the box is a consequence of the partial cancellation of the electrostatic potential by a repulsive term representing the Pauli principle. It is shown that CAB is not restricted to π -electrons but can be extended to σ -electron systems as well.

Key words: Atomic boxes

1. Introduction

Most quantum chemical models predict either the ground state properties or the excitation energies of molecules, but not both. In all methods of the Hartree–Fock

type, the ground state energies are reasonably obtained, whereas little or no physical meaning can be attributed to the unoccupied “virtual” orbitals. In order to solve the problem, it is necessary to include highly time consuming configuration interaction calculations. Semiempirical LCAO models have to be parametrized differently for ground and excited states, e.g. Hückel calculations use quite different resonance integrals β . Free electron molecular orbital (FEMO) models [1–4] have had surprising success in calculating excitation energies of π -electron systems especially for rather complex cyclic [4–8], branched [6, 7, 9, 10] and heteromolecules [7, 11, 12]. However, as long as infinite walls are assumed, FEMO models cannot give absolute energies but only energy differences. Finite potential walls were introduced [13, 14], but the potential box had to be refitted to each molecule separately. Thus FEMO’s predicting power in extrapolating the properties of other homologous molecules was lost.

On the other hand, the relatively simple model-pseudopotential method has been remarkably successful in calculating both ground and excited state energies. It was first introduced by Hellmann [15–18] and Gombás [19, 20] who both started out from Thomas–Fermi [21, 22] and Thomas–Fermi–Dirac [23] models. Semiempirically adjusted model-pseudopotentials have become extremely fruitful in solid state band calculations [24–32] and have been used as a method for obtaining descriptions of atomic and molecular valence shell and Rydberg states [15, 20, 33–41].

The aim of this paper is to present a semiempirical molecular orbital model permitting accurate calculations of both ionization and excitation energies with the same set of parameters and a minimum of mathematics. A Combination of Atomic Boxes (CAB) molecular orbital model is introduced: atoms are represented by potential boxes and explicit molecular model potentials are constructed with all the potential boxes of the atoms by bringing the box centers into the observed equilibrium distances.

It is shown in Sect. 3 that this model gives very satisfactory results for the ground and first excited states of a large variety of π -electron systems. In Sect. 4, the CAB model is shown to be a synthesis of the model-pseudopotential and free-electron methods. The crucial assumption of a constant potential is justified as a basically correct approximation for both π - and σ -electron systems.

2. Combination of Atomic Boxes Model

2.1. Atomic Boxes and Their Parametrization

It has been pointed out that the accuracy obtainable with a given model potential depends on whether it imposes the proper boundary conditions [37]. As the simplest way to fulfill this requirement, an atomic model potential is introduced as a one-dimensional potential box of finite depth U_A and of length L_A , the box-parameters being chosen to give valence electron ionization energies.

The Schrodinger equation (Eq. (2)) of an atomic box of finite depth (Fig. 1) is particularly easy to solve. It has been treated as a pedagogically valuable exercise in many textbooks on quantum mechanics [42–45].

Let $x = 0$ be at the centre of the box and $l_A = \frac{1}{2} \cdot L_A$ half of its length, then

$$U(x) = \begin{cases} -U_A & \text{for } |x| \leq l_A \\ 0 & \text{for } |x| > l_A \end{cases} \quad (1)$$

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi_n(x) = E_n \cdot \psi_n(x). \quad (2)$$

The eigenfunctions of Eq. (2) and their first derivatives must be continuous everywhere and vanish for $|x| \rightarrow \infty$

$$\psi_n(x) = \begin{cases} \alpha_n \cos(k_n x + \delta_n) & \text{for } |x| \leq l_A \\ \alpha_n \cos(k_n l_A + \delta_n) e^{-\lambda_n(|x| - l_A)} & \text{for } |x| > l_A \end{cases} \quad (3)$$

with

$$k_n^2 = \frac{2m(U_A + E_n)}{\hbar^2} \quad (4a)$$

$$\lambda_n^2 = \frac{2m|E_n|}{\hbar^2} = \frac{2mIP_n}{\hbar^2} \quad (4b)$$

$$\delta_n = \begin{cases} 0 & \text{for odd } n \\ \frac{\pi}{2} & \text{for even } n \end{cases} \quad (4c)$$

Outside the box, the eigenfunctions ψ_n diminish exponentially, i.e. proper boundary conditions are imposed. The exponent is proportional to $-\sqrt{|E_n|} = -\sqrt{IP_n}$, IP_n being the ionization potential of the n th level, therefore, ψ_n expands as IP_n decreases. The ψ_n are orthogonal and the normalization factor is:

$$\alpha_n = \left(l_A + \frac{1}{\lambda_n} \right)^{-1/2}. \quad (5)$$

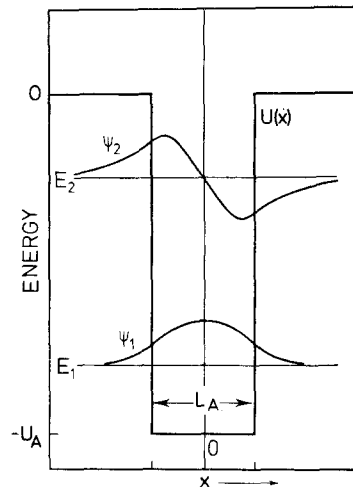


Fig. 1. Eigenenergies and eigenfunctions of an atomic potential box

The eigenvalues E_n are obtained by the requirement that $\psi_n(x)$ and $\psi'_n(x)$ are also continuous at the boundaries $|x| = l_A$. Consequently,

$$\cot k_n l_A = \frac{k_n}{\lambda_n} \quad \text{for odd } n, \quad (6a)$$

$$\tan k_n l_A = -\frac{k_n}{\lambda_n} \quad \text{for even } n. \quad (6b)$$

Using an addition-theorem, Eqs. (6a) and (6b) can be transformed into Eq. (7) valid for all n 's

$$2 \cot 2k_n l_A = 2 \cot k_n l_A = \frac{k_n^2 - \lambda_n^2}{k_n \cdot \lambda_n}. \quad (7)$$

The equations can be solved either numerically or graphically [43, 45].

There are different possible ways to parametrize an atomic potential box, namely by adjusting the box-parameters U_A and L_A to either atomic or homonuclear diatomic data. Whereas the latter may have the advantage of a better account for the electronic interactions, atomic data do not need to be regarded as parameters, but can be treated as free information for molecular studies [46]. Therefore, it is desirable to investigate to what accuracy molecular properties can be calculated by starting out from atomic data. This will be done by studying π -electron systems.

Though model potentials are eigenvalue dependent in principle [16, 20], this dependence will be neglected to a first approximation as far as np - and $(n + 1)d$ -electrons are concerned. Thus, U_A and L_A are fixed by fitting the first and second eigenenergies of the atomic potential box (Fig. 1) to the energies of the np - and $(n + 1)d$ -electrons resp. The physical reasons for this correspondence are discussed in Sect. 4. In accordance with the eigenvalue dependence, the energies of the other electrons cannot be described by the same model potential.

As an example, let us consider an atom of the configuration $K(2s)^2(2p)^m$. In general, there are several states arising from this configuration. At the present state of the model, no splitting between them is calculated and only average exchange and correlation interactions are considered. Therefore, the energies of all these states are averaged, appropriate weighting being given for multiplicity. The difference between the average energy levels of the atom and its ion has been considered as the appropriate average ionization energy for semiempirical calculations [47]. The values (Table 1) can either be found in the literature [47] or are calculated from the spectroscopic states of the atoms and ions.

The average ionization energies are close to the valence state ionization energies [48–54] but the former are well known also for the unoccupied $(n + 1)d$ -states and have the advantage to be independent of the particular ways to obtain valence states. For nitrogen, however, the average ionization energy should lead to wrong results by grossly underestimating the trivalent character of this atom. The difference between the average ionization energy $\overline{IP}_{2p} = 13.19$ eV and the valence state value for a $2p\pi$ -electron $IP_{2p} \simeq 14.15$ eV [52] is exceptionally large. In order to account

Table 1. Average ionization energies \overline{IP} , atomic box-parameters L_A , U_A , electroaffinities EA and electronegativities X

Atom	\overline{IP}_{np} (eV) ^a	$\overline{IP}_{(n+1)d}$ (eV) ^a	L_A (Å)	U_A (eV)	EA_{np} (eV) ^b	X_M ^c	X_{AR} ^d	U_A
								$2.87X_{AR} + X_M$
B	8.30	1.50	2.458	11.07		4.00	2.01	1.13
C	10.67	1.51	2.056	14.51		5.57	2.50	1.14
N	14.15 ^b	1.51	1.700	19.59		8.10 ^b	3.07	1.15
O	15.85	1.54	1.584	22.06		9.11	3.50	1.15
F	18.66	1.51	1.424	26.24		11.08	4.10	1.15
Si	7.76	1.12	2.420	10.53		4.13	1.74	1.15
P	9.64 ^e	—	(2.16)	(13.1)		5.46	2.06	(1.15)
S	11.61	1.02	1.825	16.24		6.99	2.44	1.16
Cl	13.65	0.98	1.640	19.30		8.71	2.83	1.15
Se	10.77	0.99	1.906	15.04	2.20	6.49	2.48	1.11
Br	12.27	(1.0)	1.75	17.2	3.55	7.91	2.74	(1.10)
Te	9.68	1.06	2.064	13.38	2.30	5.99	2.01	1.14
J	11.16	0.90	1.84	15.7	3.21	7.19	2.21	1.16
Xe	12.78	1.10	1.734	17.91				

H	$\overline{IP}(H_2)_{2p\pi_u}$	$\overline{IP}(H_2)_{3d\sigma_g}$	L_H (Å)	U_H (eV)
	(eV) ^f	(eV) ^f		
	3.424	1.414	4.097	4.168

^a Ref. [55]. ^b Refs. [52] and [54]. ^c Ref. [58]. ^d Ref. [57]. ^e Ref. [61]. ^f Ref. [59].

for the trivalent character of nitrogen, I shall use the value $\overline{IP}_{2p} = 14.15$ eV. The average ionization energies and the corresponding U_A and L_A values are compiled in Table 1.

It should be noted that there is a close relationship between the U_A values and the empirical (orbital-) electronegativities X . Actually, U_A is proportional to the arithmetic mean of the electronegativities X_M according to Mulliken [49] and X_P according to Pauling [56], the latter being as usual multiplied by 2.87 to obtain equal weight. This is shown in Table 1, where Pauling's thermal data are substituted by the almost identical but more precise data X_{AR} by Allred and Rochow [57]. It is appropriate to compare U_A and electronegativities, since the ionicity and the dipole moments of molecules, often analyzed in terms of electronegativity differences, will depend on the difference $\Delta U = U_A - U_B$. We can use the proportionality between U_A and X as a tool to calculate the box-parameters in cases where the $(n + 1)d$ -terms have not been observed. This is the case for phosphorus.

Hydrogen atoms represent a special case, since they do not contribute π -electrons to the molecule. But the differences between the π -electron ionization and excitation energies of e.g. C_2 , C_2H_2 and C_2H_4 or C_3 and C_3H_4 are most evident and characterize the importance of the hydrogen atoms for the energy levels of π -electron systems.

In most models for π -electron systems and especially in FEMO, hydrogen atoms are not considered at all. In this model, each hydrogen atom is taken into account

by an atomic box. It will be shown in Sect. 4 that a potential box would be appropriate for the $2p$ and $3d$ states of hydrogen. However, by adjusting to the atomic ionization energies of hydrogen, exchange and correlation interactions, which are present in molecules, would be totally neglected. Therefore, it is better to adjust U_{H} and L_{H} to the π -electron Rydberg states of the hydrogen molecule i.e. $2p\pi_u$ and $3d\pi_g$. It can then be expected that all the π -electrons of more complex molecules will experience about the same model potential (cf. Sect. 4).

The multiplicity weighted averages of the hydrogen molecule ionization energies are $\overline{IP}_{2p\pi_u} = \frac{1}{4}(3.024 + 3 \cdot 3.557) \text{ eV} = 3.424 \text{ eV}$ [59] at $\bar{r}_e = 1.037 \text{ \AA}$ and $\overline{IP}_{3d\pi_g} = 1.414 \text{ eV}$ at $\bar{r}_e = 1.060 \text{ \AA}$. Having calculated the values $U_{\text{H}_2} = U_{\text{H}} = 4.168 \text{ eV}$ and $L_{\text{H}_2} = 5.134 \text{ \AA}$, we can get L_{H} by subtracting the observed equilibrium distance r_e . Thus the box length $L_{\text{H}} = 4.097 \text{ \AA}$ is obtained.

As compared to the potential boxes of the other elements, the hydrogen box is in fact shallow and wide, as if the proton were screened to a major extent. It describes the nonpenetrability of the hydrogen atom to π -electron systems too.

2.2. Unbranched Molecules

Molecular boxes are constructed by bringing the centres of the atomic boxes into the equilibrium interatomic distances r_e . This is shown for N_2 in Fig. 2, and for other unbranched molecules in Fig. 3.

At this state of the model, nuclear repulsion and σ -bonds are not yet included, the molecular geometries used are therefore not calculated but taken from experiment. In a subsequent paper, it will be shown that a refined model allows the calculation of equilibrium distances r_e .

In this model, the energy of a particular bonding orbital is at a minimum for the boxes just touching each other, e.g. $r_{\text{AB}} = \frac{1}{2}(L_{\text{A}} + L_{\text{B}})$. Since this minimum is not necessarily coinciding with the minimum of the molecular potential energy curve,

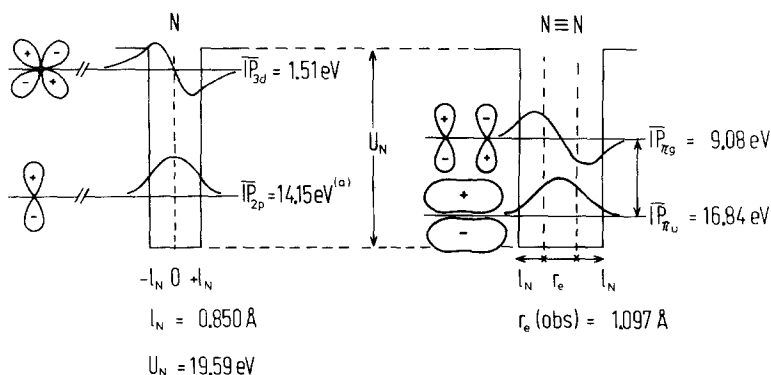


Fig. 2. The construction of the CAB model potential for the nitrogen molecule. (a) Ref. [52]

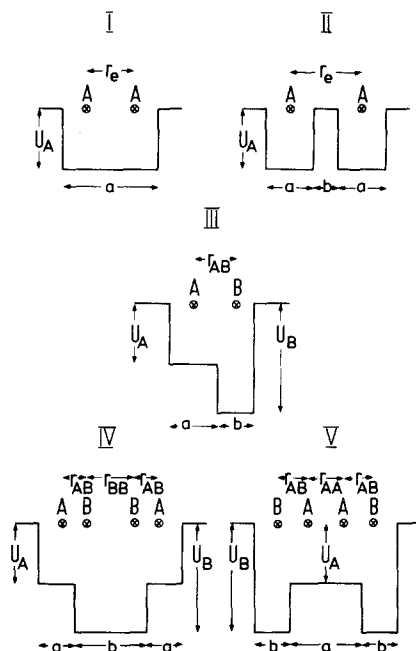


Fig. 3. Schematic CAB model potentials for unbranched molecules

the atomic boxes of the π -electrons can also overlap or leave a gap at the observed equilibrium distances.

In the case of a gap between the boxes e.g. Cl_2 (Table 2), the potential barrier reaches the vacuum level (Fig. 3, II). It can be seen that the molecules dissociate into their atomic constituents. This is not the case in LCAO MO or even in HF calculations, where the calculated dissociation products are not only the observed atoms.

If the boxes of two atoms A and B overlap (Fig. 3, III), the combined box is divided into two parts a and b of the depths U_A and U_B respectively. Their ratio is postulated to be:

$$\frac{a}{b} = \frac{L_A}{L_B}. \quad (8)$$

For polyatomic molecules with overlapping boxes and A the first, Z the last atom of the chain, this is generalized to:

$$a:b:c:\dots:z = L_A:L_B:L_C:\dots:L_Z. \quad (9)$$

The total length L_{mol} of the molecular model potential is:

$$L_{\text{mol}} = \frac{1}{2}(L_A + L_Z) + \sum_i r_{e,i}. \quad (10)$$

Thus, $U(x)$ is clearly defined and there is no open parameter left. The bond lengths and the values a and b for the model potentials of unbranched molecules (Fig. 3) are compiled in Table 2.

Table 2. Bond lengths and model potentials of unbranched molecules

Molecule	$r_e(\text{\AA})^a$	Model potential ^b	$a(\text{\AA})^b$	$b(\text{\AA})^b$
B ₂	1.589	I	4.047	—
C ₂	1.242	I	3.298	—
C ₃	1.277	I	4.610	—
N ₂	1.098	I	2.798	—
O ₂	1.208	I	2.792	—
O ₃	1.278	I	4.140	—
F ₂	1.435	II	1.424	0.011
Si ₂	2.252	I	4.672	—
P ₂	1.894	I	4.06	—
S ₂	1.889	II	1.825	0.064
Cl ₂	1.988	II	1.640	0.348
Se ₂	2.152	II	1.906	0.246
Br ₂	2.283	II	1.75	0.54
Te ₂	2.59	II	2.06	0.53
J ₂	2.666	II	1.84	0.83
HB	1.226	III	2.815	1.689
HC	1.198	III	2.847	1.428
HN	1.038	III	2.782	1.154
HO	0.970	III	2.748	1.062
HF	0.917	III	2.729	0.949
HS	1.350	III	2.982	1.329
HCl	1.275	III	2.959	1.184
HBr	1.414	III	3.04	1.30
HJ	1.609	III	3.16	1.42
HBO	HB: 1.16°	III	1.51	0.99
	BO: 1.21°			
CN	1.172	III	1.670	1.380
CO	1.128	III	1.665	1.283
CS	1.534	III	1.841	1.634
NO	1.151	III	1.446	1.347
N ₂ O	NN: 1.126	III	2.697	1.257
	NO: 1.186			
SO	1.493	III	1.712	1.486
CH ₂	$\left\{ \begin{array}{l} {}^3\Sigma_g^- \\ {}^1B_1 \end{array} \right.$	IV	2.460	1.235
	1.06		2.50	1.26
NH ₂	1.024	IV	2.545	1.056
H ₂ O	0.958	IV	2.519	0.974
H ₂ S	1.328	IV	2.761	1.230
H ₂ Se	1.460	IV	2.846	1.324
H ₂ Te	1.653	IV	2.957	1.490
NCN	1.232	V	1.569	1.297
CO ₂	1.162	V	1.538	1.185
CS ₂	1.553	V	1.777	1.577
C ₂ H ₂	CC: 1.206	IV	2.469	2.478
	CH: 1.056			
C ₂ N ₂	CC: 1.389	V	2.954	1.221
	CN: 1.154			

Table 2—Continued

Molecule	$r_e(\text{\AA})^a$	Model potential ^b	$a(\text{\AA})^b$	$b(\text{\AA})^b$	
C ₂ F ₂	CC:	1.20	V	3.14	1.09
	CF:	1.35			
C ₃ O ₂	CC:	1.28	V	4.31	1.11
	CO:	1.19			
C ₄ H ₂	C—C:	1.376	IV	2.495	5.006
	C≡C:	1.205			
	CH:	1.056			
C ₄ N ₂	C—C:	1.37	V	5.59	1.16
	C≡C:	1.19			
	CN:	1.14			
N ₂ F ₂	NN:	1.25	V	3.02	1.26
	NF:	1.44			
XeF ₂		1.90	V	2.38	1.42

^a Refs. [59] and [60].

^b Fig. 3.

^c Calc. value in Ref. [62].

The one-dimensional Schroedinger equation can be solved exactly for all possible combinations of atomic boxes. The molecular box is split up into regions of constant potentials (e.g. $U(x) = -U_A$) which belong to the different atoms.

Let $\psi_{A,n}(x_A)$ be part of the eigenfunction $\psi_n(x)$ which lies in the region of $U(x) = -U_A$.

$$\psi_n(x) = \sum_A \psi_{A,n}(x_A) \quad (11)$$

with

$$\psi_{A,n}(x_A) = \alpha_{A,n} e^{ik_{A,n} \cdot x_A} + \beta_{A,n} e^{-ik_{A,n} \cdot x_A} \quad (12)$$

and with

$$k_{A,n}^2 = \frac{2m}{\hbar^2} (U_A - IP_n). \quad (13)$$

In the case of $U_A - IP_n > 0$, $\psi_{A,n}$ is sinusoidal, otherwise it is a combination of two exponential functions. It is required that $\psi_n(x)$ and $\psi'_n(x)$ be continuous for all x 's. The consequence of this requirement is a set of linear equations in $\alpha_{A,n}$, $\beta_{A,n}$ determined by the boundary conditions of the regions with constant potential. This set of equations can be evaluated in order to obtain a characteristic equation for the eigenvalue-eigenfunction pairs. Thereby the relative values of the coefficients $\alpha_{A,n}$, $\beta_{A,n}$ are obtained. The application of the normalization condition fixes their absolute values.

This will be exemplified by the case of a heteronuclear diatomic molecule AB with $IP_n < U_A < U_B$ and $r_e \leq \frac{1}{2}(L_A + L_B)$ as shown in Fig. 3, III.

Let us introduce two coordinates x_A with $-\infty < x_A \leq a$ and x_B with $-\infty < x_B \leq b$ in opposite direction to each other and joining at the point $x_A = a$, $x_B = b$. In the following, I shall omit the index n of the wavefunction. Considering first the coordinate x_A with the condition that $\lim_{x_A \rightarrow -\infty} \psi_A(x_A) = 0$, and using λ of Eq. (4a) we find

$$\psi_A(x_A) = \begin{cases} \gamma_A e^{+\lambda x_A} & \text{for } x_A \leq 0 \\ \alpha_A \sin(k_A x_A + \delta_A) & \text{for } x_A \geq 0 \end{cases} \quad (14)$$

At $x_A = 0$, the continuity conditions impose:

$$\psi_A(0) = \gamma_A = \alpha_A \sin \delta_A, \quad (15)$$

$$\psi'_A(0) = \gamma_A \lambda = \alpha_A k_A \cos \delta_A. \quad (16)$$

By division we obtain

$$\tan \delta_A = \frac{k_A}{\lambda}. \quad (17)$$

The origin of the coordinate x_B is treated analogously:

$$\tan \delta_B = \frac{k_B}{\lambda}. \quad (18)$$

The values k_A , k_B and λ are not independent but related by the given U_A and U_B . Their absolute values are fixed by the continuity condition at the joint of x_A and x_B

$$\psi_A(a) = \alpha_A \sin(k_A a + \delta_A) = \alpha_B \sin(k_B b + \delta_B) = \psi_B(b), \quad (19)$$

$$\psi'_A(a) = k_A \alpha_A \cos(k_A a + \delta_A) = -k_B \alpha_B \cos(k_B b + \delta_B) = -\psi'_B. \quad (20)$$

Except for $\psi'_A(a) = 0 = \psi'_B(b)$, we may equate the ψ/ψ' values

$$k_A^{-1} \tan(k_A a + \delta_A) + k_B^{-1} \tan(k_B b + \delta_B) = 0. \quad (21)$$

According to the addition theorem for the tangens function and Eqs. (17) and (18) this equals:

$$\frac{k_A + \lambda \tan(k_A a)}{k_A \lambda - k_A^2 \tan(k_A a)} + \frac{k_B + \lambda \tan(k_B b)}{k_B \lambda - k_B^2 \tan(k_B b)} = 0. \quad (22)$$

Having determined the eigenenergies for the model-potential, we obtain the coefficients α_A , α_B , γ_A , γ_B for the eigenfunctions by virtue of the normalization condition and Eqs. (19), (20) and (15). For $\psi'_A(a) = 0 = \psi'_B(b)$, e.g. $a = b$, $U_A = U_B$ and n odd number, we avoid infinities by equating the ψ'/ψ values instead of Eq. (21).

The equations determining the eigenenergies for other model-potentials (Fig. 3) are obtained by similar considerations. They are listed in Table 3 without further derivation. Their systematic relations are clarified by introducing:

$$T_A = \frac{k_A + \lambda \tan(k_A a)}{k_A \cdot \lambda - k_A^2 \tan(k_A a)} \quad (23)$$

Table 3. Equations determining the eigenenergies for the model potentials of Fig. 3

Model potential	Equation*
I	$2 \cot(ka) - \frac{k}{\lambda} + \frac{\lambda}{k} = 0$
II	$2 \coth(\lambda b) + k_A T_A + (k_A T_A)^{-1} = 0$
III 1. $IP > U_A$	$H_A + T_B = 0$
2. $IP < U_A$	$T_A + T_B = 0$
IV 1. $IP > U_A$	$2 \cot(k_B b) - k_B H_A + (k_B H_A)^{-1} = 0$
2. $IP < U_A$	$2 \cot(k_B b) - k_B T_A + (k_B T_A)^{-1} = 0$
V 1. $IP > U_A$	$2 \coth(\kappa a) + \kappa T_B + (\kappa T_B)^{-1} = 0$
2. $IP < U_A$	$2 \cot(k_A a) - k_A T_B + (k_A T_B)^{-1} = 0$

* T and H are defined in Eqs. (23) and (24), respectively.

for $k_A^2 > 0$ and

$$H_A = \frac{\kappa + \lambda \tanh(\kappa a)}{\kappa \lambda + \kappa^2 \tanh(\kappa a)} \quad (24)$$

for

$$\kappa^2 = -k_A^2 > 0. \quad (25)$$

The equations on Table 3 are of such simplicity that they can be easily programmed on a pocket size calculator e.g. HP 25.

2.3. Branched Molecules

CAB's treatment of branched molecules can be exemplified by the ethene molecule (Fig. 4). Let us introduce separate coordinates x_b for each branch $b = 1, 2, 3$ originating at the "joint atom" C and ending at $x_b = c_b$, resp. In addition to their

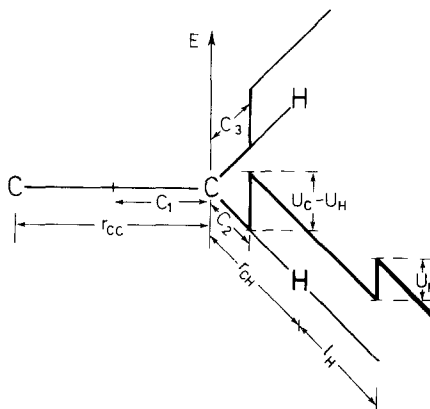


Fig. 4. Ethene and cumulenes: CAB model potential in the neighbourhood of a branching point

boundary conditions at the respective c_b 's, the branch functions $\psi_b(x_b)$ are determined by two conditions concerning their behaviour in the joint C. Different branching conditions have been discussed within the frame of the FEMO model [6, 9, 63–66]. In this paper, the branching conditions originally proposed by Kuhn [6] are used. The continuity condition demands that the branch functions $\psi_b(x_b)$ assume the same value at their joint C, i.e. for $x_b = 0$

$$\psi_1(x_1 = 0) = \psi_2(x_2 = 0) = \psi_3(x_3 = 0). \quad (26)$$

Kuhn's second condition concerns the first derivatives $\psi'_b(x_b)$ of the branch functions at the joint C

$$\sum_{b=1}^3 \psi'_b(x_b = 0) = 0. \quad (27)$$

Equation (27) has been discussed as a sufficient though not necessary condition for the "conservation of current" and for the orthogonality of the eigenfunctions [63].

If a branch represents a bond between two different atoms, it has to be divided in two parts belonging to the potential boxes of the different atoms. In analogy to the linear heteroatomic molecules, the lengths of the overlapping potential boxes (c for carbon and h for hydrogen) are postulated to have the ratio:

$$\frac{c}{h} = \frac{L_C}{L_H}. \quad (28)$$

The length attributed to a joint atom is the sum of the contributions from each branch:

$$c = \sum_{b=1}^3 c_b. \quad (29)$$

For ethene, the value of $c + 2h$ is known from Fig. 4 and Tables 1, 4.

$$c + 2h = c_1 + 2c_2 + 2h = \frac{1}{2}r_{CC} + 2r_{CH} + L_H = 6.939 \text{ \AA}.$$

Table 4. Bond lengths and model potentials of branched and cyclic molecules

Molecule	$r_e(\text{\AA})^a$	Model potential	$c_1(\text{\AA})$	$c_2(\text{\AA})$	$c_3(\text{\AA})$	$h(\text{\AA})$
Ethene	CC 1.339 CH 1.086	Fig. 4	0.670	0.363	0.363	2.772
Butatriene	CC 1.30 CH 1.09	Fig. 4	0.66	0.37	0.37	2.77
Hexapentaene	CC 1.30 CH 1.09	Fig. 4	0.66	0.37	0.37	2.77
Cyclobutadiene	CC 1.44 CH 1.09	Fig. 5	0.72	0.09	0.72	3.05
Benzene	CC 1.397 CH 1.084		0.699	0.117	0.699	3.016

^a Refs. [59] and [60].

Equation (28) is transformed into:

$$\frac{c}{c + 2h} = \frac{L_c}{L_c + 2L_H} = 0.201.$$

We obtain the values $c = 1.392 \text{ \AA}$, $h = 2.774 \text{ \AA}$ and $c_2 = 0.361 \text{ \AA}$, since $c_1 = \frac{1}{2}r_{CC} = 0.670 \text{ \AA}$ is given. The values for other branched molecules are given in Table 4.

For the ground state ionization energy of ethene, I shall derive a simplified formula, presuming that $\psi_{1\pi}$ and $IP_{1\pi}$ are affected by the potential walls at $x_2 = c_2$ and $x_3 = c_3$ only.

The symbols k and λ have been defined in Eq. (4) and κ denotes

$$\kappa = \frac{\sqrt{2m(IP - U_H)}}{\hbar}. \quad (30)$$

The branching conditions Eqs. (26) and (27) on $\psi_b(x_b) = \alpha_b \cos(kx_b + \delta_b)$ yield:

$$\alpha_1 \cos \delta_1 = \alpha_2 \cos \delta_2 = \alpha_3 \cos \delta_3, \quad (31)$$

$$\sum_{b=1}^3 k\alpha_b \sin \delta_b = 0. \quad (32)$$

Because of the symmetry, it is $\alpha_2 = \alpha_3$ and $\delta_2 = \delta_3$, thus:

$$\tan \delta_1 + 2 \tan \delta_2 = 0. \quad (33)$$

For $x_1 = c_1$, the symmetry of $\psi_{1\pi}$ demands:

$$\cos(kc_1 + \delta_1) = 1, \quad (34)$$

$$\delta_1 = n\pi - kc_1, \quad (35)$$

$$\tan \delta_1 = -\tan(kc_1). \quad (36)$$

For the potential wall at $x_2 = c_2$, the conditions for $\psi_2(c_2)$ and $[\psi'_2(c_2)]/[\psi_2(c_2)]$ become:

$$\alpha_2 \cos(kc_2 + \delta_2) = \gamma_2, \quad (37)$$

$$k \tan(kc_2 + \delta_2) = \kappa. \quad (38)$$

The addition theorem for the tangens function and the combination of Eqs. (33), (36) and (38) yield:

$$\tan(kc_2 + \delta_2) = \frac{\tan(kc_2) + \tan \delta_2}{1 - \tan kc_2 \cdot \tan \delta_2} = \frac{\tan(kc_2) + \frac{1}{2} \tan(kc_1)}{1 - \frac{1}{2} \tan(kc_2) \tan(kc_1)} = \frac{\kappa}{k}. \quad (39)$$

Finally we obtain:

$$\tan kc_1 = 2 \cdot \frac{\kappa - k \tan kc_2}{\kappa \tan kc_2 + k}. \quad (40)$$

For the excited state π^* , we get $\tan \delta_2 = -\frac{1}{2} \cot(kc_1)$ instead of Eq. (36), with the consequence that $\tan(kc_1)$ in Eq. (40) has to be substituted by $-\cot kc_1$. By taking

Table 5. Equations determining the eigenenergies for the model potentials of some branched and cyclic molecules

Molecule	Orbital	Equation ^a
Ethene	$1\pi, 2\pi$	$2 \cot(k_1 r_{CC}) + 2T_{C,i} - (2T_{C,i})^{-1} = 0$
Cumulenes	all π , with $\kappa h \geq 2$	$2 \cot(k_i \sum r_{CC}) + 2T_{C,i} - (2T_{C,i})^{-1} = 0$
Cyclobutadiene	1π	$\tan(k_1 c_1) + \tan(k_1 c_3) - T_{C,1} = 0$
	2π	$\tan(k_2 c_1) - \cot(k_2 c_3) - T_{C,2} = 0$
Benzene	$1\pi(a_{2u})$	$2 \tan(k_1 c_1) - T_{C,1} = 0$
	$2\pi(e_{1g})$	$\tan(k_2 c_1) - \cot(k_2 r_{CC}) - T_{C,2} = 0$
	$3\pi(e_{2u})$	$\cot(k_3 c_1) + \cot(k_3 r_{CC}) + T_{C,3} = 0$

^a $T_{C,i}$ is defined in Eq. (41).

into account the potential walls $\Delta U = U_H$ at the distance $c_2 + h$ from the joint atom, the value κ/k in Eq. (39) has to be multiplied by $[\lambda + \kappa \tanh(\kappa h)]/[\lambda \tanh(\kappa h) + \kappa]$. This factor is practically unity for $\kappa h \geq 2$. The equations determining the eigenenergies for the model-potentials of ethene and even cumulenes are given in Table 5.

2.4. Cyclic Molecules

For cyclic molecules, the only additional feature in the CAB model is the incorporation of cyclic boundary conditions for the continuity of ψ and ψ' along the bond skeleton. For branched cyclic molecules, the Kuhn branching conditions, Eqs. (26) and (27), are applied and the separate coordinates for each branch are introduced analogously to Sect. 2.3. Cyclobutadiene and benzene will be treated as examples for branched cyclic molecules. Figure 5 symbolizes the skeleton and the model-potential of a cyclobutadiene molecule. As the boxes of carbon and hydrogen overlap along the branch connecting the two atoms, it is divided into two parts as demonstrated for the ethene molecule in Sect. 2.3 (Eqs. (28) and (29)).

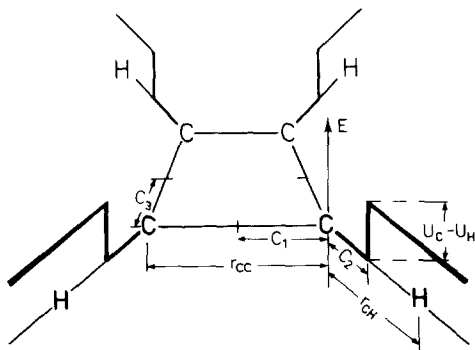


Fig. 5. Cyclobutadiene: CAB model potential along the branched bond skeleton

Since the differentiation between the singlet and triplet states of cyclobutadiene is beyond the intention of this first approximation, a non-alternating bond length of $r_{CC} = 1.44 \text{ \AA}$ is assumed for simplicity. The bond lengths and the c_b values for benzene are given in Table 4. Similarly to the derivation in Sect. 2.3, it is presumed that $\kappa h \geq 2$. The equations determining the eigenenergies for the model potentials of cyclobutadiene and benzene are given in Table 5, with $T_{C,i}$ standing for

$$T_{C,i} = \frac{\kappa_i - k_i \tan(k_i c_2)}{k_i + \kappa_i \tan(k_i c_2)} \quad (41)$$

3. Results of CAB Calculations for π -electron Systems

The calculated vertical ionization and excitation energies are collected together with the relevant experimental data in Tables 6–8. It was intended to test the model on molecules containing atoms of as many rows of the periodic system as reliable experimental data allow for. The molecules chosen for these calculations were selected accordingly. The calculated energies are in very satisfactory agreement with the experimental data not only for molecules containing first-row atoms but for those with heavy elements as well. The mean and the standard deviations are 0.540 eV and 0.731 eV resp. They drop to 0.509 and 0.647 resp., if the $IP(\pi_u)$ of F_2 is excluded. The best linear fit for 70 ground state π -orbital energies is $\overline{IP}_v(\text{cal}) = (1.002 \pm 0.025)\overline{IP}_v(\text{obs}) + (0.179 \pm 0.333) \text{ eV}$ with a correlation coefficient $r = 0.979$ (Fig. 6).

Since singlet-triplet-splitting is not yet included in the model, the calculated excitation energies have to be related to average experimental values. Thereby, appropriate weighting is given for multiplicity, e.g. for ethene $\Delta E_v(^1B_{1u}) = 7.6 \text{ eV}$, $\Delta E_v(^3B_{1u}) = 4.3 \text{ eV}$ [85], thus $\overline{\Delta E}_v = 5.1 \text{ eV}$. Adiabatic excitation energies $\overline{\Delta E}_{\text{ad}}$ may also be calculated by accounting for the different equilibrium distances in the excited state. Observed $\overline{\Delta E}$ values could be obtained for 23 molecules only. The mean and the standard deviations are 0.388 eV and 0.529 eV resp. The best linear fit is $\overline{\Delta E}(\text{cal}) = 0.933\overline{\Delta E}(\text{obs}) + 0.316 \text{ eV}$ with a correlation coefficient $r = 0.987$. For all the 93 ground and excited states allowing a comparison between the calculated and the observed ionization energies, the linear regression yields $\overline{IP}_v(\text{cal}) = (1.014 \pm 0.016)\overline{IP}_v(\text{obs}) + (0.131 \pm 0.175) \text{ eV}$ with a correlation coefficient $r = 0.990$. The mean and the standard deviations between calculations and experiments become 0.531 eV and 0.707 eV resp.

The good agreement obtained for a large variety of molecules encourages the prediction of π -electron energies of some unstable molecules (C_2 , C_3 , cyclobutadiene) and transient reaction intermediates (HBO). The values predicted by the CAB model are in good agreement with the predictions by other models¹.

¹ In calculating the $\overline{\Delta E}_v$ value for HBO, the effect of the hydrogen atom is considered. The model potential is not of the type III (Fig. 3) anymore, since the wall between the B and H atoms reaches only the level $U = -U_H = -4.17 \text{ eV}$.

Table 6. π -electron ionization and excitation energies: homonuclear molecules

Mole- cule	Orbital	$IP_v(\text{eV})$		Transition	$\overline{\Delta E}_v(\text{eV})$	
		obs. ^{a,b} ; average;	CAB		obs. ^a	CAB
B ₂	$\pi_u 2p$		9.70	$\pi_u 2p \rightarrow \pi_g 2p$		3.90
C ₂	$\pi_u 2p$	{(12.55) ^c 12.0 ± 0.6 ^d }	12.52	$\pi_u 2p \rightarrow \pi_g 2p$	(5.0 ad.) ^e	{5.67 v. 4.97 ad.
C ₃	$\pi_u 2p$	(12.92) ^f	13.33	$\pi_u 2p \rightarrow \pi_g 2p$	~ 3	3.44
N ₂	$\pi_u 2p$	16.96	16.84	$\pi_u 2p \rightarrow \pi_g 2p$	9.12 ^g	7.76
O ₂	$\pi_u 2p$	{16.82 ^h 17.73 (20.2) 24.0}	19.1			
	$\pi_g 2p$	{12.31 ^h 11.32 ^h 10.67}	11.56	11.16	$\pi_g 2p \rightarrow \pi_u 3d$	~ 11
O ₃	1 π		20.3			
	2 π	(15.57) ^h		16.08	2 $\pi \rightarrow 3\pi$	7.09
F ₂	$\pi_u 2p$	18.98	22.24			
	$\pi_g 2p$	15.83	15.19	$\pi_g 2p \rightarrow \pi_u 3d$	~ 13 ⁱ	11.97
Si ₂	$\pi_u 3p$		9.45	$\pi_u 3p \rightarrow \pi_g 3p$	(3.05) ^j	3.13
P ₂	$\pi_u 3p$	10.62 ^k	11.7	$\pi_u 3p \rightarrow \pi_g 3p$	3.4 ad. ^l	3.5 ad.
S ₂	$\pi_u 3p$	{11.82 ^m 12.33 (14.2) 15.58}	13.21	14.12		
	$\pi_g 3p$	9.41	9.61	$\pi_g 3p \rightarrow \pi_u 4d$	(> 8.3)	7.52
Cl ₂	$\pi_u 3p$	14.40	15.30			
	$\pi_g 3p$	11.59	12.09	$\pi_g 3p \rightarrow \pi_u 4d$		10.17
Se ₂	$\pi_u 4p$		11.89 ⁿ	12.41		
	$\pi_g 4p$	9.13 8.89	9.01	9.34	$\pi_g 4p \rightarrow \pi_u 5d$	7.43
Br ₂	$\pi_u 4p$	12.77 13.08	12.93	13.2		
	$\pi_g 4p$	10.56 10.95	10.74	11.2	$\pi_g 4p \rightarrow \pi_u 5d$	9.4
Te ₂	$\pi_u 5p$		10.58 ⁿ	10.56		
	$\pi_g 5p$	8.77 8.30	8.54	8.83	$\pi_g 5p \rightarrow \pi_u 6d$	7.02
J ₂	$\pi_u 5p$	11.82 11.03	11.43	11.8		
	$\pi_g 5p$	9.97 9.35	9.66	10.5	$\pi_g 5p \rightarrow \pi_u 6d$	> 8.2 ^o

^a Ref. [59].^d Ref. [68].^e Ref. [71].^f Ref. [74].^m Ref. [77].^b Ref. [61].^c Calc. in Ref. [69].^h Ref. [72].^k Ref. [75].ⁿ Ref. [78].^o Calc. in Ref. [67].^f Calc. in Ref. [70].ⁱ Ref. [73].^j Ref. [76].^o Ref. [79].

Table 7. π -electron ionization and excitation energies: unbranched heteronuclear molecules

Mole- cule	Orbital	$\overline{IP}_v(\text{eV})$		Transition	$\overline{\Delta E}_v(\text{eV})$	
		obs. ^{a,b}	CAB		obs. ^a	CAB
HB	$2p\pi$	7.2 ^c	7.28	$\pi \rightarrow \pi^*$		5.16
HC	$2p\pi$	9.24 ± 0.22^d	9.18	$\pi \rightarrow \pi^*$		7.06
HN	$2p\pi$	12.16	11.72	$\pi \rightarrow \pi^*$	10.0	9.73
HO	$2p\pi$	13.17	12.94	$\pi \rightarrow \pi^*$		11.04
HF	$2p\pi$	16.06	15.00	$\pi \rightarrow \pi^*$	13.0 ^e	13.12
HS	$3p\pi$	10.5 ± 0.1^f	10.10	$\pi \rightarrow \pi^*$		7.89
HCl	$3p\pi$	12.74	11.70	$\pi \rightarrow \pi^*$		9.54
HBr	$4p\pi$	11.62	10.8	$\pi \rightarrow \pi^*$		8.5
HJ	$5p\pi$	10.41	10.1	$\pi \rightarrow \pi^*$		7.6
HBO	1π	(14.29) ^g	13.93	$1\pi \rightarrow 2\pi$		6.66 ¹
CN	1π	—	14.97	$1\pi \rightarrow 2\pi$	6.4 ad. ^h	6.33 ad.
CO	1π	16.91	16.29	$1\pi \rightarrow 2\pi$	9.2 ¹	8.52
CS	1π	12.92	13.52	$1\pi \rightarrow 2\pi$	5.4 ^k	5.41
NO	1π	17.6	18.09			
	2π	10.0	10.02	$2\pi \rightarrow 3\pi$		9.80
N ₂ O	1π	18.23	18.68			
	2π	12.89	14.22	$2\pi \rightarrow 3\pi$	6.9 ¹	7.60
SO	1π	15.97 ¹	17.43			
	2π	9.73 ¹	9.90	$2\pi \rightarrow 3\pi$		8.87
CH ₂	$2p\pi$	9.35 ^m	9.0	$2p\pi \rightarrow 3d\pi$	7.71 ^m	6.7
NH ₂	$2p\pi$	11.4	11.58	$2p\pi \rightarrow 3d\pi$	(9.1)	9.31
H ₂ O	$2p\pi$	12.61	12.71	$2p\pi \rightarrow 3d\pi$	11.12	10.52
H ₂ S	$3p\pi$	10.47	10.13	$3p\pi \rightarrow 4d\pi$		7.57
H ₂ Se	$4p\pi$	9.88	9.64	$4p\pi \rightarrow 5d\pi$		6.96
H ₂ Te	$5p\pi$	9.14	8.95	$5p\pi \rightarrow 6d\pi$		6.10
NCN	1π		15.65			
	2π		13.11	$2\pi \rightarrow 3\pi$		7.96
CO ₂	1π	17.6	16.78			
	2π	13.8 ad.	14.40	$2\pi \rightarrow 3\pi$	$\sim 9.0^1$	9.50
CS ₂	1π	13.7	14.27			
	2π	10.08	11.74	$2\pi \rightarrow 3\pi$		5.39
C ₂ H ₂	1π	11.41	11.83	$1\pi \rightarrow 2\pi$	$\sim 6.5^1$	6.52
C ₂ N ₂	1π	15.47	15.23			
	2π	13.8	14.02	$2\pi \rightarrow 3\pi$	5.52 ¹	5.01
C ₂ F ₂	1π	18.5 ⁿ	18.4			
	2π	17.7 ⁿ	18.0			
	3π	11.3 ⁿ	10.6	$3\pi \rightarrow 4\pi$		6.8

^a Ref. [59].^b Ref. [61].^c (10.06–2.86)eV, Refs. [80] and [59].^d Weighted mean of the $\sigma^2\pi$ and $\sigma\pi^2$ states.^e Ref. [81].^f Ref. [68].^g Ref. [62].^h Ref. [59] and Schaefer III, H. F.: Electronic structure of atoms and molecules. Reading, Mass.: Addison-Wesley 1972.¹ See footnote on page 291.¹ Ref. [71].^k Ref. [82].¹ Ref. [78] and Clark, W. W., deLucia, F. C.: J. Mol. Spectry. **60**, 332 (1976).^m Weighted mean of the states \bar{X} , \bar{b} , \bar{c} with $\Delta E(\bar{X}, \bar{b}) = 1.3$ eV.ⁿ Ref. [83].^o Ref. [84], p. 207.^p Haink, H. J., Jungen, M.: Chem. Phys. Letters **61**, 319 (1979).

Table 7—Continued

Molecule	Orbital	$\overline{IP}_v(\text{eV})$		Transition	$\overline{\Delta E}_v(\text{eV})$	
		obs. ^{a,b}	CAB		obs. ^a	CAB
C ₃ O ₂	1 π	15.82	15.9			
	2 π	14.85	15.5			
	3 π	10.8	11.6	3 $\pi \rightarrow 4\pi$	4.95°	4.9
C ₄ H ₂	1 π	12.62	13.54			
	2 π	{10.17 ^b 10.79 ^a }	10.73	2 $\pi \rightarrow 3\pi$	4.4 ^p	4.27
C ₄ N ₂	1 π	14.95	14.9			
	2 π	14.16	14.5			
	3 π	11.84	12.2	3 $\pi \rightarrow 4\pi$		3.4
N ₂ F ₂	1 π	19.80	21.0			
	2 π		20.1			
XeF ₂	2a _u (3 π)	14.1	14.7	3 $\pi \rightarrow 4\pi$		6.7
	5 π_u	12.65	12.8	$\pi_u \rightarrow \pi_g$		(6.5)

In addition to the general agreement, several special features ought to be pointed out.

- 1) The good results for heteronuclear molecules together with the proportionality between the potential depth U_A and the electronegativity value X (Table 1) are particularly satisfactory from a conceptual point of view and suggest a simple interpretation of the empirical electronegativity scales.
- 2) The effect of hydrogenation on π -electron systems is accounted for as shown by the series of compounds: C₂, C₃H₂ and C₂H₄. This is further illustrated by the results with mono- and dihydrides.

Table 8. π -electron ionization and excitation energies: branched and cyclic molecules

Molecule	Orbital	$\overline{IP}_v(\text{eV})$		Transition	$\overline{\Delta E}_v(\text{eV})$	
		obs. ^a	CAB		obs.	CAB
Ethene	1 π	10.51	9.83	1 $\pi \rightarrow 2\pi$	5.1 ^b	4.80
Butatriene	1 π	11.78°	13.01			
	2 π	9.30°	9.49	2 $\pi \rightarrow 3\pi$		3.51
Hexapentaene	1 π		13.84			
	2 π		11.96			
	3 π		9.33			
Cyclobutadiene	1 π	11.66 ^d	11.76			
	2 π	8.50 ^d	8.11	2 $\pi \rightarrow 3\pi$		4.0
Benzene	1 π (a _{2u})	12.25	11.78			
	2 π (e _{1g})	9.25	10.03	e _{1g} → e _{2u}	4.85 ad. ^o	4.72

^a Ref. [61].^b Ref. [85].^c Ref. [86].^d Ref. [87].^o Parmenter, C. S.: *Advan. Chem. Phys.* **22**, 365 (1972).

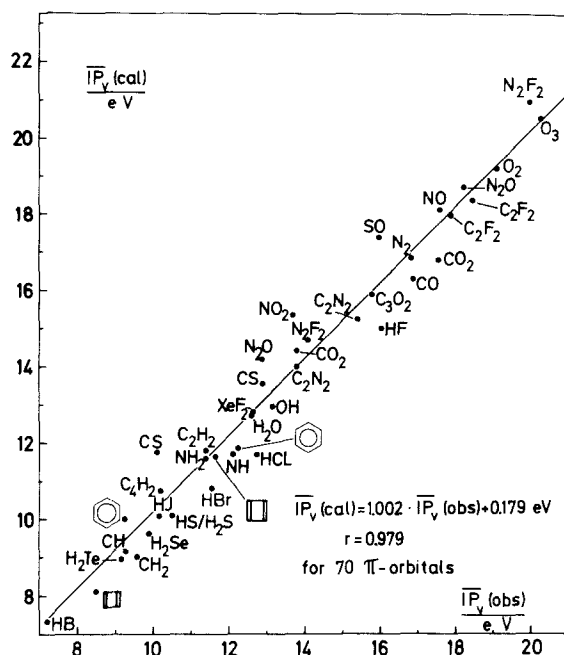


Fig. 6. Calculated and observed ground state ionization energies

- 3) Free radicals like CH_2 , NH_2 , OH , and NO are calculated to the same accuracy as closed-shell molecules, provided we compare to singlet-triplet-averaged values.
- 4) Polyenes and other molecules with alternating bond lengths are not treated. A refined model will take care of the alternation through the introduction of small potential barriers. However, the highest occupied MO can be calculated by this simple model, since the barriers coincide with the nodes of the HOMO wavefunction, e.g. diacetylene. Then, as far as IP_{HOMO} is concerned, the potential barriers become ineffective. The same applies to the ground state of XeF_2 . Although the boxes leave a gap, the barriers can be neglected and the model potential V (Fig. 3) is adequate. On the other hand, the excitation energy will be too small without barriers.

Summarizing the results, it can be stated that despite their simplicity, the CAB calculations of first and higher π -electron ionization energies are about as good as those of any other model available. This holds especially if we include molecules with heavy elements such as Br, Te, J and Xe. The CAB model is superior to most other models concerning its efficiency to calculate excitation energies using the same parametrization as for ground state calculations.

4. The Physical Basis of the CAB Model

In this section, it will be shown that the assumptions made in the CAB model are physically meaningful and reasonable. Physical arguments will be given explaining

the good results obtained in Sect. 3. It will be shown that the CAB model can be extended to σ -electron systems.

The crucial assumption is that of a constant potential within an atom. In fact, the FEMO assumption of a constant potential within a homonuclear molecule has also been criticized [13, 88] by arguing that the potential experienced by an electron should be a superposition of shielded Coulomb-potentials. For the special case of $2p\pi$ -electron systems, H. Kuhn and collaborators [7, 89, 90] have shown that the projected electron density method [7, 89–92] leads to a flat one-dimensional wave shape potential. For $2p\pi$ -electron systems with nonalternating bond lengths, this flat potential can be replaced by a potential box [7, 90]. Until now, no theoretical arguments have been presented for the similar adequacy of a box-model in the case of $np\pi$ - and $nd\pi$ -electrons with $n \geq 3$. Apparently, the radial nodes of such atomic orbitals overcomplicate the picture. Finally, for σ -electron systems, a constant potential around the nuclei has been considered to be particularly unrealistic [88]. On the other hand, FEMO was applied to σ -electron systems with remarkable success [12, 93–97]. This cannot be explained, as was attempted, by “the overriding importance of distance parameters in calculating energies” [93].

The explanation is that the arguments against a constant potential were concerned only with the electrostatic part of the problem and the Pauli principle must also be considered. In the discussions pro and contra FEMO it has remained completely unnoticed that the fundamental theoretical arguments for a constant potential were given by Hellmann [15–18] and Gombás [19, 20].

Hellmann showed that the influence of the atom core on the valence electrons including the orthogonality requirement can be represented by a pseudopotential, i.e. a superposition of the electrostatic potential and a repulsive potential representing the Pauli exclusion principle. The core electrons enter the picture only to determine the exact form of the pseudopotential, and the problem is effectively reduced to the valence electrons. The theoretical derivations [16–20, 98–100] show that pseudopotentials are nonlocal and very complicated inside the core. Yet, it is possible to use simple model-pseudopotentials to reproduce many advantages of the pseudopotential theory.

Hellmann's first model-pseudopotential [15] was derived by treating the atom core according to Thomas–Fermi [21, 22] and the valence electrons according to Schroedinger. A valence electron experiences the potential of the Thomas–Fermi ion core of radius R_0 :

$$U(r) = \begin{cases} -U_0 = -\frac{(Z - N) e^2}{R_0} & r \leq R_0 \\ -\frac{(Z - N) e^2}{r} & r > R_0 \end{cases} \quad (42)$$

N is the number of electrons in the core. The valence electrons are free within a sphere of radius R_0 , dependent on the nuclear charge Z and the quantum numbers n and l [17, 18, 20]. Since the values of R_0 are often larger than the bond radii [20,

27–29, 33–39, 101], regions with free valence electrons can overlap in molecules and solids. It is important for molecular calculations that the repulsive part of a pseudo-or model potential is equivalent to the Pauli principle with respect to *all* valence electrons in a molecule, independent of the atom from which they originate [16–20].

Corrections accounting for exchange [23, 101], correlation [102, 103], and the electron density near the nucleus [17, 104, 105] do not change the form of this model pseudopotential [18, 20]. The corrections permit the extension of the Thomas–Fermi approximation to small atoms and even to hydrogen [18, 20, 103]. However, Hellmann’s model is not justified for $1s$ -orbitals, since there is no lower orbital to do any cancelling of the electrostatic potential². For p -, d -, f - etc. orbitals, the centrifugal kinetic energy term $[\hbar^2 l(l + 1)]/2mr^2$ in the radial Schrodinger equation should be added. In the case of $2p$ - and $3d$ -orbitals, it somewhat compensates for the lack of a “ $1p$ ” and “ $2d$ ” orbital, respectively [17, 108].

Comparing different forms of model pseudopotentials, Abarenkov and Heine [27] obtained the best results with potentials $U_{n,l}(r)$ that are constant inside the core. According to Weeks, Hazi and Rice [38], the model pseudopotentials suggested by the exact pseudopotential theory of Phillips and Kleinmann [100] are also of this type. For some purposes this model pseudopotential can be treated as local and eigenvalue independent [17, 26].

The eigenfunctions of the pseudo-wave equation with $U(r)$ as given in Eq. (42) are separable into a “smooth”, nodeless radial part and the appropriate spherical harmonic [16, 18]. The mathematical problem has been solved explicitly by different authors [106, 109–111]. Taking into account the centrifugal kinetic energy term $[\hbar^2 l(l + 1)]/2mr^2$, the np - and $(n + 1)d$ -pseudowave functions correspond closely to the $2p$ - and $3d$ -Slater functions, respectively [16, 18]. Thus, the complications caused by the radial nodes are circumvented by this approach. For $np\pi$ -electrons the proof of a flat and eventually constant one-dimensional box-potential is effectively reduced to the $2p\pi$ -problem treated by Kuhn *et al.* [90]. Obviously, the projections of ns - and nd -electron densities lead to similar, but probably not identical flat potentials inside the core. Therefore, constant one-dimensional core potentials are reasonable for both π - and σ -electron systems.

Outside the core region, the model potential may be simplified for mathematical convenience. However, in studying interatomic interactions, the valence electron wavefunctions outside the core are eminently important. It has been pointed out [112] that both Huckel and SCF calculations are not able to describe the properties of the ground state and excited states with the same set of parameters, because no care is taken of the considerably different orbital exponents. The accuracy obtainable with a given model potential depends on whether it imposes the proper boundary conditions [37]. It is therefore highly relevant for its good results that the CAB model potential imposes exponential eigenfunctions outside the box and

² On the other hand, Hauk and Parr [106] have had very satisfying results for the $1s\sigma$ ground state of H_2^+ by using a “phantom centre molecular puff” potential which has the shape of that in Eq. (42). For a proton-pseudo-potential based on dielectric screening see Ref. [107].

that their orbital exponents have the correct relation to the respective orbital energies. Thus, in the approximation used in this paper (cf. Sect. 2.1), the first and second eigenfunctions of the atomic potential box (Figs. 1, 2) closely correspond to the projected electron densities of the $2p$ - and $3d$ -orbitals in the case of first-row atoms, of the np - and $(n + 1)d$ -pseudo-orbitals of heavier elements respectively.

It can be stated that the potential chosen for the CAB model, far from being unrealistic, accounts fairly well for the influence of the core on a valence electron. Being based on the correlation-corrected Thomas–Fermi–Dirac model, it even takes into account the Coulomb, exchange and correlation interactions of the core electrons.

The interactions between the valence electrons are not considered formally. But, by fitting to experimental data involving atomic ground and excited states, the semiempiricism of the model potential will include effects not considered in formal theory, such as exchange and correlation interactions including the valence electrons [16–18, 113]. Relativistic effects for molecules with heavier atoms are also taken into account semiempirically. It has been pointed out by Chang *et al.* [41] that model potentials are the only simple device to do so.

5. Conclusions and Outlook

The study in this paper has shown that it is possible to calculate good values for the first and higher ionization and the first excitation energies of π -electron systems by a conceptually and mathematically very simple model. One important feature is that no change in parametrization is needed for the ground and excited states. The physical reasons for this success have been established.

The next step in the development will account for all valence electrons and the nuclear repulsion, in order to calculate equilibrium distances, dissociation energies and dipole moments. Electron interactions responsible for the singlet-triplet-splitting will also be considered. According to first calculations, good results can be obtained without essentially complicating the picture. This will be published in forthcoming papers.

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For CS₂ the $\overline{IP}_{1\pi} = 13.7$ eV (Table 7) is the centre of mass of the bands discussed by Schirmer, J., Domcke, W., Cederbaum, L. S., von Niessen, W., Asbrink, L.: *Chem. Phys. Letters* **61**, 30 (1979).