

University of Newcastle upon Tyne

Calculation of the π -Electronic Structures of Vinyl Boron Compounds by the Free-Electron Method

By

D. R. ARMSTRONG and P. G. PERKINS

The free-electron model has been used to investigate the π -electronic structures and spectra of two vinylboranes. It is concluded that none of the simple F. E. methods is satisfactory alone and agreement between calculated and observed spectral quantities is only obtained when electron interaction is explicitly included in the calculations.

Das Elektronengasmodell wurde zur Untersuchung der π -Elektronenstrukturen und Spektren von zwei Vinylboranen angewendet. Es wurde gefunden, daß keine der einfachen Elektronengasmethoden allein befriedigend ist und daß ein Übereinstimmen zwischen berechneten und beobachteten Spektralwerten nur dann erreicht werden kann, wenn die Elektronenwechselwirkung explizit berücksichtigt wird.

Le modèle de l'électron libre a été utilisé pour étudier les niveaux d'énergie électronique et les bandes d'absorption de deux boranes vinyliques. C'est trouvé que les méthodes simples ne sont pas satisfaisantes et l'accord entre les spectres calculés et observés est obtenu seulement quand l'interaction électronique est comprise dans les calculs.

It is now accepted that atoms attached to trigonal boron which have electrons in orbitals antisymmetric to the molecular plane can be involved in π -bonding with the boron atom. Further situations arise where the surrounding moieties have group orbitals of π -symmetry e. g. the vinyl and phenylboranes. Such effects might be expected to be manifest in the electronic spectrum of the compound and this point has been discussed by other authors [6, 9, 19]. GOOD and RITTER [9], using simple Hückel theory, obtained good agreement between the observed and calculated positions of the first intense electronic bands in several vinylboranes. The calculations also predicted small π -charges on the boron atoms. It seemed, therefore, of interest to carry the calculation of the spectral quantities further.

Most other theoretical investigations in boron chemistry have dealt with those compounds in which boron is directly linked to nitrogen [4, 8, 13] and all have been studied by the L. C. A. O.-M. O. approximation. In this paper we present the results of calculations on the π -electronic structures and spectra of the two vinyl boranes, $\text{CH}_2 = \text{CHBX}_2$ and $(\text{CH}_2 = \text{CH})_2 \text{BX}$, based on free electron models. Here X is a substituent, such as hydrogen or the methyl group which interacts little with the π -electron system of the molecule. This restriction was applied for simplicity so that a non-branched core potential only need be considered. The free electron models described in the literature have been mainly used for predicting the average positions of the first transition bands of polyenes and dyes, [1a, 14, 15] the higher energy bands being, in general, neglected. These were extended and are discussed first. Electronic interaction was then explicitly superimposed by

employing determinantal wave functions built from antisymmetrised products of free electron molecular orbitals (A.S.F.E.M.O.) to describe the electronic states of the molecules.

1. Simple Free-Electron Methods

A non-branched molecule may be approximated by a narrow cylindrical tube inside which the electrons are confined, and if the σ - π separability condition is assumed, then the nuclei and σ -electrons may be regarded as providing a core potential in which the π -electrons move. To simplify the situation mathematically the radius of the tube is allowed to tend to zero (since electronic excitation is more readily achieved along the chain than transversely) and so the Schrödinger equation has the one dimensional form,

$$\frac{d^2 \psi}{dx^2} + \frac{8 \pi^2 m}{h^2} (E - V) \psi = 0. \quad (1.1)$$

The solution of this problem is well-known [3] and if the external potential is infinite and V , being constant, can be assumed to vanish then the eigenfunctions are,

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (1.2)$$

which form satisfies homogeneous Cauchy conditions at each end of the chain.

The corresponding eigenenergies are,

$$E_n = \frac{n^2 h^2}{8 m L^2} \quad (1.3)$$

where L is the length of the potential well.

The treatment need not lose sight of the real three-dimensional nature of the molecule nor its true symmetry. Thus the eigenfunctions in a well where V is symmetric are themselves alternately symmetric and antisymmetric to inversion through the point $L/2$ which corresponds (in a molecule having C_{2v} symmetry) to the reflection plane perpendicular to the plane of the molecule. Refinements to the simple model have been described in the literature, these include a) superimposition of a sinusoidal potential on the well [14] b) allowance for non-infinite end walls [1] c) insertion of subsidiary potential wells or barriers to simulate the position of heteroatoms in the molecule [15].

For a system of $2n$ π -electrons, using (1.3), the wavelength of the first electronic transition band is given by,

$$\lambda_{n \rightarrow n+1} = \frac{8 m c L^2}{h (2n+1)}. \quad (1.4)$$

Clearly the magnitude of λ is sensitive to the quantity L since this enters the expressions as L^2 and hence it is necessary to consider the best choice of this. We cite three possibilities,

- (a) the distance along the chain between the two extreme nuclei.
- (b) as (a) plus one half the average polyene bond length at each end (0.7 Å).
- (c) as (a) plus one whole bond length each end.

For the present purpose this bond length has been taken as the 'long bond' in butadiene. (i. e. 1.46 Å).

RUEDENBERG and SCHERR [28] have shown that direct equivalence between L.C.A.O.-M.O. and F.E.M.O. theories may only be established if choice (c) is made. In the section of the paper dealing with simple free electron models the three different alternatives have been employed for comparison, but later we have used the third exclusively.

The geometry of neither borane is known, and the following bond lengths have been assumed for both compounds.

C = C 1.35 Å as in butadiene

B - C 1.55 Å [average of B - C in BH_3CO (1.54 Å) and in $\text{B}(\text{CH}_3)_3$ (1.56 Å)].

Thus for the three choices of L we have (a) 5.80 Å, (b) 7.20 Å, (c) 8.72 Å for divinylborane.

2. Form of the Potential

It is convenient to consider first the divinylborane for which the potential, independent of its analytical form, is symmetric to a plane through the B atom. A first approximation to this may be obtained by calculating the potential energy of an electron with the assumption that it moves along the line of the nuclei in one dimension at a distance b from them. This recognises the three dimensional nature of the model whilst preserving the simplicity of the one dimensional case. The potential energy of the electron between 0 and L is [16],

$$V(x) = - \sum_i Z_i^{\text{eff}} \frac{e^2 (1 - x_i/a)}{V(b^2 + x_i^2)} \quad (2.1)$$

where Z_i^{eff} is the Slater nuclear charge of the i^{th} atom (C, 3.25; B, 2.25) and $b = 0.61$ Å. The attraction is assumed zero at distances $x_i > a \approx 2$ Å from the i^{th} nucleus. The form of $V(x)$ for divinyl borane is shown in Fig. 1a. For such a potential function the Schrödinger equation may only be solved numerically and further approximations for which analytical solutions exist have been proposed. One such is the finite well [1] in which the potential is of the form,

$$V(x) = V_0 \left(\cos^2 \frac{\pi x}{L} - 1 \right). \quad (2.2)$$

(Fig. 1 b). This allows the Schrödinger equation to be put in the form of Mathieu's equation and the eigenfunctions are then simply Mathieu functions.

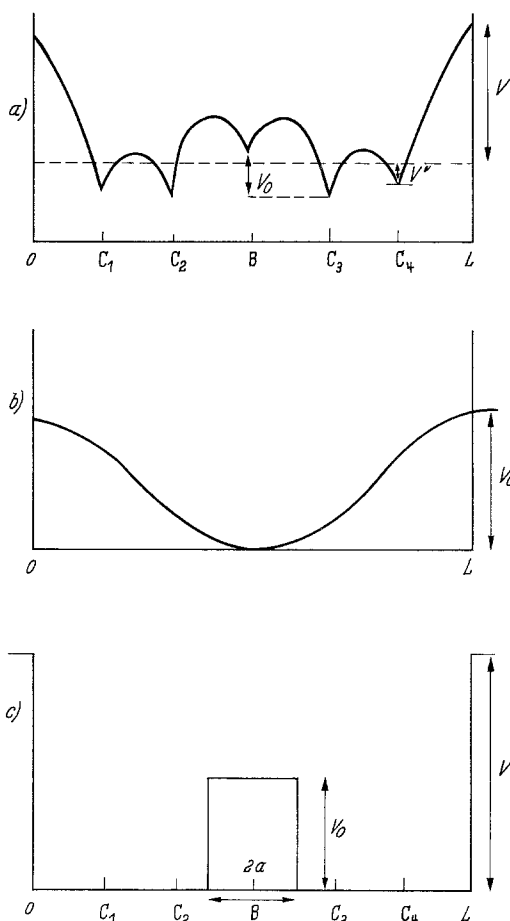


Fig. 1. Potential functions for divinylborane

It is clear from Fig. 1a that neither the simple linear well (with or without finite end walls), the regular sinusoidal well, or the "cos²" well, are realistic for a molecule containing a boron atom and are not therefore expected to yield reliable spectral information without arbitrary parameter adjustment. A refinement which improves the situation employs a potential which is a step function (Fig. 1c) and which leads to an exactly soluble barrier problem. The eigenfunctions are alternately symmetric and antisymmetric about $L/2$ as in the simple case. For a potential of this form, when the energies are less than the barrier height, the wave functions are sinusoidal in the troughs but exponential in the barrier region. The latter arises because $\sqrt{(E - V_0)}$ is imaginary here and only tunneling is allowed. Thus,

$$\begin{aligned} \psi_1 &= Ae^{i\alpha x} + Be^{-i\alpha x} & 0 < x < L/2 - a, & \quad L/2 + a < x < L \\ \psi_2 &= Ce^{-\beta x} + De^{\beta x} & L/2 - a < x < L/2 + a \end{aligned} \quad (2.3)$$

$$\alpha = \sqrt{HE}, \beta = \sqrt{H(V_0 - E)}, H = \frac{8\pi^2 m}{h^2} = 2 \text{ a. u.}$$

Both increasing and decreasing exponential components are needed since the antisymmetric wave functions must be zero at $L/2$. The continuity requirements of the functions and their gradients at the barriers lead to the quantum conditions,

$$\sin \alpha (L/2 - a) = K \left\{ \frac{e^{\beta(L/2+a)} - e^{\beta(L/2-a)}}{e^{-\beta(L/2-a)} - e^{\beta(L/2+a)}} \right\} e^{-\beta(L/2-a)} + e^{\beta(L/2-a)} \quad (2.4)$$

for the symmetric levels

where,

$$K = \frac{\beta \sin \alpha (L/2 - a) + \alpha \cos \alpha (L/2 - a)}{2 \beta e^{\beta(L/2-a)}}$$

and for the antisymmetric levels,

$$\sin \alpha (L/2 - a) = -2 K e^{\beta L/2} \sinh \beta a. \quad (2.5)$$

The transcendental equations may be solved numerically and in the present work this was accomplished by an Algol 60 programme. The symmetric eigenfunctions are attenuated considerably by the barrier and the corresponding energies of a simple well of the same length are raised appreciably and converge towards the next higher antisymmetric level as the barrier height and width are increased. The antisymmetric levels are but little affected by a narrow barrier since they have a node at $L/2$. This is the basis of NIKITIN's approximation [21]. Inclusion of finite end walls (outside which the wave functions are again exponential) allows for ionisation as before. The quantum conditions are then more complex and for the symmetric levels,

$$\begin{aligned} & \frac{\alpha}{\gamma} \cos \alpha (L/2 - a) + \sin \alpha (L/2 - a) \\ &= K \left\{ \frac{e^{\beta(L/2+a)} - e^{\beta(L/2-a)}}{e^{-\beta(L/2-a)} - e^{\beta(L/2+a)}} \right\} e^{-\beta(L/2-a)} + e^{\beta(L/2-a)} \end{aligned} \quad (2.6)$$

where

$$K = \frac{\cos \alpha (L/2 - a) \left(\alpha + \frac{\beta \alpha}{\gamma} \right) + \sin \alpha (L/2 - a) \left(\beta - \frac{\alpha^2}{\gamma} \right)}{2 \beta e^{\beta(L/2-a)}}$$

$$\gamma = \sqrt{H(V - E)}$$

and

$$V = \text{height of end walls.}$$

Whilst for antisymmetric levels,

$$\frac{\alpha}{\gamma} \cos \alpha (L/2 - a) + \sin \alpha (L/2 - a) = -2 K e^{\beta L/2} \sinh \beta a. \quad (2.7)$$

The height of the barrier, V_0 , may be chosen semi-empirically *a priori* as the difference between the binding energies of an electron situated on a positively charged carbon and a neutral boron atom. For carbon the energy difference of the two valence states C (*tritrtri* π) and C⁺ (*tritrtri*) is 11.22 eV and the corresponding quantity for boron is its π -electron affinity in the trigonal valence state, i.e. B (*tritrtri*) \rightarrow B⁻ (*tritrtri* π) i.e. 0.96 eV [25]. These are not the only figures which may be taken; a combination of the corresponding data for C (*sxyz*) $V_4 \rightarrow$ C⁺ (*sxy*) V_3 and B⁻ (*sxy*²) $V_2 \rightarrow$ B (*sxy*) V_3 [11, 26] lead to a barrier height of 11.22 eV and a third value, 9.78 eV, may also be derived [11].

Calculations were carried out for all three cases so that the effect of small variations of the barrier height on the transition energies could be judged. Now the above figures refer to free atoms and if the Virial theorem is to be satisfied then the average potential energy difference between the boron and adjacent carbon atoms should be twice as great. (~ 20 eV). It seems however that this is a high extreme for the molecular situation since the σ -electron drift from boron to carbon will tend to lower the trigonal π -valence state ionisation potential of carbon concomitantly raising that of boron. The net effect is to lower the potential barrier. In deriving the curve of Fig. 1 a the Slater nuclear charges appropriate to free boron and carbon atoms were used. These should clearly be amended to take account of the σ -electron distribution and indeed for carbon compounds much reduced values have been suggested [1, 18].

Other methods allowing for a heteroatom

The problem may also be treated by orthodox first order perturbation theory employing the unperturbed eigenfunctions of the simple well. This introduces integrals of the form $\int \psi_i V_0 \psi_i dx$ as first order corrections to the energies [15]. Such a treatment becomes less appropriate with increased barrier height, however.

If the barrier is high but narrow then to a first approximation it attenuates only the symmetric wave functions since all others have a node at the mid point. This leads to two sets of energy levels [21],

$$\begin{aligned} E_{\text{anti.}} &= \frac{\hbar^2 k^2}{8 m L^2} \\ E_{\text{sym.}} &= \frac{\hbar^2 k^2}{8 m L^2} (1 - \mathcal{E})^2, \quad \mathcal{E} = \frac{2 \hbar^2}{8 \pi^2 m V_0 a (L/2)} \quad * \\ k &= 2, 4, 6 \dots \end{aligned} \quad (2.8)$$

The method is necessarily limited to cases in which the potential is symmetric. When the barrier cannot be considered narrow NIKITINE and KOMOSS [20] proposed also a second model in which the energies are approximated by the expression,

$$\frac{E}{V_0} = \sin^2 \alpha (L/2 - a) ** \quad (2.9)$$

* a equals $2a$ on Fig. 1 (c).

** α as in eq. (2.3).

For energies $> V_0$ the wave functions are periodic in all regions of the well. This may also be used for an unsymmetrical potential.

3. Results and Discussion

The results of the calculations made on the symmetrical borane are presented first. In the ground state of divinylborane the two lowest levels are doubly occupied and single excitation of any of these electrons to the two lowest unfilled levels only were considered. Since the symmetry of the compound is at most C_{2v} both the ground and the excited states are spatially non-degenerate and thus the approximate positions of the first three bands may be predicted directly from the sequence of energy levels. These are given in Tab. 1 in $m\mu$ ($\lambda_i \rightarrow k$).

The ultra-violet spectra of divinylmethylborane and vinylmethylborane between 190 and 300 $m\mu$ have been measured by GOOD and RITTER [9]. The trace of the former exhibits an intense main band which has a weak shoulder on the low energy side and is also overlapped at shorter wavelengths by the trailing edge of a third band out of the range of observation. The two lower energy bands were isolated by Gaussian analysis and in this process a fourth band, on the high energy side of the main peak, was uncovered. The procedure was facilitated by a programme written for the Newcastle University KDF 9 computer. In the spectrum of the latter the low energy shoulder was again apparent and its position was fixed in a similar way. The wavelengths (in $m\mu$) and oscillator strengths of the peaks are as follows:

$$\begin{aligned} (\text{C}_2\text{H}_3)_2 \text{BMe}; & 252, .0303; 221, .3065; 201, .1074; \\ (\text{C}_2\text{H}_3) \text{B}(\text{Me})_2; & 228, .0254; 195, .2820. \end{aligned}$$

More detailed discussion of these figures will be deferred until later but it is immediately apparent that the first transition band associated with the vinyl group which might have been expected to be close to that of ethylene (162 $m\mu$) has undergone a pronounced bathochromic shift in both cases. For a symmetric potential the lowest energy transition, from the n 'th to the $(n+1)$ 'th level is symmetry allowed and is polarized in the x -direction. It should then correspond to the lowest energy *intense* band in both spectra (221, 195 $m\mu$ respectively). In the symmetrical borane both overtone transitions ($n-1 \rightarrow n+1$, $n \rightarrow n+2$), are space-forbidden but are allowed in the non-symmetric case. The appearance of the second band at 201 $m\mu$ [in $(\text{C}_2\text{H}_3)_2 \text{BMe}$] stems from violation of the selection rule due to the real 3-dimensional nature of the molecule. A second component of transition density in the molecular plane is then allowed. Comparison with the figures given in Tab. 1 may now be made and clearly none of the simple methods can give a satisfactory account of the two bands at 221 and 201 $m\mu$. Independent variation of the two parameters V and L does not improve the situation although of course either band may be fitted exactly by an arbitrary choice. Superimposition of finite end walls depresses the energy levels of the simple well which, as BAYLISS has pointed out [1a] is physically more realistic since in the infinite well they diverge with increasing quantum number. The eigenvalues of Mathieu's equation lead to a prediction for the first energy gap which is far too large even when L is increased to 9.8 Å. Consequently the second and third energies were not calcu-

Table 1. *Models not allowing for boron*

Length L (Å)	Simple potential well (infinite walls)		Simple well (finite walls)		Periodic potential well			Potential well fitted to Mathieu's equation				
	$V = 0$	7.20	8.72	$V = -72.0$ eV**	(wave amplitude = 2.4eV†)	(amplitude = 7.2eV††)	$V_0 = 61.2$ eV	$V_0 = 45.0$ eV				
E_1	1.117	0.725	0.494	0.650	0.445	absolute energies not calculated for these models	7.20	7.20	7.20	7.20	9.80	
E_2	4.468	2.899	1.978	2.590	1.780		5.80	7.20	8.72	103	123	157
E_3	10.053	6.523	4.450	5.760	4.310		167	227	289	not calculated for this model	157	177
E_4	17.872	11.597	7.910	—	7.020		144	140	177	95	61	61
$\lambda_{2 \rightarrow 3}$	221	340	499	391	488	167	227	289	157	103	123	157
$\lambda_{1 \rightarrow 3}$	138	214	312	241	319	114	140	177	95	not calculated for this model	123	157
$\lambda_{2 \rightarrow 4}$	92	142	208	—	235	70	96	127	61	—	—	—

* The energies are positive and are measured relative to the bottom of the well.

** Value taken from Fig. 1 a. If this value is decreased $\Delta E_{2,3}$ is lowered.

† From ref. [14]. The transition energy is given by

$$\Delta E_{n,n+1} = \frac{\hbar^2 (2n+1)}{8mL^2} + V' \left(1 - \frac{1}{2n}\right) \cdot V' = \text{wave amplitude.}$$

If V' is decreased to 0.83 V' some allowance for electronic interaction is introduced. However, the ΔE values are only slightly altered by this.

†† Taken from Fig. 1 a.

lated. The improvement attendant on a sinusoidal potential encourages the view that a flat-bottomed well is an adequate approximation provided that explicit account is taken of the heteroatom, e. g. by allowing a finite barrier to represent it. This is the most important feature neglected by the simple models where the boron compound is considered simply as a polyene chain. The necessary modifications have already been described and the results of their application are listed in Tab. 2. In all cases the length of the well was 8.72 Å and the barrier width a was taken as 1.55 Å, *i. e.* from mid-point to mid-point of the B — C bonds. As before the energies are measured relative to the bottom of the well.

Inspection of the values of Tab. 2 shows that, as expected, the inclusion of a potential barrier simulating the boron atom improves the agreement between the observed and calculated positions of the spectral bands. This improvement over the simple infinite well is particularly marked when the corresponding figures derived for a length of 8.72 Å are compared, and is due to the differential effect of the barrier on the symmetric and antisymmetric levels. Application of perturbation theory to the problem reverses the sequence of the first and second energy levels and is thus not a reliable procedure. Such a result is perhaps not surprising from the first order theory.

Although the agreement is still not completely satisfactory for any particular calculation all the other models yield energies which are open to improvement by the inclusion of electron interaction.

Since none of the foregoing methods take this into account singlet and triplet states (V and T) are not interdistinguished. HAM and RUEDENBERG [10] and OLSZEWSKI [22, 23] have independently incorporated free electron theory into an antisymmetrised molecular orbital scheme. As is usual the total Hamiltonian is explicitly defined as the sum of the core Hamiltonian and the electron interaction operator $\frac{e^2}{|r - r_0|}$ where r and r_0 are the vector distances of electrons i and j from the origin. The configurational state functions are Slater determinants built from antisymmetrised products of free electron molecular spinorbitals. The energy of the lowest configurational singlet state is [17],

$$\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \sum_{i=0}^{n/2} I_i + \frac{1}{2} \sum_{i,j=0}^{n/2} \sum_{i,j=0}^{n/2} (J_{ij} - K_{ij}). \quad (3.1)$$

The summation runs over all occupied spinorbitals and J_{ij} , K_{ij} are the coulomb and exchange repulsion integrals defined in terms of the free electron orbitals. Since the core integrals are the eigenenergies of the initial unperturbed problem they can be calculated in the most suitable way by any of the simple F. E. methods.

An elegant technique for the evaluation of all the two-electron repulsion integrals has been developed by OLSZEWSKI [22]. Since the entity $\frac{1}{|r - r_0|}$ is the Green's function for the three dimensional Laplacian operator it satisfies the δ -function equation,

$$\nabla^2 G = -4\pi\delta(r - r_0). \quad (3.2)$$

Solution of this equation in cylindrical polar coordinates under homogeneous

Table 2. Models which allow for boron

Method	Barrier height (eV)	Energies (eV)				Predicted Spectral bands (m μ)			
		E_1	E_2	E_3	E_4	$\lambda_{2 \rightarrow 3}$	$\lambda_{1 \rightarrow 3}$	$\lambda_{2 \rightarrow 4}$	
Unapproximated Well (Eq. 2.4, 2.5, 2.6, 2.7)	<i>a</i>	2.027	2.231	7.741	8.871	225	217	187	
	<i>b</i>	1.850	2.000	7.034	7.945	246	239	209	
	<i>c</i>	1.741	1.891	6.653	7.469	260	252	222	
	<i>a</i>	1.996	2.204	7.524	8.802	233	224	188	
	<i>b</i>	1.809	1.986	6.857	7.891	255	246	210	
	<i>c</i>	1.714	1.877	6.503	7.428	268	259	223	
	<i>a</i>	1.973	2.218	7.428	8.762	238	227	189	
	<i>b</i>	1.782	1.986	6.775	7.864	259	248	211	
	<i>c</i>	1.687	1.877	6.422	7.401	273	262	224	
Nikitine's Approximation (Model 1)	<i>a</i>	1.600	1.978	6.401	7.910	279	257	209	
	<i>b</i>	1.440	1.780	5.680	7.020	318	292	236	
	<i>a</i>	1.567	1.978	6.268	7.910	289	264	209	
	<i>b</i>	1.411	1.780	5.563	7.020	328	299	236	
	<i>a</i>	1.548	1.978	6.192	7.910	294	267	209	
	<i>b</i>	1.393	1.780	5.496	7.020	334	302	236	
Nikitine's Approximation (Model 2)	11.22	2.137	4.261	8.265	*	202	—		
Perturbation method	11.22	4.381	2.367	8.228	9.201	210	321	180	

a - infinite end walls.*b* - finite end walls, height 72 eV.*c* - finite end walls, height 30 eV. This value was taken for compatibility with the magnitude of the barrier.

* This energy could not be obtained as the functions diverge.

Dirichlet conditions for the whole range of the variables yields an integral representation* of $\frac{1}{|r-r_0|}$.

The use of this as the interaction operator in J_{ij} , K_{ij} leads to integrals uniformly convergent in the whole chain region (z, z') . The passage to the limit $r \rightarrow 0$ is taken after integration (as in Gauss' theorem). This condition must be imposed because of the δ -function behaviour of $\frac{1}{|z-z'|}$ at $z = z'$. The final forms of the integrals are, [23],

$$K_{nm} = \frac{e^2}{\pi L} \left\{ Si [(n+m)\pi] \left(\frac{1}{n+m} - \frac{n+m}{nm} \right) + Si [(n-m)\pi] \left(\frac{1}{n-m} + \frac{n-m}{nm} \right) \right\} \quad (3.3)$$

$$J_{nm} = \frac{e^2}{\pi L} \left\{ \pi + \frac{m^2}{(n^2-m^2)n} Si (2m\pi) - \frac{n^2}{(n^2-m^2)m} Si (2m\pi) \right\} \quad (3.4)$$

$$J_{nn} = K_{nn} = \frac{e^2}{\pi L} \left\{ \pi - \frac{3}{2} \frac{Si (2n\pi)}{n} \right\} \quad (3.5)$$

where n, m refer to the n 'th and m 'th free electron MO's and

$$Si(x) = si(x) + \frac{\pi}{2}$$

$$si(x) = \int_0^x \frac{\sin x}{x} dx.$$

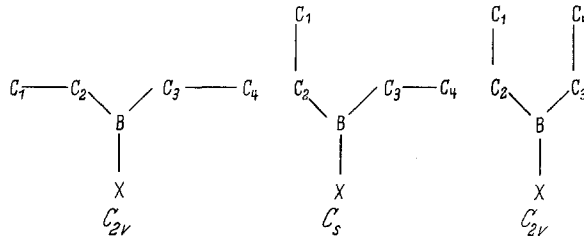
In the present work the eigenfunctions used in expressing the interaction integrals were those of the linear infinite well. The integrals most affected by this simplification are those which incorporate symmetric eigenfunctions, notably the lowest in energy. The error introduced is expected to be small.

Electronic states of the boranes

Under the influence of a cylindrical potential the wave functions, with the exception of the lowest would span the two dimensional representations of the axial rotation group. The descent in symmetry due to the real symmetry of the molecule completely removes the degeneracy and the electronic states may be classified accordingly.

Planar monovinylborane has C_s symmetry and, since the antisymmetry of π -orbitals with respect to the molecular plane is implicit, all its electronic states belong to the irreducible representation A' . For divinylborane three planar forms are possible.

* Since in the actual physical model the eigenfunctions vanish on the walls at the small value $r = a$, and z , in general, will not be infinite then it would seem preferable to represent the Green's function by an infinite series of Bessel functions. However, such a series may not be readily summable.



In model (b) all states are A' whereas for models (a) and (c) single excitations from both filled levels generate the states (ground state V_0 is 1A_1)

$$T_{13}, V_{13}, {}^3,{}^1A_1; T_{14}, V_{14}, {}^3,{}^1B_1; T_{23}, V_{23}, {}^3,{}^1B_1; T_{24}, V_{24}, {}^3,{}^1A_1.$$

The energies of these states relative to V_0 are given by [27],

$$E^{1,3} \Psi_{i,a} - E {}^1\Psi_0 = I_a + \sum_j (2 J_{ja} - K_{ja}) - I_i - \sum_j (2 J_{ij} - K_{ij}) - (J_{ia} - K_{ia}) \pm K_{ia} \quad (3.6)$$

and the singlet-triplet separation is $2 K_{ia}$. Since the ground state is not self-consistent then configurational interaction with the 1A_1 excited states will lower its energy. This may be included in the framework of the previous scheme by the usual linear variational procedure,

$$\Omega_s = \sum_i \lambda_i \Psi_i \quad s = 1, 2 \dots \quad (3.7)$$

where the Ψ_j are A.S.F.E.M.O. determinantal functions for states of the same spin and space symmetry (since the Hamiltonian matrix diagonalises). The off-diagonal elements of the configuration interaction matrices were calculated from the expressions [5, 2A],

$$\langle V_0 | V_{ik'} \rangle = \sqrt{2} \{ I_{ik'} + \langle ii | ik' \rangle + \sum_{j \neq i} (2 \langle fj | ik' \rangle - \langle fi | fk' \rangle) \} \quad (3.8)$$

$$\langle V_{ik'} | V_{jl'} \rangle = 2 \langle ik' | jl' \rangle - \langle ij | k' l' \rangle \quad (3.9)$$

$$\langle T_{ik'} | T_{jl'} \rangle = - \langle ij | k' l' \rangle \quad (3.10)$$

where,

$$\langle ij | kl \rangle = \iint \varphi_i^*(\mu) \varphi_j(\mu) \frac{e^2}{r_{\mu\nu}} \varphi_k^*(\nu) \varphi_l(\nu) d\tau_\mu d\tau_\nu.$$

These integrals are of the form explicitly considered by OLSZEWSKI. The eigenvalues and eigenvectors of the configuration interaction matrices were obtained using a programme based on the Householder-Wilkinson-Sturm sequence method [30]. The results of including electron interaction in the previous free electron calculations are listed in Tab. 3. The ground state, 1A_1 , was taken as zero for reference in all cases and configuration interaction between all electron states involving the first four energy levels was included. The squares of the elements of the corresponding normalised ground state eigenvectors are grouped in Tab. 4.

From the first column of Tab. 3 it is immediately obvious that, for the simple well, the inclusion of electron interaction does not compensate for the lack of a central potential barrier. NIKITINE's approximation yields results which are quite good and, providing the barrier is not too wide (i. e. does not extend over more

Table 3. *Electronic states of divinylborane*

Model V (eV)	Simple well	Unapproximated well (Eqns. 2.4, 2.5, 2.6, 2.7)						Nikifore's approximation (Eqns. 2.8)								
		11.22		10.26		9.78		11.22		10.26		9.78				
		c	d	e	c	d	e	c	d	e	c	d	e	c	d	
${}^3B_1(T_{23})$	a	2.504	5.529	5.066	4.794	5.352	4.903	4.658	5.243	4.821	4.576	3.932	4.322	3.815	4.264	3.748
	b	2.783	5.707	5.261	5.001	5.537	5.105	4.871	5.432	5.028	4.893	4.182	4.549	4.110	4.493	4.048
	λ	4.45	217	236	248	224	243	254	228	247	253	265	273	302	276	306
${}^1B_1(V_{23})$	a	3.687	6.712	6.249	5.977	6.535	6.086	5.841	6.426	6.004	5.759	5.638	5.504	4.998	5.429	4.931
	b	3.990	6.930	6.483	6.223	6.759	6.328	6.094	6.655	6.251	6.017	5.898	5.769	5.331	5.695	5.268
	λ	3.11	179	191	199	183	196	203	186	198	206	210	229	215	233	218
${}^3A_1(T_{13})$	a	4.829	6.588	6.058	5.786	6.402	5.922	5.663	6.330	5.867	5.609	5.675	5.578	5.026	5.518	4.977
	b	5.005	6.572	6.025	5.739	6.420	5.917	5.648	6.353	5.871	5.603	5.731	5.653	5.148	5.603	5.112
	λ	2.48	188	206	216	193	209	219	195	211	221	216	239	219	241	221
${}^1A_1(V_{13})$	a	4.869	6.628	6.098	5.826	6.442	5.962	5.703	6.370	5.907	5.649	5.714	5.615	5.066	5.558	5.017
	b	5.198	6.846	6.338	6.078	6.574	6.214	5.969	6.606	6.164	5.966	5.988	5.895	5.669	5.841	5.631
	λ	2.39	181	196	204	186	199	207	188	201	209	207	227	210	212	220
${}^3A_1(T_{24})$	a	6.516	7.222	6.528	6.161	7.181	6.488	6.134	7.127	6.460	6.107	6.516	6.515	5.823	6.515	5.823
	b	6.981	7.781	7.156	6.835	7.711	7.092	6.780	7.655	7.059	6.746	7.061	7.044	6.450	7.035	6.444
	λ	1.78	159	173	181	161	175	183	162	176	184	176	193	176	176	192
${}^1A_1(V_{24})$	a	6.703	7.409	6.716	6.348	7.369	6.675	6.321	7.314	6.647	6.294	6.703	6.703	6.010	6.703	6.010
	b	7.313	8.006	7.368	7.036	7.958	7.323	7.002	7.906	7.295	6.975	7.332	7.318	6.532	7.316	6.529
	λ	1.70	155	168	174	156	169	177	157	170	178	169	185	169	169	190
${}^3B_1(T_{13})$	a	8.855	8.282	7.534	7.166	8.245	7.520	7.153	8.228	7.534	7.153	7.749	7.782	7.048	7.801	7.066
	b	9.216	8.646	7.934	7.587	8.608	7.918	7.570	8.590	7.929	7.569	8.128	8.158	7.502	8.176	7.521
	λ	1.35	143	156	163	144	157	164	144	156	164	153	167	152	152	165
${}^1B_1(V_{14})$	a	8.958	8.386	7.637	7.270	8.349	7.624	7.256	8.331	7.624	7.256	7.852	7.885	7.151	7.904	7.169
	b	9.296	8.711	7.999	7.652	8.662	7.982	7.635	8.654	7.980	7.633	8.194	8.225	7.568	8.243	7.587
	λ	1.33	142	155	162	143	155	162	143	155	162	151	166	151	164	163
${}^1A_1(V_{15})$	a	13.42	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	b	13.76	—	—	—	—	—	—	—	—	—	—	—	—	—	—

 a - before configuration interaction. b - after configuration interaction. c - infinite walls. d - finite walls, $V = 72$ eV. e - finite walls, $V = 30$ eV.

Table 4

V (eV)	11.22		10.26		9.78	
	a	b	a	b	a	b
State						
V_0	0.957	0.953	0.956	0.953	0.956	0.951
V_{13}	0.007	0.007	0.007	0.008	0.007	0.008
V_{24}	0.036	0.040	0.037	0.040	0.037	0.041
Ground state depression (eV)	-0.298	-0.314	-0.300	-0.316	-0.301	-0.317

a - walls 72 eV. b - walls 30 eV.

than one atom), it seems to be a very simple and reliable technique. The remainder of the figures illustrate that the wells with infinite walls yield energies which are somewhat too high but these are lessened by the superposition of finite end walls. With end walls of 30 eV and a central barrier 10.26 or 9.78 eV the results for the first three transitions correspond fairly well with experiment. The second ($1 \rightarrow 3$) transition is forbidden in free electron theory but is weakly allowed by the C_{2v} perturbation and is polarized in the z -direction. Hence on an intensity basis the main peak in the spectrum of divinylmethylborane may be assigned to the ${}^1A_1 \rightarrow {}^1B_1$ transition and the next higher energy band to ${}^1A_1 \rightarrow {}^1A_1$. Both the above calculations place the first 1B_1 state too high in energy by ~ 0.4 eV and the first 1A_1 state too low (~ 0.2 eV). The second totally symmetric singlet state is predicted to be out of the range of observation (7.00 eV, 178 $m\mu$) and indeed no band is observed from 200 $m\mu$ down to 180 $m\mu$ although there is further absorption beyond this point. The shoulder (resolved at 253 $m\mu$) is difficult to assign. The calculated position of the 3B_1 state would correspond to absorption very close to this wavelength but the observed intensity (~ 0.03) seems too great for a singlet-triplet transition which can, at most, be only very weakly allowed by spin orbit coupling. Such bands are generally 10 times less intense. It is noteworthy that a similar spread of intensity is observed in ethylene itself, where it has been considered, by analogy with oxygen, to be part of the main band system [31].

On the other hand BERRY [2] has assigned the weak low energy shoulder which appears in the U. V. spectra of alkylated ethylenes (in solution) to the transition of an electron from the highest filled C - H bonding orbital to the lowest π^* orbital. Further discussion of this point, with reference to a series of vinylboranes, will appear in a subsequent publication.

A third possibility also arises; the vinylboranes undergo a slow reaction at room temperature and produce "daughter compounds", which may be dimeric [12]. However, since the boron atom in such a dimer would presumably be non-planar then we would perhaps expect absorption at higher energies than in the monomer.

Monovinylborane

The potential function employed in this case is shown in Fig. 2. For simplicity the barrier region was assumed to extend from the mid-point of the B - C bond to a point one bond length beyond boron as before. The barrier and end wall

heights and the boundary conditions are the same as before and the energy levels are obtained in a similar way. Since the potential is not symmetric here then the inversion symmetry of the eigenfunctions is lost and NIKITINE'S simplified method is not applicable. The eigenvalues are, however, simply related to

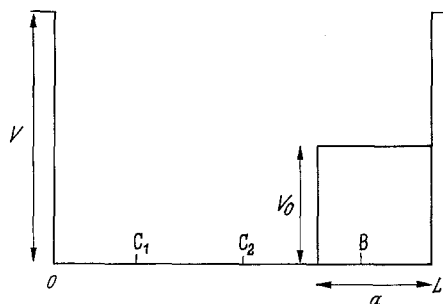


Fig. 2. Potential for monovinylborane

those of the symmetric well, the antisymmetric levels of the latter becoming the complete energy level set which yields the core energies. Electron and configuration interaction (between ground and first excited singlet states) was then included. The results are given in Tab. 5.

Comparison of the data shows that the overall agreement with experiment (section 3) is good.

Table 5. *Electronic states of monovinylborane*

Barrier height (eV)		Energies		${}^3A'$ (T_{12})		${}^1A'$ (V_{12})		
		E_1	E_2		λ	d	e	λ
11.22	<i>a</i>	2.136	8.231	5.832	213	7.110	7.224	172
	<i>b</i>	1.918	7.442	5.261	236	6.539	6.662	186
	<i>c</i>	1.823	7.034	4.948	251	6.226	6.356	195
10.26	<i>a</i>	2.107	8.062	5.696	218	6.974	7.090	175
	<i>b</i>	1.905	7.306	5.138	241	6.416	6.542	189
	<i>c</i>	1.796	6.911	4.853	255	6.131	6.262	198
9.78	<i>a</i>	2.095	7.973	5.614	221	6.892	7.010	177
	<i>b</i>	1.891	7.238	5.084	244	6.362	6.489	191
	<i>c</i>	1.769	6.803	4.771	260	6.049	6.182	201

a - infinite walls.

b - finite walls (72 eV).

c - finite walls (30 eV).

d - before C. I.

e - after C. I.

4. Electron Densities and Bond Orders

These have been defined [28] in terms of normalised free electron eigenvectors which may be substituted directly into the COULSON equations [7, 29]. The equivalence depends directly on the extension of the space by one bond length beyond each terminal atom. Alternatively electron densities and bond orders may be obtained by integration thus,

$$P = \sum n_j \int_a^b \psi_j^* \psi_j dx \quad (4.1)$$

over all occupied orbitals

where,

$$P = \begin{cases} \text{electron density if } ab \text{ is an atom region} \\ \text{bond order if } ab \text{ is a bond region} \end{cases}$$

and n_j is the occupation number of the j 'th orbital.

Although the above functions are readily integrable in closed form they are most conveniently evaluated by numerical quadrature and the figures for the two boranes are listed in Tab. 6. The normalizing constants were calculated from a combination of equations 2.4, 2.5 and the condition

$$A^2 \int_0^{L/2-a} \sin^2 \alpha x dx + B^2 \int_{L/2-a}^{L/2+a} e^{-2\beta x} dx + C^2 \int_{L/2-a}^{L/2+a} e^{2\beta x} dx + D^2 \int_{L/2+a}^L \sin^2 \alpha (L-x) dx = 1. \quad (4.2)$$

The two lowest eigenfunctions for divinylborane are shown in Fig. 3.

In all cases an appreciable π -charge resides on the boron atom in these compounds and the B - C bond is multiple. Both features reflect the known electron acceptor properties of boron when linked to groups or atoms providing electrons in orbitals of π -symmetry, the classic case being borazine.

Throughout this paper the substituent X has been considered non interacting but in the more readily available vinylboranes this will not be the case and substituents such as Cl or N will contribute to the π -system. Such effects complicate the mathematics of the free electron approach and are perhaps better estimated by the L.C.A.O. technique.

In conclusion it may be said that the free electron method may yield detailed and reasonable results which compare quite well with experiment. Furthermore, these results are not oversensitive to small variations in the semi-empirical parameters chosen. However, there seems no possibility of quantitative agreement with the experimental spectra unless explicit account is taken of the boron atom.

Table 6. Bond orders and charge densities

V_0	C_1, C_4	C_2, C_3	B	B - C
11.22	<i>a</i> 1.020	0.915	0.131	0.405
	<i>b</i> 0.971	0.946	0.083	0.454
10.26	<i>a</i> 1.014	0.930	0.112	0.407
	<i>b</i> 0.968	0.964	0.068	0.451
9.78	<i>a</i> 1.003	0.924	0.146	0.423
	<i>b</i> 0.954	0.970	0.076	0.466

a - divinylborane, *b* - monovinylborane.

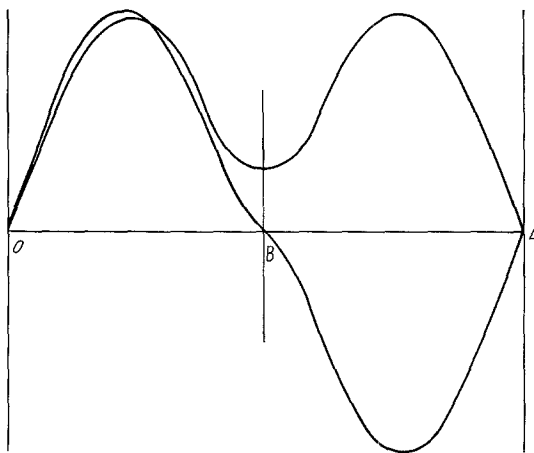


Fig. 3. Bonding free-electron wave functions for divinylborane

The authors thank Dr. B. J. DUKE (University Computing Laboratory) for invaluable help and the D. S. I. R. for a maintenance grant (to D. R. A.). We are also indebted to Prof. D. M. RITTER for supplying copies of spectra.

References

- [1] BAYLISS, N. S.: Austral. J. Sci. Res. A **3**, 109 (1950).
[1a] - Quart. Rev. (Lond.) **6**, 319 (1952).
[2] BERRY, R. S.: J. chem. Physics **38**, 1934 (1963).
[3] BUCKINGHAM, R. A.: Quantum Theory. 1. Ed. D. R. BATES. New York and London: Academic Press 1961.
[4] CHALVET, O., R. DAUDEL, and J. J. KAUFMAN: J. Amer. chem. Soc. **87**, 399 (1965).
[5] CONDON, E. U., and G. H. SHORTLEY: The theory of Atomic Spectra. Cambridge: University Press. 1951. P. 69.
[6] COYLE, T. D., S. L. STAFFORD, and F. G. A. STONE: J. chem. Soc. (Lond.) **1961**, 3103.
[7] COULSON, C. A.: Proc. Roy. Soc. London A **169**, 413 (1939).
[8] DAVIES, D. W.: Trans. Faraday Soc. **56**, 1713 (1960).
[9] GOOD, C. D., and D. M. RITTER: J. Amer. chem. Soc. **84**, 1162 (1962).
[10] HAM, N. S., and K. RUEDENBERG: J. chem. Physics **25**, 1 (1956).
[11] HINZE, J., and H. H. JAFFÉ: J. Amer. chem. Soc. **84**, 540 (1962).
[12] KAESZ, H. D., and F. G. A. STONE: Organometallic Chemistry. New York: Reinhold 1960, P. 104.
[13] KAUFMAN, J. J., and J. R. HAMANN: Boron-Nitrogen Chemistry, Advances in Chemistry Series, 42. American Chemical Society, p. 95, 1964; HOFFMAN, R.: *ibid.* p. 78; DEWAR, M. J. S.: *ibid.* p. 227.
[14] KUHN, H.: J. chem. Physics **17**, 1198 (1949).
[15] - Helv. chim. Acta **34**, 2371 (1951).
[16] - Experientia **9**, 41 (1953).
[17] MULLIKEN, R. S.: J. Chim. physique **46**, 497, 675 (1949).
[18] MURAI, T.: Progr. theoret. Physics **7**, 345 (1952).
[19] NIKITINA, A. N., V. A. VAYER, N. S. FEDOTOV, and B. M. MIKHAILOV: Optics and Spectroscopy **7**, 389 (1959).
[20] NIKITINE, S., and S. G. EL-KOMOSS: J. Chim. physique **47**, 798 (1950).
[21] - J. Chim. physique **50**, 407 (1953).
[22] OLSZEWSKI, S.: Acta physica Polonica **14**, 419 (1955).
[23] - Acta physica Polonica **16**, 211, 369 (1957).
[24] PARISER, R.: J. chem. Physics **24**, 250 (1956).
[25] PILCHER, G., and H. A. SKINNER: J. inorg. nucl. Chem. **24**, 937 (1962).
[26] PRITCHARD, H. O., and H. A. SKINNER: Trans. Faraday Soc. **49**, 1254 (1953).
[27] ROOTHAAN, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
[28] RUEDENBERG, K., and C. W. SCHERR: J. chem. Physics **21**, 1565 (1953).
[29] WHELAND, G. W. and L. PAULING: J. Amer. chem. Soc. **57**, 2086 (1935).
[30] WILKINSON, J. H.: Numerische Mathematik **4**, 254 (1962).
[31] WILKINSON, P. G., and R. S. MULLIKEN: J. chem. Physics **23**, 1895 (1955).

(Received July 15, 1965)