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Commentationes

Molecular Orbitals and the Virial Theorem

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It is shown that for H_2^+ and H_2 an atomic orbital exponent ξ chosen from the condition $\overline{\Delta T} = -\Delta E_{\text{obs.}}$ gives calculated total energies which are insignificantly different from those obtained using a ξ obtained through a variational treatment. A scheme is proposed in which the atomic orbital exponents of π-electron molecular orbitals are taken to be a function of the orbital energies, such that these molecular orbitals qualitatively satisfy the virial theorem.

Es wird gezeigt, daß für H_2^+ und H_2 ein Atomorbital-Exponent ξ, der entsprechend der Bedingung $\overline{\Delta T} = -\Delta E_{\text{obs.}}$ gewählt wurde, zu Gesamtenergien führt, die nur unwesentlich von jenen abweichen, die man nach der Variations-Methode erhält. Es wird ein Verfahren vorgeschlagen, in welchem der Exponent ξ der Atomorbitale eines π-Elektronensystems als Funktion der Orbitalenergien angesetzt wird, so daß diese Orbitale dem Virial Theorem qualitativ genügen.

On montre que l'exposant ξ que l'on choisit pour les orbitales atomiques de H_2^+ et H_2 en se servant de la condition $\overline{\Delta T} = -\Delta E_{\text{obs.}}$ diffère d'une façon insignifiante de celui calculé par la méthode variationelle. On propose un procédé dans lequel les exposants ξ des orbitales atomiques de systèmes π sont fonction de l'énergie des orbitales moléculaires de manière que le théorème du viriel est qualitativement satisfait.

Introduction

For a system of particles in equilibrium, which are interacting by Coulomb forces, the total energy relative to the energy of the particles infinitely separated from one another is equal to the negative of the kinetic energy or half the potential energy. This is a special case of the virial theorem which is valid for classical and quantum mechanical systems.

$$-E = \overline{T}\,, \qquad E = \overline{V}/2\,. \tag{1}$$

Löwdin has written a comprehensive review on the virial theorem in quantum mechanics and a bibliography of early work is given therein [4].

The description of the electronic states of atoms based on atomic orbitals is at least qualitatively compatible with the virial theorem. Although the energy of an atomic orbital is not precisely defined, one can say roughly that the higher the energy of an atomic orbital, the larger the orbital and the lower its associated kinetic energy. In the LCAO molecular orbital theory, however, one usually takes a basis of atomic orbitals of the separated atoms which is the same for all the molecular orbitals. For a small basis set it is not clear that this satisfies the virial

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theorem. If one writes a molecular orbital in the form

$$\psi_r = \sum_{\mu} c_{r\mu} \varphi_{\mu} ,$$

then should the size of the orbital φ_{μ} depend on the energy of ψ_r, and if so how sensitive is the size to the energy ? In addition, could such an effect be introduced into the calculation without making the mathematics too complicated ? These are the questions we shall examine in this paper.

H_2^+ and H_2

As an introduction we first look at H_2^+ and H_2. It is well known that a LCAO wave function based on hydrogen $1s$ orbitals does not satisfy the virial theorem unless orbital contraction is allowed for [*8*, *9*]. Thus for a wave function

$$\psi = (2 + 2S)^{-\frac{1}{2}} (1s_a + 1s_b) \tag{2}$$

where $1s_a = (\xi^3/\pi)^{\frac{1}{2}} e^{-\xi r_a}$ and S is the overlap integral between the two orbitals at distance R, one finds ($\varrho = \xi R$)

$$\overline{\Delta T} = \frac{(\xi^2 - 1)\,[1 + e^{-\varrho}\,(1 + \varrho)] - (\xi^2 + 1)\,\frac{1}{3}\,\varrho^2 \cdot e^{-\varrho}}{2\,[1 + e^{-\varrho}\,(1 + \varrho + \frac{1}{3}\,\varrho^2)]} \tag{3}$$

$$\overline{\Delta V} = \frac{-\xi\left[1 + \frac{1}{\varrho} - \left(\frac{1}{\varrho} + 1\right) e^{-2\varrho} + 2\,(1 + \varrho)\,e^{-\varrho}\right]}{1 + e^{-\varrho}\,(1 + \varrho + \frac{1}{3}\,\varrho^2)} + 1 \tag{4}$$

for the average kinetic and potential energies relative to those for infinitely separated nuclei.

If no orbital contraction is allowed for ($\xi = 1$) then it can be seen that $\overline{\Delta T}$ is negative, for all internuclear distances whereas from the virial theorem we know it must be positive at the equilibrium separation.

By the variation principle the best value of ξ has been found to be 1.239 at the observed internuclear distance of $R = 2a_0$. Fig. 1 shows the values of $-\overline{\Delta V}$, $\overline{\Delta T}$, $-\Delta E$ and $\overline{\Delta V} + 2\,\overline{\Delta T}$ for ξ in the range 1.23 to 1.26. It is seen that whereas $\overline{\Delta V}$, $\overline{\Delta T}$ and $\overline{\Delta V} + 2\,\overline{\Delta T}$ are varying quite rapidly in this region ΔE is varying very slowly and is an insensitive test of the best ξ. Applying the virial condition to this wave function ($\overline{\Delta V} + 2\,\overline{\Delta T} = 0$) at $2a_0$ gives the solution $\xi = 1.238$. (By FOCK's scaling theorem they would coincide if the energies were evaluated for that internuclear distance which gives the minimum energy for this wave function [*2*, *4*].)

Since the kinetic energy is much easier to calculate than the total energy one is tempted to use the virial theorem rather than the variation principle to obtain good wave functions. For example, if one chooses ξ such that $\overline{\Delta T} = -E_{\text{obs.}}$ (which an exact calculation for H_2^+ gives as 0.1026 a.u.) then one obtains $\xi = 1.255$. Fig. 1 shows that the energy calculated using this value is insignificantly worse than that obtained using the variation principle.

It might be argued that the reason for the satisfactory result for H_2^+ is that the molecular orbital wave function is close to an exact wave function in this case. However, Fig. 2 shows the corresponding results for H_2, where due to the underestimation of electron correlation, the MO function is not very good. Nevertheless, the ξ obtained by equating $-\overline{\Delta T}$ to the observed energy is still close to that obtained by the variation principle, and the calculated energy is insignificantly worse.

Thus for the two cases we have considered, a wave function can be obtained from the condition $\overline{\Delta T} = -E_{\text{obs.}}$ which gives as good energies as that obtained from the variation principle, although the virial theorem in the form $2\,\overline{\Delta T}_{\text{calc.}} + \overline{\Delta V}_{\text{calc.}} = 0$ is not satisfied so well (c. f. appendix).

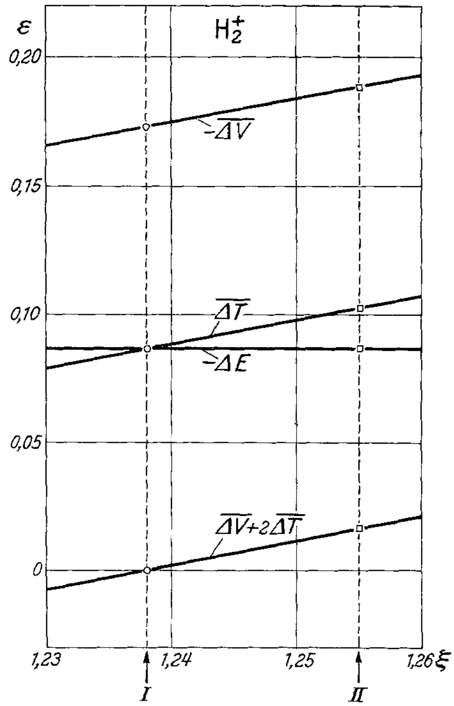

Fig. 1

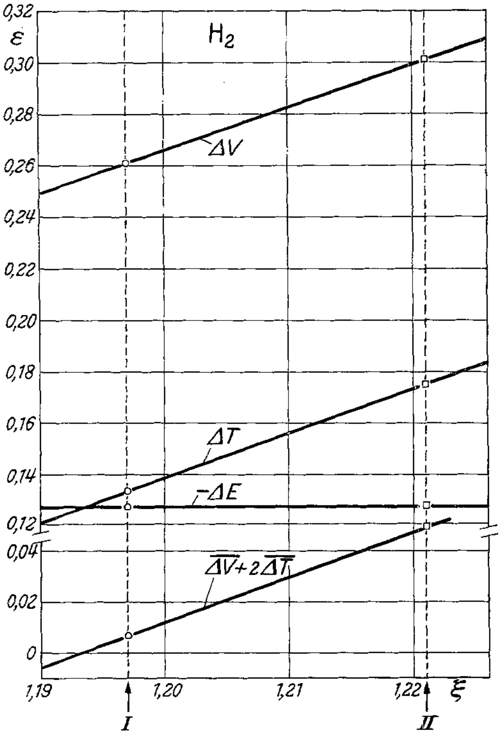

Fig. 2

Fig. 1. Hydrogen molecule ion H_2^+. ε = Energy in atomic units, I: ξ-value for which $\overline{\Delta V} + 2\overline{\Delta T} = 0$, II: ξ-value for which $\overline{\Delta T} = \Delta E_{\text{obs}}$, (In the range indicated, the value of ΔE changes only in the fourth decimal)

Fig. 2. Hydrogen molecule H_2. ε = Energy in atomic units, I: Best ξ-value according to variational principle, II: ξ-value for which $\overline{\Delta T} = -\Delta E_{\text{obs}}$

Application of the virial theorem to π-electron systems

Although the satisfaction of the virial theorem is a necessary condition for an exact solution of the Schrödinger equation it is not sufficient for, by Fock's scaling theorem, even poor wave functions can be made to satisfy it.

For the heteronuclear molecules the orbital exponents of each atomic orbital in the basis can by the variation principle be varied to obtain a unique energy minimum. The virial theorem, however, will only be sufficient to determine the best value of one of these exponents for chosen values of all others. At the present time we have insufficient information from variation calculations to suggest how the exponents should vary for heteronuclear systems.

It is therefore only for homonuclear molecules that the virial theorem may be a useful method of determining orbital exponents. In this class one might include the π-electron systems of conjugated hydrocarbons. MURAI [*6*] has calculated the energies of different electronic states of ethylene assuming the σ-electron core to be fixed and the π-electron molecular orbitals to be based on atomic orbitals with orbital exponents which were optimized for each state. Although this approach is incomplete in the sense of having invariant σ-orbital exponents, it nevertheless would seem to be a useful extension of the usual π-electron theory. Moreover, it is consistent with the deduction, from the vibrational fine structure of π-π^*-absorption bands that excitation of the π-electrons does not lead to an overall expansion of the molecule [*5*]; which is what is to be expected if this excitation were accompanied by σ-electron expansion.

Let us first consider Hückel orbitals, written as

$$\psi_r = \sum_{\mu} c_{r\mu}\, \varphi_{\mu} \,. \tag{5}$$

These are eigenfunctions of a Hamiltonian matrix having a constant element α on the diagonal, and a constant element β on the off diagonal elements $H_{\mu\nu}$ when μ and ν are bonded together. The eigenvalues E_r of this matrix are related to the set of values which are eigenvalues of the topological matrix having 1 in positions where there are β in the Hückel matrix, and zero elsewhere:

$$m = (\alpha - E)/\beta \,. \tag{6}$$

In the Hückel scheme all off diagonal elements of the overlap matrix are put equal to zero. In the Wheland scheme they are put equal to S for all bonded pairs of atoms. However, the orbitals given in the Wheland scheme only differ by a normalising factor from the Hückel orbitals, since the parameter m is redefined as

$$m = (\alpha - E)/(\beta - ES) \tag{7}$$

or

$$E = \frac{\alpha - m\beta}{1 - mS} \,. \tag{8}$$

In general we can say that the set of orbitals

$$\psi_r = N_r \sum_{\mu} c_{r\mu}\, \varphi_{\mu}$$

are non interacting in the Hückel scheme ($N_r = 1$) and in the Wheland scheme $\left(N_r = (1 - m_r S)^{-\frac{1}{2}}\right)$. That is, for $r \neq s$

$$\langle \psi_r \,|\, \mathscr{H} \,|\, \psi_s \rangle = N_r N_s \left\{ \sum_{\mu} c_{r\mu}\, c_{s\mu}\, \alpha + \sum_{\mu} \sum_{\mu \to \nu} c_{r\mu}\, c_{s\nu}\, \beta \right\} = 0 \,. \tag{9}$$

But, from the orthogonality of the Hückel orbitals

$$\sum_{\mu} c_{r\mu}\, c_{s\mu} = 0 \tag{10}$$

hence

$$\sum_{\mu} \sum_{\nu \to \mu} c_{r\mu}\, c_{s\nu} = 0 \,. \tag{11}$$

If we now define integrals of kinetic energy by

$$\begin{aligned} \tau &= \langle \varphi_{\mu} \,|\, -\tfrac{1}{2}\nabla^2 \,|\, \varphi_{\mu} \rangle \\ \omega &= \langle \varphi_{\mu} \,|\, -\tfrac{1}{2}\nabla^2 \,|\, \varphi_{\nu} \rangle \end{aligned} \tag{12}$$

and take all integrals between non bonded atoms equal to zero, then the orbitals (8) will also be eigenfunctions of the kinetic energy matrix, and, drawing the analogy between α and τ, β and ω we can see from (8)

$$\overline{T}_r = \frac{\tau - m_r\,\omega}{1 - m_r\,S} \tag{13}$$

(where S is put equal to zero for the Hückel scheme).

We can now ask whether the virial theorem is satisfied for this set of orbitals. That is, if we assume that there exist states of the hydrocarbon which differ only in the allocation of electrons to the π-orbitals and which have the same unchanged σ-electron structure and nuclear structure, then we should find that the kinetic energy $\overline{T}_r$ decreases as r increases.

If we evaluate ω for Slater type $2p\pi$ atomic orbitals with exponential factor ξ one finds [7]:

$$\langle 2p\pi_\mu \,|\, -\tfrac{1}{2}\nabla^2 \,|\, 2p\pi_\nu \rangle = -\tfrac{1}{2}\,\xi^2 \{S - S'\}\ , \tag{14}$$

where S is the overlap integral between the two orbitals, and S' is proportional to the overlap integral between a $2p\pi$ and a Slater-type $1p\pi$ orbital, as defined by ROOTHAAN [7]:

$$S' = \frac{4}{\sqrt{3}}\,\langle 2p\pi_\mu \,|\, 1p\pi_\nu \rangle\ . \tag{15}$$

These overlap integrals have the form ($\varrho = \xi\,R$)

$$S = \left[1 + \varrho + \tfrac{2}{5}\,\varrho^2 + \frac{1}{15}\,\varrho^3\right] e^{-\varrho}$$

$$S' = 2\,[1 + \varrho + \tfrac{1}{3}\,\varrho^2]\,e^{-\varrho} \tag{16}$$

so that

$$\omega = \tfrac{1}{2}\,\xi^2\,(1 + \varrho + \frac{4}{15}\,\varrho^2 - \frac{1}{15}\,\varrho^3)\,e^{-\varrho}\ . \tag{17}$$

For ϱ less than 6.6 (for C–C bonds ϱ is in the range 4 — 4.5) ω is positive, which means that the Hückel scheme satisfies the virial theorem at least qualitatively, $\overline{T}_r$ decreasing with growing quantum number r, i. e. with increasing E_r. However, from expression (14) it is clearly inconsistent to put $S = 0$ in a Hückel scheme and yet not take ω to be zero.

In the Wheland scheme we have for small values of m_r that $m_r\,S < 1$ and therefore we can approximate (13) by

$$\overline{T}_r = \tau - m_r\,(\omega - \tau S)\ . \tag{18}$$

τ has the value $\frac{1}{2}\,\xi^2$, hence

$$\omega - \tau S = \tfrac{1}{2}\,\xi^2\,(S' - 2\,S) = \frac{-\,\xi^2}{15}\,\varrho^2\,(1 + \varrho)\,e^{-\varrho}\,. \tag{19}$$

$\omega - \tau\,S$ is now negative for all values of ϱ, hence $\overline{T}_r$ increases as the energy of the orbitals increases — which is in violation of the virial theorem. If one calculates the energies of π-molecular orbitals according to an independent electron scheme without neglect of overlap, one finds as for the H_2 and H_2^+ system, that if all exponents are kept constant, then the kinetic energy associated with an orbital increases as the energy of the orbital increases. For H_2 and H_2^+ this fault can be remedied by contracting the bonding orbitals and expanding the antibonding. Can one introduce a similar variation of π-molecular orbitals which will likewise bring the system into line with the virial theorem?

The simplest approach is to allow the exponent of the atomic orbitals ξ to depend on the nature of the molecular orbital ψ_r, but still take all the $\varphi_{\mu r}$ to be identical. The α and β will be functions of r and s and (9) will become

$$\langle\psi_r \mid \mathscr{H} \mid \psi_s\rangle = N_r\, N_s \left\{\sum_{\mu} c_{r\mu}\, c_{s\mu}\, \alpha_{rs} + \sum_{\mu} \sum_{\nu\to\mu} c_{r\mu}\, c_{s\nu}\, \beta_{rs}\right\} . \tag{20}$$

However, since α_{rs} and β_{rs} are independent of μ and ν we have from (10) and (11)

$$\langle\psi_r \mid \mathscr{H} \mid \psi_s\rangle = 0 . \tag{21}$$

It follows that even if we allow for the size of the atomic orbitals $\varphi_{\mu r}$ to be a function of r, the set of orbitals (8) will still be noninteracting.

In order to have some idea as to how much the orbital exponents should vary with m_r we will assume that the ξ appropriate for a molecular orbital ψ_r is a linear function of m_r

$$\xi_r = \xi_0 - k m_r . \tag{22}$$

The expression for $\overline{T}_r$ can then be expanded as a power series in k and to first order one finds

$$\overline{T}_r = \overline{T}{}_r^0 - k m_r\, \xi_0 + \frac{e^{-\varrho_0}\, k m_r^2\, \xi_0\, \varrho_0^2}{15}\,(\varrho_0^2 - 4\,\varrho_0 - 4) \tag{23}$$

where $\overline{T}{}_r^0$ is the kinetic energy evaluated with $k = 0$ and $\varrho_0 = \xi_0\, R$. Taking $\xi_0 = 1.625$, $R = 1.4$ Å one finds

$$\overline{T}{}_r^0 = \frac{\xi_0^2}{2}\,(1 + 0.178\, m_r) \tag{24}$$

and that the third term in (23) is small compared with the second. It follows that we have

$$\overline{T}_r = \frac{\xi_0^2}{2} + (0.089\, \xi_0^2 - k\, \xi_0)\, m_r . \tag{25}$$

We now evaluate k by making the decrease in kinetic energy for the excitation from the highest occupied molecular orbital ψ_1 to the lowest vacant molecular orbital ψ_{-1} of aromatic hydrocarbons, equal to the energy of the ${}^1L_a$ band. A linear correlation has been found between the energy of this band and the difference in Hückel energies which has the form

$$\Delta E_{\text{obs.}} = A + B\,(m_{-1} - m_1) \tag{26}$$

where $B = 2.19 \cdot 10^4\ \text{cm}^{-1} = 0.101$ a.u. and where A is small [*3*].

Our calculated decrease in kinetic energy is

$$\overline{T}_1 - \overline{T}_{-1} = (0.089\, \xi_0^2 - k\, \xi_0)\,(m_1 - m_{-1}) \tag{27}$$

which means that the virial theorem would hold for

$$\xi_0\,(k - 0.089\, \xi_0) = 0.101 \tag{28}$$

where

$$k = 0.207 .$$

For example, for the ${}^1L_a$ band of naphthalene (36400 cm^{-1}) one would have excitation from a bonding orbital ψ_1 with $\xi_1 = 1.753$ to an antibonding orbital ψ_{-1}, with $\xi_{-1} = 1.497$.

The value of k is sufficiently small for the approximation of the Hückel or Wheland model of only considering nearest neighbour interactions to be valid. For example, the most antibonding orbitals have $m \approx 2.5$ and for these we would have $\xi \approx 1.1$.

A further conclusion is that any correlation which is found between Hückel energies and some observed quantity (e. g. spectroscopic energies, polarographic reduction potentials, resonance energies) would still be valid for calculations based on orbitals with variable exponents according to the scheme we have suggested. For example, suppose one relates some observed energy to the difference of energies calculated according to the Hückel independent electron model. Then

$$E_{\text{obs.}} = E_r - E_s = -(m_r - m_s)\,\beta\,.$$

In the Wheland scheme this becomes for $mS < 1$

$$E_{\text{obs.}} = -(m_r - m_s)\,(\beta - \alpha\, S)$$

and if the linear relationship is found between $E_{\text{obs.}}$ and the Hückel energies it will also be found between $E_{\text{obs.}}$ and the Wheland energies. Likewise if one expands α_r, β_r and S_r in the scheme we suggest,

$$\alpha_r = \alpha_0 + \alpha_1\, k m_r\,; \qquad \beta_r = \beta_0 + \beta_1\, k m_r$$

$$S_r = S_0 + S_1\, k m_r$$

then

$$E_{\text{obs.}} = -(m_r - m_s)\,(\beta_0 - \alpha_0\, S_0 - \alpha_1\, k)$$

plus smaller terms. In other words, the fact that there are good correlations between some experimental results and theoretical energies based on fixed atomic orbitals is not evidence against orbital expansion in the manner we have suggested.

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Appendix

The raison d'être of the covalent bond has often been attributed, on the basis of the "particle-in-a-box" model to a reduction in kinetic energy. Although the virial theorem shows

Table 1

	$\overline{T}_x$	$\overline{T}_z$	$\overline{T}$
Separate atoms	0.17	0.17	0.50
Ground state $\xi = 1$	0.15	0.09	0.39
Excited state[a] $\xi = 1$	0.24	0.46	0.94
Ground state[b] $\xi = 1.25$	0.23	0.14	0.60
Excited state[a][b] $\xi = 0.90$	0.21	0.41	0.81

[a] $\psi = (2 - 2S)^{-\frac{1}{2}}(1s_a - 1s_b)$.

[b] Deduced by the variation method for $R = 2$ a.u.

that this interpretation is incorrect*, the model has some validity as one can see by evaluating the three components of the kinetic energy for the H_2^+ wave function. Tab. 1 shows the values of the component along the internuclear axis ($\overline{T}_z$) and at right angles to this ($\overline{T}_x = \overline{T}_y$) for both the ground and excited state wave functions, with and without variable ξ.

Thus along the internuclear axis the kinetic energy is less than for separate atoms, as one would surmise from the "particle-in-a-box" model, but for the ground state this is offset when orbital contraction is allowed for by an increase perpendicular to this axis. (Further details shall be published elsewhere [*1*]).

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* RUEDENBERG has given a very detailed account of the changes in kinetic and potential energies which accompany bond formation [*8*].

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