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Annotatio

The Kinetic Energy Components of LCAO-Molecular Orbitals: A Comment on the "Electron-in-a-Box"-"LCAO-MO-Model" Analogy

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In many textbooks attention is drawn to the close analogy that seems to exist between the "Electron-in-a-Box"-wave functions Ψ_n and their LCAO–MO counterparts ψ_J $(J = n)$ for the movement of an electron in a π-system. It is often implied that the "wave lengths" Λ of Ψ_n and λ of ψ_J $(J = n)$ which satisfy to a high degree the relation $\Lambda = \lambda$, have the same physical meaning. It is shown that this is not the case. Λ for a linear system (e.g. a one-dimensional "Electron-in-a-Box"-model) is directly connected with the momentum of the electron and therefore with its kinetic energy according to the deBroglie relation. However, there is no such simple relationship between λ and the corresponding kinetic energy component in LCAO–MO's ψ_J. (The necessary two-center kinetic energy integrals have been computed for 1s-type atomic orbitals.)

Dans les textes élémentaires de chimie théorique on attire souvent l'attention sur l'analogie qui semble exister entre les fonctions d'onde Ψ_n pour un modèle «Electron-in-a-Box» et les fonctions correspondantes LCAO–MO ψ_J $(J = n)$ décrivant le mouvement d'un électron dans un système π. En particulier cette comparaison implique que les «longueurs d'onde» Λ de Ψ_n et λ de ψ_J $(J = n)$, qui satisfont pratiquement la relation $\Lambda = \lambda$, ont la même signification physique. Dans ce travail on montre, que ceci n'est pas le cas. Pour un système linéaire (c.à.d. un modèle linéaire du type «Electron-in-a-Box») Λ est reliée directement à la quantité de mouvement et par là à l'énergie cinétique, par la relation de deBroglie. Par contre on ne trouve pas une dépendance analogue entre λ et la composante correspondante de l'énergie cinétique dans une orbitale moléculaire LCAO ψ_J. (Les intégrales bicentriques pour les composantes d'énergie cinétique nécessaires à ce calcul ont été déterminées pour des orbitales atomiques du type 1s.)

In vielen elementaren Textbüchern wird die Aufmerksamkeit auf die scheinbar enge Verwandtschaft hingelenkt, die zwischen den Wellenfunktionen Ψ_n für ein „Electron-in-a-Box"-Modell und den entsprechenden LCAO–MOs ψ_J $(J = n)$ für die Bewegung eines Elektrons in einem π-System besteht. Unter anderem wird oft implizit angenommen, daß die „Wellenlängen" Λ der Funktion Ψ_n und λ von ψ_J $(J = n)$, die weitgehend der Bedingung $\Lambda = \lambda$ genügen, die gleiche physikalische Bedeutung haben. In dieser Arbeit wird gezeigt, daß dies nicht der Fall ist. Für ein lineares System (z. B. ein eindimensionales „Electron-in-a-Box"-Modell) ist Λ über die deBroglie'sche Beziehung direkt mit dem Impuls und damit mit der kinetischen Energie des Elektrons verknüpft. Im Gegensatz dazu existiert keine einfache Beziehung zwischen λ und der entsprechenden Komponenten der kinetischen Energie in einem LCAO–MO ψ_J. (Die notwendigen Zweizentrenintegrale der kinetischen Energie wurden für Atomorbitale vom 1s-Typus berechnet.)

A free electron which moves unrestricted and therefore with constant velocity v along an axis (e.g. the x-axis) posesses the kinetic energy

$$E = \tfrac{1}{2} mv^2 = \frac{p^2}{2m} \tag{1}$$

where m is the mass of the electron and $p = mv$ its momentum. The movement of the electron is described by a periodic wave-function

$$\Psi(x) = \Psi(x \pm \Lambda) . \tag{2}$$

The periodicity Λ of $\Psi(x)$ depends on the momentum p according to the deBroglie-relation (h = Planck's constant):

$$\Lambda = \frac{h}{p} . \tag{3}$$

Λ is called the deBroglie wave length associated with the momentum p. Inserting (3) into (1), one obtains for the kinetic energy of a free moving electron

$$E = \frac{h^2}{2m\Lambda^2} \tag{4}$$

or expressed in atomic units*:

$$E = \frac{2\pi^2}{\Lambda^2} = \frac{19.74}{\Lambda^2} . \tag{5}$$

As the simplest example for a bound electron, the one-dimensional "electron-in-a-box"-model is discussed in most elementary texts on quantum chemistry. The aim is to acquaint the student with the behaviour of an electron, the movement of which is restricted by a potential $V(x)$ to a limited space (here the "box" of length L). For the "box"-model the potential $V(x)$ is assumed to be of the form:

$$\begin{aligned} V(x) &= 0 \quad \text{if} \quad 0 < x < L \\ V(x) &= \infty \quad \text{if} \quad x < 0 \text{ or } x > L . \end{aligned} \tag{6}$$

Therefore the wave function $\Psi(x)$ describing the movement of the electron inside the "box" [where $V(x) = 0$] must be of the type (2). However, according to well known principles, the wave function $\Psi(x)$ has to vanish for $x \leq 0$ and $x \geq L$:

$$\Psi(0) = \Psi(L) = 0 . \tag{7}$$

This leads to the quantum condition (8) for the periodicity Λ of the electron wave function $\Psi(x)$ in the interval 0 to L:

$$\Lambda = \frac{2L}{n} \tag{8}$$

where n, the quantum number, can take the values $n = 1, 2, 3, \ldots$ Insertion of (8) into (4) yields the eigenvalues E_n for the system:

$$E_n = \frac{h^2}{8mL^2} \cdot n^2 . \tag{9}$$

$$n = 1, 2, 3, \ldots$$

Expressed in atomic units:

$$E_n = \frac{\pi^2}{2L^2} \cdot n^2 = \frac{4.93}{L^2} \cdot n^2 . \tag{10}$$

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* 1 a.u. of energy = 27.2 eV, 1 a.u. of length = 0.53 Å.

To each eigenvalue E_n of the energy of the electron in a "box" of length L, there corresponds an eigenfunction $\Psi_n(x)$ ("wave-function") which can be shown to have the normalized form (c.f. Fig. 1):

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n x}{L}\right) \qquad (0 < x < L)\,. \tag{11}$$
$$n = 1, 2, 3, \ldots$$

The functions $\Psi_n(x)$ form an orthonormal set (Integration domain from 0 to L).

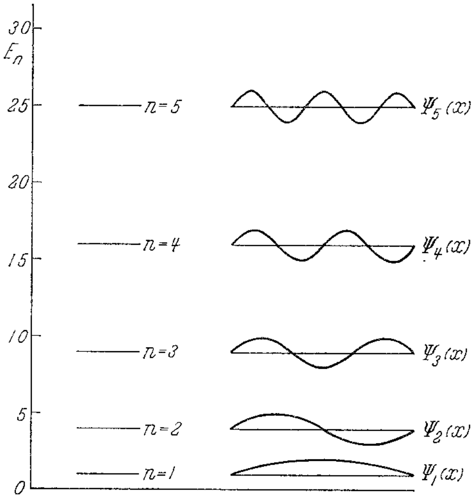

Fig. 1. "Electron-in-a-box"-model. (E_n in units of $\pi^2/2L^2$)

If the electron moves in a three-dimensional box of length, width and depth L_x, L_y, L_z, then by a simple extension of the previous arguments the following set of eigenvalues [corresponding to (9)] is obtained:

$$\begin{aligned} E_{n_x n_y n_z} &= E^{(x)}_{n_x} + E^{(y)}_{n_y} + E^{(z)}_{n_z} \\ &= \frac{h^2}{8\,m}\left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2\right] \\ n_x &= 1, 2, 3, \ldots;\; n_y = 1, 2, 3, \ldots;\; n_z = 1, 2, 3, \ldots \end{aligned} \tag{12}$$

Assuming that the "box" is a tetragonal prism with $L_y = L_z = L$ and $L_x = Z \cdot L$ where $Z > 1$, then the lowest M eigenvalues with

$$M < \sqrt{3} \cdot Z \tag{13}$$

depend on n_x only: $n_x = 1, 2, \ldots M$; $n_y = n_z = 1$. It is in this sense that the movement of an electron in an elongated, three-dimensional box may be treated as an essentially one-dimensional problem.

Note that all the energies E, E_n and $E_{n_x\,n_y\,n_z}$ [formulae (4), (9) and (12)] are purely the kinetic energy of the electron.

In LCAO molecular orbital models the space to which the electron is restricted is determined by the set of atomic orbitals ϕ_μ over which the linear combination

ψ extends

$$\psi = \sum_{\mu} c_{\mu}\, \phi_{\mu}\,. \tag{14}$$

The square of the coefficients, c_{μ}^{2} is a measure for the probability of finding the electron in the space spanned by ϕ_{μ} (or more precisely by ϕ_{μ}^{2}, assuming ϕ_{μ} to be a real function). The crossterms $2c_{\mu}c_{\nu}$ measures the probability of finding the electron in the overlap region $\phi_{\mu}\,\phi_{\nu}$.

We shall restrict our considerations to an LCAO–MO-model of the Wheland-type, that is to one in which the overlap integrals

$$S_{\mu\nu} = \langle \phi_{\mu} \mid \phi_{\nu} \rangle \tag{15}$$

are different from zero only for bound centers μ and ν.

$$\begin{aligned} S_{\mu\mu} &= 1 \text{ (normalized AO's)} \\ S_{\mu\nu} &= S \text{ (if } \mu \text{ bonded to } \nu;\ = 0 \text{ otherwise)}\,. \end{aligned} \tag{16}$$

Considering a chain of Z equally spaced AO's ϕ_{μ} one obtains under the above assumptions the following solutions to the corresponding eigenvalue-eigenvector problem:

$$\begin{aligned} \varepsilon_{J} &= (\alpha + x_{J}\beta)/(1 + S x_{J}) \\ J &= 1, 2, 3, \ldots, Z\,. \end{aligned} \tag{17}$$

In this expression the coefficients x_J are defined as

$$x_{J} = 2\cos\left(\frac{\pi J}{Z+1}\right); \qquad J = 1, 2, 3, \ldots, Z \tag{18}$$

and the parameters α and β have their usual meaning with respect to a model hamiltonian $\mathscr{H}$:

$$\alpha = \langle \phi_{\mu} \mid \mathscr{H} \mid \phi_{\mu} \rangle; \qquad \beta = \langle \phi_{\mu} \mid \mathscr{H} \mid \phi_{\nu} \rangle\,,\ \mu \text{ bonded to } \nu\,. \tag{19}$$

The linear combinations corresponding to the eigenvalues (17) are

$$\psi_{J} = \sqrt{\frac{2}{(J+1)(1 + x_{J} S)}} \cdot \sum_{\mu=1}^{Z} \sin\left(\frac{\pi J \mu}{Z+1}\right) \cdot \phi_{\mu}\,. \tag{20}$$

In the case of a purely linear system, the Wheland-model (neglecting overlaps between non bonded centers) may be used only if $S < \frac{1}{2} \cdot \cos\left(\frac{\pi}{Z+1}\right)$ [$\approx \frac{1}{2}$ if Z is large]. Otherwise the overlap matrix will be no longer positive definite and the results of the eigenvalue-eigenvector-problem relativ to $\mathscr{H}$ become meaningless.

Many textbooks point to the close analogy that exists between the functions $\Psi_{n}(x)$ for an electron in a one-dimensional "box" and the linear combinations ψ_J if $n = J$ [c.f. formulae (11) and (20)]. This analogy is emphasised in graphical representations in which both functions are superimposed, as shown in Fig. 2. From this, certain conclusions are either drawn explicitely or are at least tacitely implied by the graphical representations. The one we are going to investigate more closely concerns the kinetic energy of an electron in an LCAO–MO ψ_J of the type (20).

A change in sign between two consecutive coefficients $c_{J\mu}$ and $c_{J\mu+1}$ of ψ_J [formula (20)]

$$c_{J\mu} = \sqrt{\frac{2}{(Z+1)(1 + x_{J} S)}} \cdot \sin\left(\frac{\pi J \mu}{Z+1}\right); \ \psi_{J} = \sum_{\mu=1}^{Z} c_{J\mu}\, \phi_{\mu} \tag{21}$$

corresponds to a node in ψ_J. For linear systems the number of nodes in ψ_J is $J-1$ that is the same number as in the "electron-in-a-box"-wave function $\Psi_n(x)$ [formula (11)] with $n=J$. If the length of the space spanned by the linear combination (14) and therefore by ψ_J is l, then we may associate with each wave function (linear combination) ψ_J a "wave length" λ, in the same sense we did for the "electron-in-a-box":

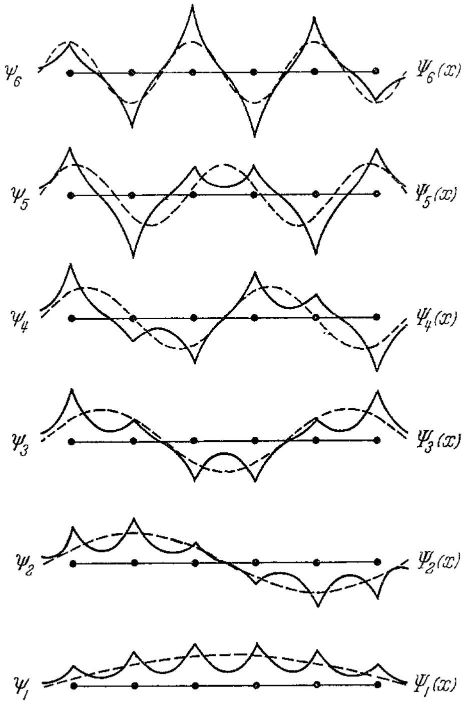

Fig. 2. Comparison of the "electron-in-a-box"-wavefunction $\Psi_n(x)$ with the corresponding LCAO–MOs ψ_J ($Z=6$)

$$\begin{array}{lccr} & \text{“Electron-in-a-box”} & \text{LCAO–MO (Wheland)} & \\ \text{Wave fct.} & \Psi_n(x) & \psi_J=\sum_\mu c_{J\mu}\,\phi_\mu & \\ \text{nodes; length} & n-1;\,L & J-1;\,l & (22) \\ \text{wave-length} & \Lambda=\dfrac{2L}{n} & \lambda=\dfrac{2l}{J}\,. & \end{array}$$

This means that a periodicity λ can be associtated with each LCAO–MO ψ_J of a linear system and we may have the tendency to think of it as a sort of deBroglie wave length. This is in fact what Fig. 2 tries to suggest (wrongly as we shall see!).

The kinetic energy T_J of an electron in the orbital ψ_J can be split into the components

$$T_J = T_{Jx} + T_{Jy} + T_{Jz}\,, \tag{23}$$

x referring to the long axis of the system as in the analogous threedimensional "box" model discussed previously. As a corrollary to (22), and by an intuitive extension of the results quoted under (12) and (13), we would expect that the

x-component T_{Jx} of the kinetic energy for an electron in the orbital ψ_J is given — at least in a first approximation — by the expression (24):

$$T'_{Jx} = \frac{h^2}{8\,m\,l^2} \cdot J^2 \,. \tag{24}$$

T'_{Jy} and T'_{Jz} should be independent of J, if we assume that relation (13) still holds. (The length l of our system is proportional to Z and the maximum value of $J = Z$). Primed values refer to the "guess" suggested by the comparison (22). From (24) follows that

a) T'_{Jx} is proportional to J^2 for a system of fixed number (Z) of AOs (and therefore of fixed length l), and that

b) T'_{Jx} decreases for fixed values of J with increasing length l, proportional to $\frac{1}{l^2}$.

More precisely, if l is of the general form $l = a + bZ$ [see later; formula (36)], then $T'_{Jx} \sim (a + bZ)^{-2}$ or:

$$(T'_{Jx})^{\frac{1}{2}} \sim J/(a + bZ) \tag{25}$$

and

$$(T'_{Jx})^{-\frac{1}{2}} \sim (a/J) + (b/J)\cdot Z \,. \tag{26}$$

This expected behaviour of T_{Jx} is represented schematically in Figs. 3 and 4, where we have chosen the constants $a = b = 1$. Note that under these assumptions the kinetic energy component $T'_{\frac{Z+1}{2}x}$ of the orbital $\psi_{\frac{Z+1}{2}}$ (Z = odd) is independent of Z, according to (24). Conclusion a) is in strong qualitative contradiction to what would be expected on the basis of the virial theorem, according to which T_J and therefore T_{Jx} should decrease with increasing J. However, the assumption of linear combinations ψ_J with fixed basis functions ϕ_μ (i.e. with constant orbital exponent ζ) presupposes a rather particular type of potential, which deviates considerably from a potential which is simply the sum of Coulomb terms.

We shall now show that these conclusions suggested by the seemingly close analogy between the "electron-in-a-box" model and the LCAO–MO-model are not valid and that the periodicity λ defined for the latter can not be identified even qualitatively with the deBroglie wave-length Λ.

For simplicity we are going to use $1s$-type AOs ϕ_μ as basis functions in the linear combinations (14) and (20).

$$\phi_\mu = (1s)_\mu = \frac{1}{\sqrt{\pi}} \exp(-\zeta\, r_\mu) = \frac{1}{\sqrt{\pi}}\, e^{-\varrho_\mu} \tag{27}$$

r_μ is the distance from the electron to the center μ, ζ is the orbital exponent and $\varrho_\mu = \zeta \cdot r_\mu$. The kinetic energy (in atomic units) associated with an electron in ϕ_μ is given by

$$T_\mu = \frac{\xi^2}{2} \,. \tag{28}$$

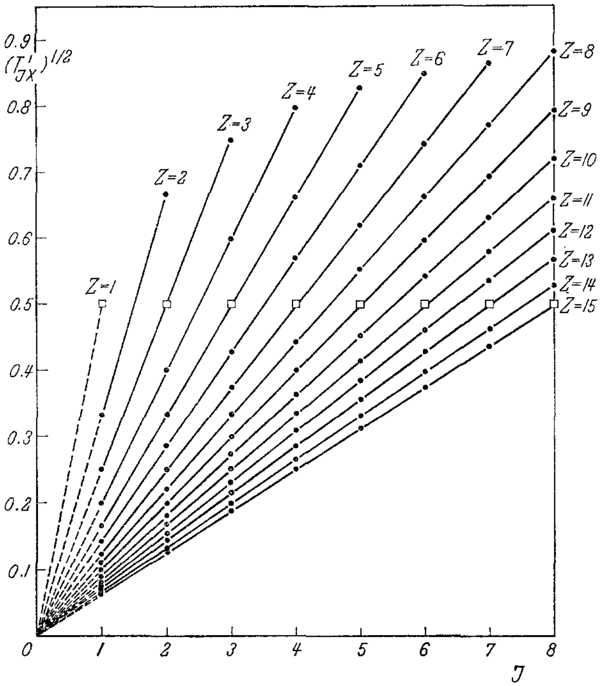

Fig. 3

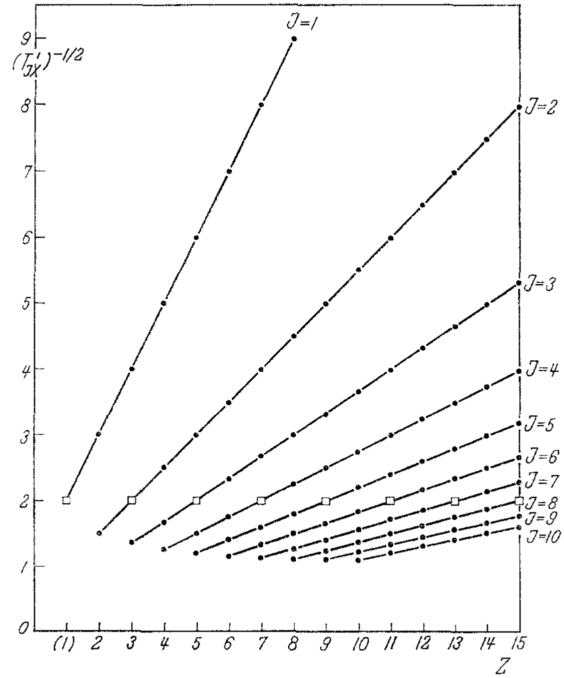

Fig. 4

Figs. 3 and 4. Expected behaviour of the kinetic energy component T_{Jx} of an electron in a LCAO-MO ψ_J of 1s AOs, according to the comparison (22). $(T'_{Jx})^{\frac{1}{2}}$ and $(T'_{Jx})^{-\frac{1}{2}}$ calculated from (25) and (26) with $a = b = 1$. (□ = Values for $J = (Z + 1)/2$ when Z = odd)

According to (12) the same energy would be that of an electron in a cubic box ($L_x = L_y = L_z = L$) of length

$$L = \frac{\pi \cdot \sqrt{3}}{\xi} = \frac{5.4}{\xi}\,\text{a. u.} \tag{29}$$

The kinetic energy T_J associated with the orbital ψ_J (20) is calculated from (30) where $\vec{T}$ is the kinetic energy operator

$$T_J = \langle \psi_J \mid \vec{T} \mid \psi_J \rangle \tag{30}$$

$\vec{T}$ can be written as the sum of the operators corresponding to the components T_{Jx}, T_{Jy}, T_{Jz} of T_J

$$\vec{T} = \vec{T}_x + \vec{T}_y + \vec{T}_z \,. \tag{31}$$

Inserting (20), (28) and (31) into (30) we obtain:

$$T_{Jx} = (\zeta^2/6 + x_J\, T_{\mu\nu,x})/(1 + x_J S) \tag{32}$$

$$T_{Jy} = T_{Jz}\,(\zeta^2/6 + x_J\, T_{\mu\nu,y})/(1 + x_J S)\,. \tag{33}$$

S is defined according to (15) and (16), x_J is given by (18) and $T_{\mu\nu,x}$, $T_{\mu\nu,y} = T_{\mu\nu,z}$ are the kinetic energy corrections associated with the overlap region $\varphi_\mu\,\varphi_\nu$ of bonded centers:

$$T_{\mu\nu,x} = \langle \phi_\mu \mid \vec{T}_x \mid \phi_\nu \rangle \tag{34}$$

$$T_{\mu\nu,y} = T_{\mu\nu,z} = \langle \phi_\mu \mid \vec{T}_y \mid \phi_\nu \rangle = \langle \phi_\mu \mid \vec{T}_z \mid \phi_\nu \rangle\,. \tag{35}$$

These integrals, computed by numerical methods are given in the appendix (Tab. 2, Fig. 7). Note that these corrections can be negative.

In Tab. 1 and in Fig. 5, 6 we show the results obtained for chains of Z $1s$-AOs (27) equally spaced at distances l_0 such that the overlap between nearest neighbours is $S = 0.25$. This is a value close to the one found for neighbouring $2p$-AOs in π-electron systems and one for which the Wheland scheme (16) is a satisfactory approximation. (For $\zeta = 1$ this would correspond to a bond length $l_0 = 3.56$ a.u.)

Comparing Figs. 3 and 4 with Figs. 5 and 6 it is immediately apparent that certain aspects of the dependence of the kinetic energy components calculated according to (32) and (33) are in serious disagreement with the expectations based on the intuitive "electron-in-a-box" analogy.

$T_{Jy} = T_{Jz}$ depend markedly on J, increasing with increasing values of J. The absolute change in T_{Jy} (or T_{Jz}) going from T_{1y} to T_{2y} is roughly $\frac{1}{4}$ of the corresponding change in the x component T_{Jx}, so that $T_{Jy} + T_{Jz}$ contribute about $\frac{1}{3}$ to the total change in kinetic energy when going from $J = 1$ to $J = Z$. From the box model we would have expected no change in T_{Jy} and T_{Jz}, the increase in the kinetic energy being absorbed in its totality in the x-component (13).

A comparison of Figs. 3 and 5 shows that for the "inner" orbitals (i.e. those which yield orbital energies ε_J nearest to α), the dependence of $(T_{Jx})^{\frac{1}{2}}$ on J, as obtained from (25) and (32), is qualitatively the same. Also for systems with Z = odd the component $T_{\frac{Z+1}{2}x}$ associated with the MO $\psi_{\frac{Z+1}{2}}$ is again a constant. However, the limiting values T_{1x} and T_{2x} converge for $Z \to \infty$ to limits which are quite different from those expected for the box model: T_{1x} ($Z \to \infty$) does not go to zero and T_{Zx} ($Z \to \infty$) converges to a much lower value than expected.

Table 1. *Kinetic energy components* T_{Jx}, T_{Jy} *and* T_{Jz} *associated with a* LCAO–MO ψ_J *of* 1s − *AOs*

Wheland approximation with $S = \frac{1}{4}$ for nearest neighbours

Z	J	T_{Jx}	$T_{Jy} = T_{Jz}$	T_J
2	1	0.10256	0.15064	0.40384
	2	0.27350	0.19338	0.66026
3	1	0.08295	0.14573	0.37441
	2	0.16667	0.16667	0.50000
	3	0.34196	0.21050	0.76295
4	1	0.07436	0.14358	0.36152
	2	0.12377	0.15594	0.43565
	3	0.22524	0.18131	0.58786
	4	0.38438	0.22111	0.82660
5	1	0.06982	0.14245	0.35471
	2	0.10256	0.15064	0.40384
	3	0.16667	0.16667	0.50000
	4	0.27350	0.19338	0.66026
	5	0.41144	0.22788	0.86719
6	1	0.06712	0.14177	0.35067
	2	0.09049	0.14762	0.38573
	3	0.13458	0.15864	0.45186
	4	0.20679	0.17670	0.56019
	5	0.31184	0.20297	0.71777
	6	0.42941	0.23237	0.89415
7	1	0.06539	0.14134	0.34807
	2	0.08295	0.14573	0.37441
	3	0.11519	0.15379	0.42277
	4	0.16667	0.16667	0.50000
	5	0.24250	0.18563	0.61376
	6	0.34196	0.21050	0.76295
	7	0.44183	0.23548	0.91278
8	1	0.06421	0.14104	0.34630
	2	0.07790	0.14447	0.36684
	3	0.10256	0.15064	0.40384
	4	0.14106	0.16026	0.46158
	5	0.19714	0.17429	0.54571
	6	0.27350	0.19338	0.66026
	7	0.36564	0.21642	0.79848
	8	0.45072	0.23770	0.92610
9	1	0.06337	0.14083	0.34504
	2	0.07436	0.14358	0.36152
	3	0.09386	0.14846	0.39079
	4	0.12377	0.15594	0.43565
	5	0.16667	0.16667	0.50000
	6	0.22524	0.18131	0.58786
	7	0.30007	0.20002	0.70011
	8	0.38438	0.22111	0.82660
	9	0.45727	0.23934	0.93593

Table 1 (Continued)

Z	J	T_{Jx}	$T_{Jy} = T_{Jz}$	T_J
10	1	0.06275	0.14068	0.34412
	2	0.07177	0.14293	0.35764
	3	0.08761	0.14689	0.38140
	4	0.11154	0.15288	0.41730
	5	0.14537	0.16134	0.46806
	6	0.19122	0.17281	0.53683
	7	0.25069	0.18768	0.62604
	8	0.32270	0.20568	0.73407
	9	0.39936	0.22485	0.84906
	10	0.46222	0.24057	0.94336
11	1	0.06228	0.14056	0.34341
	2	0.06982	0.14245	0.35471
	3	0.08295	0.14573	0.37441
	4	0.10256	0.15064	0.40384
	5	0.12994	0.15748	0.44490
	6	0.16667	0.16667	0.50000
	7	0.21431	0.17858	0.57146
	8	0.27350	0.19338	0.66026
	9	0.34196	0.21050	0.76295
	10	0.41144	0.22788	0.86719
	11	0.46605	0.24153	0.94911
12	1	0.06192	0.14047	0.34286
	2	0.06831	0.14207	0.35245
	3	0.07938	0.14484	0.36906
	4	0.09577	0.14894	0.39364
	5	0.11840	0.15459	0.42759
	6	0.14845	0.16211	0.47267
	7	0.18722	0.17181	0.53083
	8	0.23574	0.18394	0.60361
	9	0.29381	0.19846	0.69073
	10	0.35836	0.21460	0.78756
	11	0.42130	0.23034	0.88197
	12	0.46907	0.24229	0.95364
13	1	0.06163	0.14040	0.34243
	2	0.06712	0.14177	0.35067
	3	0.07659	0.14414	0.36487
	4	0.09049	0.14762	0.38573
	5	0.10953	0.15238	0.41428
	6	0.13458	0.15864	0.45186
	7	0.16667	0.16667	0.50000
	8	0.20679	0.17670	0.56019
	9	0.25546	0.18887	0.63320
	10	0.31184	0.20297	0.71777
	11	0.37237	0.21811	0.80858
	12	0.42941	0.23237	0.89415
	13	0.47150	0.24289	0.95728
14	1	0.06140	0.14034	0.34208
	2	0.06617	0.14153	0.34924
	3	0.07436	0.14358	0.36152

Table 1 (Continued)

Z	J	T_{Jx}	$T_{Jy} = T_{Jz}$	T_J
	4	0.08632	0.14657	0.37946
	5	0.10256	0.15064	0.40384
	6	0.12377	0.15594	0.43565
	7	0.15075	0.16268	0.47611
	8	0.18434	0.17108	0.52651
	9	0.22524	0.18131	0.58786
	10	0.27350	0.19338	0.66026
	11	0.32781	0.20696	0.74173
	12	0.38438	0.22111	0.82660
	13	0.43617	0.23406	0.90428
	14	0.47347	0.24339	0.96023
15	1	0.06121	0.14029	0.34179
	2	0.06539	0.14134	0.34807
	3	0.07255	0.14313	0.35881
	4	0.08295	0.14573	0.37441
	5	0.09699	0.14924	0.39547
	6	0.11519	0.15379	0.42277
	7	0.13818	0.15954	0.45726
	8	0.16667	0.16667	0.50000
	9	0.20131	0.17533	0.55196
	10	0.24250	0.18563	0.61376
	11	0.28994	0.19749	0.68492
	12	0.34196	0.21050	0.76295
	13	0.39472	0.22370	0.84211
	14	0.44183	0.23548	0.91278
	15	0.47509	0.24379	0.96267

This is brought out more dramatically in Fig. 6 which clearly shows the strong deviation from linearity of the plot of $(T_{Jx})^{-\frac{1}{2}}$ vs. Z. As a matter of fact the curves for fixed J do not even diverge if Z goes to infinity, but converge to a finite limit. This means that the "wave length" λ – in sharp contrast to the deBroglie periodicity Λ – can go to infinity without the corresponding energy component T_{Jx} going to zero. Furthermore the kinetic energy T_{Jx} is not even linked in a unique way to λ, as it is quite easy to pick two orbitals from two systems with differing Z such that $2l/J = \lambda$ is the same for both orbitals which will nevertheless exhibit different kinetic energy components T_{Jx}.

It follows that the analogy suggested by graphical representations such as that shown in Fig. 2, or more explicitely by the comparison (22) are misleading. One cannot compare λ to the periodicity Λ of a corresponding "electron-in-a-box"-model.

If l_0 is the distance between two consecutive centers, the length l of the system is

$$l = (Z - 1)\, l_0 + k \tag{36}$$

where k is a correction which allows for the "overshooting" of the electron beyond the centers 1 and Z. We can construct an "electron-in-a-box" model with $L_x = l$ which will yield a constant value $E_{\frac{Z+1}{2}}$, independent of Z, if $k = 2l_0$ so that

Table 2. *Kinetic energy corrections (34) and (35) associated with the overlap region of bonded* 1*s*-AOs ϕ_μ, ϕ_ν

ζl_0	$\zeta^{-2}\, T_{\mu\nu,x}$ $= \zeta^{-2}\, \langle \mu \mid \vec{T}_x \mid \nu \rangle$	$\zeta^{-2}\, T_{\mu\nu,\, y} = \zeta^{-2}\, T_{\mu\nu,z}$ $= \zeta^{-2}\, \langle \mu \mid \vec{T}_y \mid \nu \rangle$	$\zeta^{-2}\, T_{\mu\nu}$ $= \zeta^{-2}\, \langle \mu \mid \vec{T} \mid \nu \rangle$
0.0	0.16667	0.16667	0.50000
0.1	0.16435	0.16589	0.49615
0.2	0.15828	0.16375	0.48578
0.3	0.14937	0.16052	0.47041
0.4	0.13849	0.15643	0.45134
0.5	0.12629	0.15167	0.42962
0.6	0.11334	0.14639	0.40612
0.7	0.10004	0.14075	0.38154
0.8	0.08673	0.13487	0.35646
0.9	0.07385	0.12875	0.33135
1.0	0.06130	0.12263	0.30656
1.1	0.04936	0.11651	0.28238
1.2	0.03814	0.11044	0.25902
1.3	0.02770	0.10447	0.23664
1.4	0.01807	0.09865	0.21536
1.5	0.00928	0.09298	0.19523
1.6	0.00133	0.08750	0.17632
1.7	−0.00580	0.08222	0.15863
1.8	−0.01215	0.07715	0.14215
1.9	−0.01772	0.07230	0.12688
2.0	−0.02258	0.06768	0.11277
2.1	−0.02676	0.06328	0.09980
2.2	−0.03031	0.05911	0.08790
2.3	−0.03327	0.05515	0.07703
2.4	−0.03570	0.05142	0.06713
2.5	−0.03764	0.04789	0.05814
2.6	−0.03914	0.04458	0.05001
2.7	−0.04024	0.04146	0.04267
2.8	−0.04097	0.03853	0.03608
2.9	−0.04138	0.03578	0.03017
3.0	−0.04150	0.03320	0.02489
3.1	−0.04138	0.03079	0.02019
3.2	−0.04106	0.02855	0.01603
3.3	−0.04053	0.02644	0.01235
3.4	−0.03984	0.02448	0.00912
3.5	−0.03903	0.02266	0.00629
3.6	−0.03808	0.02095	0.00382
3.7	−0.03707	0.01938	0.00168
3.8	−0.03596	0.01791	−0.00014
3.9	−0.03479	0.01654	−0.00172
4.0	−0.03360	0.01528	−0.00305
4.1	−0.03236	0.01410	−0.00417
4.2	−0.03110	0.01301	−0.00509
4.3	−0.02984	0.01200	−0.00585
4.4	−0.02858	0.01106	−0.00646
4.5	−0.02732	0.01019	−0.00694
4.6	−0.02609	0.00940	−0.00730
4.7	−0.02485	0.00865	−0.00756
4.8	−0.02366	0.00797	−0.00773
4.9	−0.02249	0.00733	−0.00783
5.0	−0.02135	0.00675	−0.00786

ζ = Orbital exponent in 1*s*-AO (27). l_0 = Distance between centers μ and ν in a.u. Energy of $\zeta^{-2}\, T_{\mu\nu,x}$, $\zeta^{-2}\, T_{\mu\nu,y} = \zeta^{-2}\, T_{\mu\nu,z}$ and $\zeta^{-2}\, T_{\mu\nu} = \zeta^{-2}\, T_{\mu\nu,x} + 2\, \zeta^{-2} T_{\mu\nu,y}$ in atomic units.

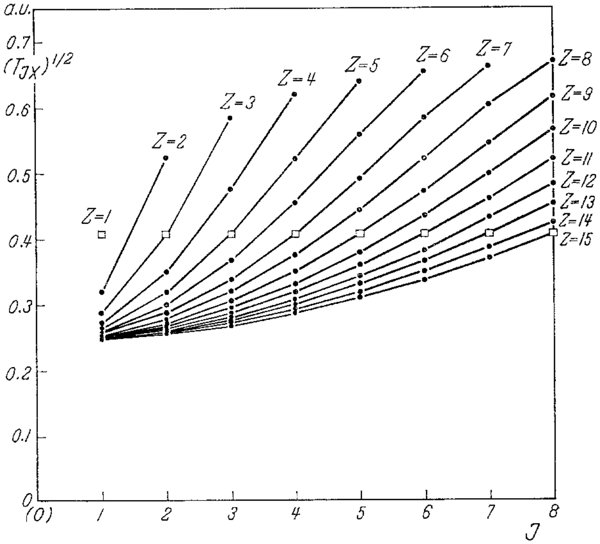

Fig. 5

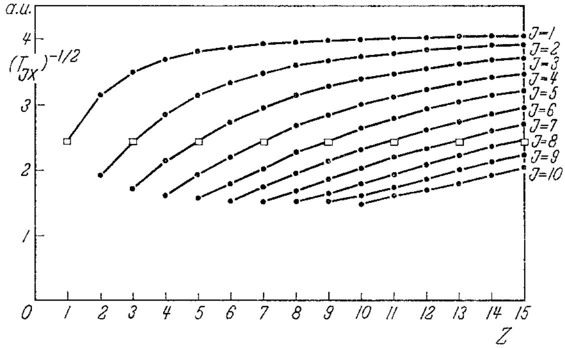

Fig. 6

Figs. 5 and 6. Behaviour of the kinetic energy component T_{Jx} of an electron in a LCAO–MO ψ_J of 1*s* AOs, according to (32). T_{Jx} calculated with an overlap $S = 0.25$ and $T_{\mu v,x} = -0.03845$ a.u. (see Tab. 2

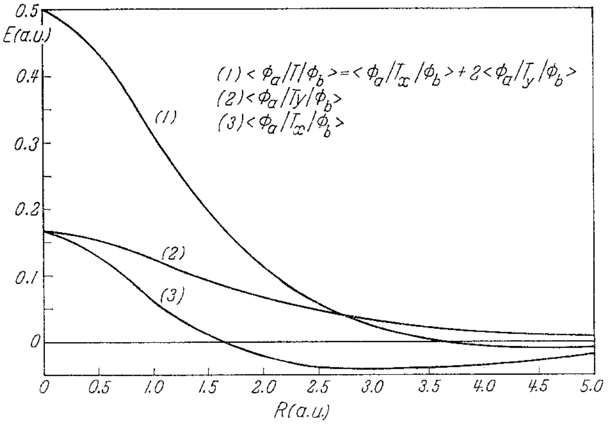

Fig. 7. Kinetic energy corrections $T_{\mu v,x}$ (34), $T_{\mu v,y} = T_{\mu v,z}$ (35) and $T_{\mu v} = T_{\mu v,x} + 2T_{\mu v,y}$ for 1*s* AOs (27). Energy for interatomic distance $d = \zeta l_0$ in units of ζ^2 a.u.

expression (36) becomes $l = l_0(1 + Z)$. If we set $E_{\frac{Z+1}{2}} = \frac{1}{6}$ a.u., to make it identical with $T_{\frac{Z+1}{2}x}$ of the non bonding MOs $\psi_{\frac{Z+1}{2}}$ (Z = odd), we find that $l_0 = 2.72$ a.u., which would correspond to an LCAO model of $1s$-AOs having an overlap $S = 0.4$ between bonded centers. Note that according to (33) the kinetic energy for non bonding MOs is independent of the value of S.

Appendix

Computation of the kinetic energy compounts $T_{\mu\nu,x}$ and $T_{\mu\nu,y} = T_{\mu\nu,z}$ for $1s$ AOs [c.f. (34); (35)].

The distance between two bonded $1s$-AOs (27) of orbital exponent ζ is l_0. Setting $l_0\,\zeta = R$ we obtain in atomic units:

$$[\mu = (\varrho_\mu + \varrho_\nu)/R, \qquad \nu = (\varrho_\mu - \varrho_\nu)/R]$$

$$\langle\mu \mid \vec{T}_x \mid \nu\rangle = R^2\,\zeta^2/8\,\pi \int\limits_{\mu=1}^{\infty}\int\limits_{\nu=-1}^{+1}\int\limits_{\varphi=0}^{2\pi} e^{-R\mu}\left\{(\mu + \nu) - \frac{(\mu + \nu)\,(\mu\nu - 1)^2}{(\mu - \nu)^2} - \frac{R(\mu + \nu)\,(\mu\nu - 1)^2}{2(\mu - \nu)}\right\} d\mu\,d\nu\,d\varphi \tag{37}$$

$$\langle\mu \mid \vec{T}_y \mid \nu\rangle = R^2\,\zeta^2/8\,\pi \int\limits_{\mu=1}^{\infty}\int\limits_{\nu=-1}^{+1}\int\limits_{\varphi=0}^{2\pi} e^{-R\mu}\left\{(\mu + \nu) - \frac{(\mu + \nu)\,(\mu^2 - 1)\,(1 - \nu^2)\cos^2\varphi}{(\mu - \nu)^2} - \frac{R(\mu + \nu)\,(\mu^2 - 1)\,(1 - \nu^2)\cos^2\varphi}{2(\mu - \nu)}\right\} d\mu\,d\nu\,d\varphi\,. \tag{38}$$

Partial integration over ν and φ yields

$$T_{\mu\nu,x} = \langle\mu \mid \vec{T}_x \mid \nu\rangle = [e^{-R}\,(-R^2/6 + R/6 - \tfrac{5}{6} - 3/R - 3/R^2) + A]\,\zeta^2 \tag{39}$$

$$T_{\mu\nu,y} = \langle\mu \mid \vec{T}_y \mid \nu\rangle = [e^{-R}\,(R/6 + \tfrac{2}{3} + 3/2R + 3/2R^2) - A/2]\,\zeta^2 \tag{40}$$

$$T_{\mu\nu} = T_{\mu\nu,x} + 2\,T_{\mu\nu,y} = [e^{-R}\,(-R^2/6 + R/2 + \tfrac{1}{2})]\,\zeta^2\,. \tag{41}$$

A stands for the integral

$$A = R^2/4\int\limits_{1}^{\infty} e^{-R\mu}\log\frac{(\mu + 1)}{(\mu - 1)}\,[-R\mu^5 + 5\mu^4 + 2\,R\mu^3 - 6\mu^2 - R\mu + 1]\,d\mu \tag{42}$$

which has to be integrated numerically. The results for the integrals (39) to (41) in the interval $R = 0$ to 5 a.u. are shown in Tab. 2 and Fig. 7.

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