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Invited Review

Today's View of the Chemical Bond

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Summary. The chemical bond is a stabilization of a system with a characteristic nuclear configuration, electronic structure, and a set of physico-chemical properties. The physical origin of the chemical bond lies in an acceleration of the electrons by a joint potential of several nuclei. The quantitative description of the chemical bond in the dihydrogen molecule can be treated within the MO or VB method. Both of them have some intrinsic drawbacks which can be overcome when the MO method is followed by the configuration interaction, and the limited VB method by its complete counterpart that includes the "ionic structures". In the end, both results are equivalent as they include the correlation energy. The amplitudes of the two-electron wave functions show that the maximum probability is obtained when the electrons are correlated – kept apart at the individual centers. This condition is very natural for the limited VB; it includes a part of the correlation energy. Therefore the VB method is a better reference for the evaluation of the exchange coupling constant that separates the ground singlet state from the lowest triplet one.

Keywords. Chemical bond; Molecular orbital method; Valence bond method; Configuration interaction; Electron density.

Introduction

The ambition of the present communication is to bring a review of basic formulae for the energies of the lowest energy states in the prototypal molecule of the chemical bond – the dihydrogen molecule and the related molecular cation and anion.

The project involves hand, but *ab initio* calculations at different levels of sophistication: the simple molecular orbital (MO) method, the limited valence bond (LVB) method, the MO method improved by the configuration interaction (MO + CI), and finally, the complete VB (CVB) method. Each of these stages

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results in some energy formulae in which integrals over the basis set functions (the atomic 1s orbitals) occur.

However, these formulae are method-dependent and bring little insight into the physical nature of the chemical bond [1–22]. In no case it could be concluded that the chemical bond results as a consequence of the exchange integral; such an integral is absent in the dihydrogen cation which is bound by the chemical bond either. Within the MO method the sign of the hybrid integral plays a key role in stabilisation of the ground state of the dihydrogen molecule. The only correct statement is that the chemical bond appears as a consequence of the acceleration of electrons by a joint potential of several nuclei – the result following from the application of the virial theorem.

Both, the MO and the LVB methods, possess some intrinsic defects. We will see that the MO method involves the "valence structures" and the "ionic structures" with the same weight whereas the LVB ignores the "ionic structures" completely. The results of the MO + CI method and the CVB method are exactly the same: they involve the maximum correlation energy in the given basis set. The impact of the electron correlation is not only in the improvement of the energy of the ground state. It has a serious consequence in the amplitude of the two-electron wave function: this show a maximum probability when the electrons are correlated – kept apart at the individual centers.

The Virial Theorem

The kinetic energy operator and the potential energy operator in atoms and molecules have a definite form. This fact implies that a relationship between the mean values of the kinetic energy and the potential energy exists. The relationship is fulfilled for the exact wave function as well as for the best trial wave function in terms of the variation principle. We will derive that the virial ratio in atoms and in equilibrium geometry of molecules is exactly $v = \langle V\rangle/\langle T\rangle = -2$ (atomic units are used throughout this chapter).

Let $\Psi(r_1, \ldots, r_n)$ be an n-electron wave function yielding the mean value described by Eq. (1).

$$\langle A\rangle = \langle\Psi|\hat{A}|\Psi\rangle = \int\cdots\int \Psi^*(r_1,\ldots,r_n)\hat{A}\Psi(r_1,\ldots,r_n)\mathrm{d}r_1\cdots\mathrm{d}r_n \qquad (1)$$

Now we introduce a scaling factor, s, which stretches all coordinates uniformly; thus we have the scaled wave function $\Psi_s(sr_1,\ldots,sr_n)$ which gives the following mean value (Eq. (2)).

$$\langle A_s\rangle = \langle\Psi_s|\hat{A}|\Psi_s\rangle = \int\ldots\int \Psi^*(sr_1,\ldots,sr_n)\hat{A}\Psi(sr_1,\ldots,sr_n)\mathrm{d}(sr_1)\cdots\mathrm{d}(sr_n) \qquad (2)$$

This relationship can be modified as follows in Eq. (3).

$$\langle A_s\rangle = s^m\int\cdots\int \Psi^*(sr_1,\ldots,sr_n)[s^{-m}\hat{A}(r_1,\ldots,r_n)]\Psi(sr_1,\ldots,sr_n)\mathrm{d}(sr_1)\ldots\mathrm{d}(sr_n) \qquad (3)$$

Let us assume that our operator obeys the following relationship (Eq. (4)).

$$s^{-m}\hat{A}(r_1,\ldots,r_n) = \hat{A}_s(sr_1,\ldots,sr_n) \qquad (4)$$

Then the mean values in scaled and unscaled coordinates interrelate as shown in Eq. (5) where we utilize a property that the scaling leaves the integration limits $(-\infty, +\infty)$ unaffected.

$$\langle A_s \rangle = s^m \langle \Psi_s | \hat{A} | \Psi_s \rangle = s^m \langle A \rangle \tag{5}$$

The fulfillment of the scaling hypothesis should be examined for every operator separately. As a result of the analysis, the power m results.

In an n-electron atom the kinetic energy operator (expressed in polar coordinates) has the form shown in Eq. (6).

$$\hat{T}(r) = (-1/2) \sum_i^n \frac{1}{r_i^2} \frac{\mathrm{d}}{\mathrm{d}r_i} \left(r_i^2 \frac{\mathrm{d}}{\mathrm{d}r_i} \right) + (-1/2) \sum_i^n \left[\frac{1}{r_i^2} \nabla_i^2(\theta_i, \varphi_i) \right] \tag{6}$$

The scaled kinetic energy operator, from simple algebra, is given by Eq. (7) so that we arrive at $m = 2$. The potential energy operator is described by Eq. (8).

$$\hat{T}(sr) = s^{-2} \hat{T}(r) \tag{7}$$

$$\hat{V}(r) = -\sum_i^n \frac{Z_i}{r_i} + \sum_{i<j}^n \frac{1}{r_{ij}} \tag{8}$$

The scaled potential energy operator obeys the relationship shown in Eq. (9) giving rise to $m = 1$.

$$s^{-1} \hat{V}(r) = \hat{V}(sr) \tag{9}$$

On summary, the following relations hold true (Eqs. (10) and (11)) and the total energy of the atom becomes as given by Eq. (12).

$$\langle T_s \rangle = s^2 \langle T \rangle \tag{10}$$

$$\langle V_s \rangle = s \langle V \rangle \tag{11}$$

$$\langle E_s \rangle = \langle T_s \rangle + \langle V_s \rangle = s^2 \langle T \rangle + s \langle V \rangle \tag{12}$$

The total atomic energy is subject to variation with respect to the scaling factor s (Eq. (13)) and we arrived at the optimum value (Eq. (14)).

$$\frac{\partial \langle E_s \rangle}{\partial s} = 2s \langle T \rangle + \langle V \rangle = 0 \tag{13}$$

$$s_{\mathrm{opt}} = -\langle V \rangle / [2 \langle T \rangle] \tag{14}$$

If our trial wave function is already the optimum wave function, the scaling of coordinates is incapable of energy lowering. Then $s_{\mathrm{opt}} = 1$ applies and consequently the virial ratio (for atoms) is given by Eq. (15).

$$v = \frac{\langle V(s_{\mathrm{opt}}) \rangle}{\langle T(s_{\mathrm{opt}}) \rangle} = -2, \quad \text{[exactly]} \tag{15}$$

For a diatomic molecule the wave function includes an internuclear distance R in the role of a parameter (the *Born-Oppenheimer* approximation is utilized), so that we have $\Psi(r_1,\ldots,r_n;R)$ and its scaled counterpart $\Psi_s(sr_1,\ldots,sr_n;sR)$. Using a substitution of $t = sR$ we can write Eqs. (16)–(18).

$$\langle T_s\rangle = \langle T(s,t)\rangle = s^2\langle T(1,t)\rangle \tag{16}$$

$$\langle V_s\rangle = \langle V(s,t)\rangle = s\langle V(1,t)\rangle \tag{17}$$

$$\langle E_s\rangle = \langle T_s\rangle + \langle V_s\rangle = s^2\langle T(1,t)\rangle + s\langle V(1,t)\rangle \tag{18}$$

The variation of the total molecular energy brings Eq. (19).

$$\frac{\partial\langle E_s\rangle}{\partial s} = 2s\langle T(1,t)\rangle + \langle V(1,t)\rangle + s^2\frac{\partial\langle T(1,t)\rangle}{\partial s} + s\frac{\partial\langle V(1,t)\rangle}{\partial s} = 0 \tag{19}$$

This equation can be rewritten into the following form (Eq. (20)).

$$2s\langle T(1,t)\rangle + \langle V(1,t)\rangle + s^2R\frac{\partial\langle T(1,t)\rangle}{\partial t} + sR\frac{\partial\langle V(1,t)\rangle}{\partial t} = 0 \tag{20}$$

We utilized the identity (Eq. (21)) fulfilled for any function.

$$\frac{\partial}{\partial s}f(t) = \frac{\partial}{\partial t}\left(\frac{\partial t}{\partial s}\right)f(t) \tag{21}$$

In our case of $t = sR$ we get Eq. (22).

$$\frac{\partial}{\partial s}f(t) = R\frac{\partial}{\partial t}f(t) \tag{22}$$

Under the assumption that the wave function is already optimum, the scaling factor becomes $s_{\mathrm{opt}} = 1$. Collecting the kinetic and the potential energy terms into the total molecular energy (Eq. (23)) we finally get Eq. (24).

$$\frac{\partial\langle T(1,t)\rangle}{\partial t} + \frac{\partial\langle V(1,t)\rangle}{\partial t} = \frac{\partial\langle E(1,t)\rangle}{\partial t} = \frac{\partial\langle E\rangle}{\partial(s_{\mathrm{opt}}R)} = \frac{\partial\langle E\rangle}{\partial R} \tag{23}$$

$$2\langle T\rangle + \langle V\rangle + R\left(\frac{\partial\langle E\rangle}{\partial R}\right) = 0 \tag{24}$$

This is a form of the virial theorem for diatomic molecules. In the optimum geometry, however, the energy gradient vanishes and thus we arrive at the same expression for the virial ratio as for atoms.

For a diatomic molecule there is a problem of two variables: R (internuclear distance) and a (orbital exponent). For a fixed R there exists a value of $a_{\mathrm{opt}}(R)$ for which the virial equation is fulfilled. Only a single pair $\{a_{\mathrm{opt}}, R_0\}$ yields the virial ratio $v = -2$ (exactly). For different molecular states the $a_{\mathrm{opt}}(R)$ are different functions.

The Physical Nature of the Chemical Bond

A bound system is more stable relative to its constituents: it has a lower energy relative to the sum of the energies of the constituents so that the bonding energy is given by Eq. (25).

$$E_{\mathrm{b}} = \sum_i E_i(\text{constituents}) - E(\text{system}) > 0 \tag{25}$$

The chemical bond is the *raison d'être* of molecules whereas the intermolecular interactions are responsible for the existence of the condensed phase. Individual subsystems bound due to intermolecular interactions retain partially their chemical individuality and chemical properties.

Although the border between the systems stabilized by the chemical bond and the intermolecular interaction is not well established, the systems bound by the chemical bond, in general, possess much higher stabilization (binding) energy and the equilibrium separation appears at lower distances.

Balance of the Kinetic and Potential Energy

In atoms, the virial theorem implies that Eq. (26) is valid.

$$\langle E\rangle_{\mathrm{at}} = -\langle T\rangle_{\mathrm{at}} = \langle V\rangle_{\mathrm{at}}/2 \tag{26}$$

In the equilibrium geometry of a molecule, when $\partial\langle E\rangle/\partial R = 0$, the virial theorem adopts a similar form (Eq. (27)).

$$\langle E\rangle_{\mathrm{mol}} = -\langle T\rangle_{\mathrm{mol}} = \langle V\rangle_{\mathrm{mol}}/2 \tag{27}$$

Since the molecular binding energy is positive (Eq. (28)) the application of the virial theorem ends up in two conditions (Eqs. (29) and (30) or (31) and (32)).

$$E_{\mathrm{b}} = \langle E\rangle_{\mathrm{at}} - \langle E\rangle_{\mathrm{mol}} > 0 \tag{28}$$

$$-\langle T\rangle_{\mathrm{at}} > -\langle T\rangle_{\mathrm{mol}} \tag{29}$$

$$\langle V\rangle_{\mathrm{at}}/2 > \langle V\rangle_{\mathrm{mol}}/2 \tag{30}$$

$$\langle T\rangle_{\mathrm{mol}} > \langle T\rangle_{\mathrm{at}} \tag{31}$$

i.e., the kinetic energy increases upon formation of a molecule

$$\langle V\rangle_{\mathrm{mol}} < \langle V\rangle_{\mathrm{at}} \tag{32}$$

i.e., the potential energy decreases (becomes more negative).

This means that in any molecule: *the electrons are moving faster as they are accelerated by the increasing potential of several nuclei*. Such a situation applies only when the electrons are concentrated in the internuclear region.

The binding of a hydrogen molecule is $E_{\mathrm{b}}(\mathrm{H_2}) = 4.7\,\mathrm{eV}$. Using the statement of the virial theorem we arrive at Eqs. (33) and (34).

$$E_{\mathrm{b}} = -2\langle T(\mathrm{H})\rangle + \langle T(\mathrm{H_2})\rangle = 4.7\,\mathrm{eV} \tag{33}$$

$$E_{\mathrm{b}} = [2\langle V(\mathrm{H})\rangle - \langle V(\mathrm{H_2})\rangle]/2 = 4.7\,\mathrm{eV} \tag{34}$$

This means that the kinetic energy increased by 4.7 eV whereas the potential energy decreased by 9.4 eV. The potential energy of a molecule, however, includes the internuclear repulsion term V_{NN}, which is easily evaluated knowing the internuclear distance ($R_0 = 74.1\,\mathrm{pm}$): $V_{\mathrm{NN}}(R_0) = 19.4\,\mathrm{eV}$.

Energy Functions

Let us consider the molecular energy as a function of the number of electrons, N, and the external potential (the electron-nuclear attraction plus any other potential

Table 1. Derivatives of the electronic energy [23–25]

Order	Scalars (molecule characteristics)	Functions (site characteristics)
0	Energy $E = E[N, v(\vec{r})]$	
1	Chemical potential $\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})}$	Electron density $\rho(\vec{r}) = \left(\frac{\partial E}{\partial v(\vec{r})}\right)_N$; $\int \rho(\vec{r})\mathrm{d}\vec{r} = N$
2	Hardness $\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})}$ Softness $S = 1/\eta$	*Fukui* function $f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} = \left(\frac{\partial^2 E}{\partial v(\vec{r})\partial N}\right)$; $\int f(\vec{r})\mathrm{d}\vec{r} = 1$ Response function $\chi_1(\vec{r}, \vec{r}') = \left(\frac{\partial \rho(\vec{r})}{\partial v(\vec{r}')}\right)_N$

applied to the molecule), $v(\vec{r})$. Then it is legitimate to write Eq. (35) and a different degree of differentiation yields the energy functions as listed in Table 1.

$$E = E[N, v(\vec{r})] \tag{35}$$

A contemporary definition says that the *electronegativity* equals to the negative of the *chemical potential* of an electron: the resistance of the system (an atom or molecule) against the change of the number of electrons (*N*) (Eq. (36)).

$$\chi(A) = -\mu_\mathrm{e} = -\frac{\partial E(A)}{\partial N} \tag{36}$$

Such a differential definition does not allow a direct measurement since the number of electrons can alter only by discrete quanta.

Some theoretical arguments allow expressing the electronegativity in the form introduced by *Mulliken* (Eq. (37)) where the ionization energy, I_A, and the electron affinity, A_A, occurs (a recommended sign convention of the electron affinity is applied: this is positive for the energy given to the system).

$$\chi(A) = \frac{I_A - A_A}{2} + O_3 \tag{37}$$

Table 2. Some electronegativity scales

Type	Key formula
1. *Pauling*	$\lvert\chi_A - \chi_B\rvert = C[E_{A-B} - (E_{A-A}E_{B-B})^{1/2}]^{1/2}$; $\chi_\mathrm{H} = 2.1$ – origin of the scale; E_{A-B} – bond dissociation energy
2. *Mulliken*	$\chi_A = \frac{I_A - A_A}{2}$; I_A – ionisation energy; A_A – electron affinity defined as a supplied energy
3. *Allred-Rochow*	$\chi_A = a\frac{Z_{\mathrm{eff},A}}{r^2_{\mathrm{cov},A}} + b$; $Z_{\mathrm{eff},A}$ – effective nuclear charge according to *Slater* rules; $r_{\mathrm{cov},A}$ – covalent radius
4. *Gordy*	$\chi_A = a\frac{Z_{\mathrm{eff},A}}{r_{\mathrm{cov},A}} + b$
5. *Sanderson*	$\chi_A = \frac{D_A}{D_{\mathrm{interpol},A}}$, $D = a\frac{Z_{\mathrm{eff},A}}{r^3_{\mathrm{cov},A}}$

However, some other definitions (or scales) are available among which the *Pauling* and the *Allred-Rochow* definition are well known (Table 2).

Electronegativity expresses the ability of the system to attract its electrons and thus the lower the electronegativity the greater the amplitude of electrons and consequently the higher their mobility, and *vice versa*. Therefore the electronegativity is helpful in explaining differences between different types of chemical bond.

Types of the Chemical Bond

There are three principal kinds of chemical bond: the covalent, metallic, and the ionic bond (Table 3) whose key features are shortly reviewed.

1) When the electronegativity of both bonding partners is high, the *covalent bond* is formed (like in H_2O and $H_2C{=}CH_2$):
    a) the bonding electrons tend to be localized in the direction of the atomic linkage;
    b) in addition to the single bond, multiple bonds with the nodal structure (π and δ) also appear;
    c) a saturation property means that only a limited number of bonds are formed (*e.g.* the carbon atom has a maximum of four).
2) When the electronegativity of both bonding partners is low, the *metallic bond* is formed (like in metallic Al):
    a) the electrons possess a high mobility and are shared by a whole solid which allows us to speak about an electron gas;
    b) the bond is delocalised over a number of centers and has no saturation property.
3) When the bonding partners differ in their electronegativities substantially, the *ionic bond* is formed (like in NaCl):
    a) it has neither the directional nature nor the nodal structure;
    b) it does not depend upon the quality of the ions since the cohesive forces are the *Coulomb* interactions among ions;
    c) it does not possess a saturation property.

Table 3. Characteristic features of the individual types of the chemical bond

Covalent bond	Metallic bond	Ionic bond
High electronegativity of the bonding partners	Low electronegativity of the bonding partners	Different electronegativity of the bonding partners
Saturation property	No saturation	No saturation
Directional, almost localized	Delocalized	No directional
Multiplicity		No multiple bonds
Nodal structure		No nodal structure
Strong overlap of atomic wave functions	Strong overlap of atomic wave functions	Low overlap of atomic wave functions
Low amplitude and low mobility of electrons (insulators)	High amplitude and high mobility of electrons (conductors, electron gas)	Low amplitude and no mobility of electrons (insulators)

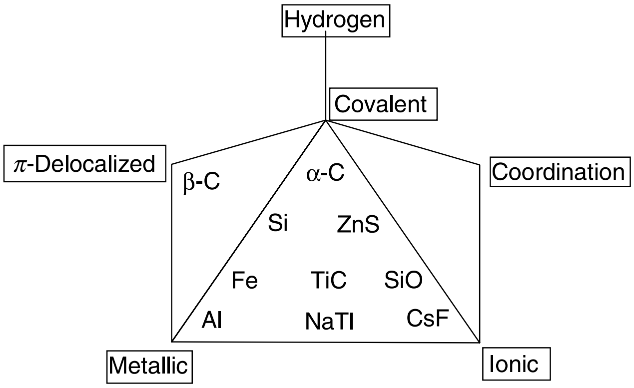


Fig. 1. Types and examples of the chemical bond

Frequently the actual chemical bond is a combination of the limiting cases as shown by the central triangle in Fig. 1.

Description of the Chemical Bond

Several theoretical approaches were developed that are capable of describing the chemical bond:

1. the molecular orbital (MO) method (eventually followed by the configuration interaction – CI) plays a central role at present;
2. the valence bond (VB) method, which is rarely used at present;
3. the method of localized MOs preceded by the hybridisation of atomic orbitals and eventually followed by the perturbative CI (the PCILO method), which is again rarely used at present;
4. the density functional theory (DFT), which is of increasing popularity;
5. the methods for periodic solids – the crystal orbital (CO) method, the ASW (Augmented Spherical Waves), the APW (Augmented Plane Wave), *etc*.

The MO and VB methods will be described in detail later.

Angular Momentum

The angular momentum of a massive particle about the origin is introduced as the vector normal to the plane of motion and can be expressed in the form of Eq. (38).

$$\vec{l} = \vec{r} \times \vec{p} \tag{38}$$

If we apply the operator expression for $\vec{p} = -\mathrm{i}\hbar\vec{\nabla}$ in its differential form, then the following commutation relations can be derived (Eqs. (39)–(44)) where $\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$ is the square of the angular momentum, and $\hat{H}$ – the Hamiltonian; for $a = x, y, z$

$$\hat{l}_x\hat{l}_y - \hat{l}_y\hat{l}_x = \mathrm{i}\hbar\hat{l}_z \tag{39}$$

$$\hat{l}_y\hat{l}_z - \hat{l}_z\hat{l}_y = \mathrm{i}\hbar\hat{l}_x \tag{40}$$

$$\hat{l}_z\hat{l}_x - \hat{l}_x\hat{l}_z = \mathrm{i}\hbar\hat{l}_y \tag{41}$$

$$[\hat{l}^2, \hat{l}_a] = 0 \tag{42}$$

$$[\hat{H}, \hat{l}^2] = 0 \tag{43}$$

$$[\hat{H}, \hat{l}_a] = 0 \tag{44}$$

Only three of these operators commute simultaneously: $\hat{H}$, $\hat{l}^2$, and one component (say the third component $\hat{l}_z$) of the angular momentum. Thus we can use an indexation $|\Psi_i\rangle \equiv |E, \lambda, \mu\rangle$ for a set of eigenstates which simultaneously are eigenstates of the operators $\hat{H}$, $\hat{l}^2$, and $\hat{l}_z$. This result plays a key role in the theory of the electronic structure of atoms: *an arbitrary eigenfunction can be expanded as a sum over eigenfunctions common for the operators* $\hat{H}$, $\hat{l}^2$ *and* $\hat{l}_z$ (Eq. (45)).

$$|\Psi_i\rangle = \sum_i C_i |E, \lambda, \mu\rangle_i \tag{45}$$

Using the shift operators, the following results can be derived (Eqs. (46)–(49)).

$$\hat{l}_z|l, m\rangle = m\hbar|l, m\rangle \tag{46}$$

$$\hat{l}^2|l, m\rangle = l(l+1)\hbar^2|l, m\rangle \tag{47}$$

$$\hat{l}_x|l,m\rangle = \frac{1}{2}[(l-m)(l+m+1)]^{1/2}\hbar|l,m+1\rangle + \frac{1}{2}[(l-m+1)(l+m)]^{1/2}\hbar|l,m-1\rangle \tag{48}$$

$$\hat{l}_y|l,m\rangle = \frac{1}{2\mathrm{i}}[(l-m)(l+m+1)]^{1/2}\hbar|l,m+1\rangle - \frac{1}{2\mathrm{i}}[(l-m+1)(l+m)]^{1/2}\hbar|l,m-1\rangle \tag{49}$$

The last two equations are nothing else but the statement quoted above: the eigenfunctions of $\hat{l}_x$ and $\hat{l}_y$ operators are expanded as a sum over eigenfunctions common for the operators $\hat{H}$, $\hat{l}^2$, and $\hat{l}_z$, *i.e.* $|l, m\rangle$.

The eigenfuctions of the orbital angular momentum can be explicitly expressed in the form of the spherical harmonic functions Y_{lm}. The restriction of $l = 0, 1, 2, \ldots$ is accepted for the orbital angular momentum in order to keep a geometrical meaning that the rotation about the angle 2π leaves its wave function invariant. However, the quantum number l could adopt also half-integer values, say $1/2$, $3/2$, *etc*. This set is reserved for the spin; the spin of the electron is $s = 1/2$. Then the rotation about the angle 4π leaves its wave function invariant.

Wave Functions

In a many-electron system the appropriate wave function should fulfill two basic requirements:

1. it is antisymmetric with respect to interchange of two electrons;
2. it is an eigenfuction of the compound angular momenta.

Table 4. List of the wave functions in the H_2 molecule

Wave function	Eigenfunction	Form	Number
One-electron functions			
Atomic 1s orbitals	$\hat{l}^2$, $\hat{l}_z$	$\psi_A = (a^3/\pi)^{1/2} \mathrm{e}^{-ar_A}$	2
Molecular orbitals		$\varphi_\pm(i) = (2 \pm 2S_{AB})^{-1/2}[\psi_A(i) \pm \psi_B(i)]$	2
Spin functions	$\hat{s}^2$, $\hat{s}_z$	$\alpha(m_s = +1/2)$, $\beta(m_s = -1/2)$	2
Spin-orbitals		ϕ_1 through ϕ_4; *e.g.*, $\phi_1(i) = \varphi_+(i)\alpha(i)$	4
Two-electron functions			
Two-electron spin functions	$\hat{S}^2$, $\hat{S}_z$	$\eta(S, M_S)$; *e.g.*, $\eta(0,0) = [\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$	4
Spatial wave function	$\hat{L}^2$, $\hat{L}_z$	Θ_1 through Θ_4; *e.g.*, $\Theta_1(^1\Sigma_g) = \varphi_+(1)\varphi_+(2)$	4
Product functions		Ω_1 through Ω_4	4
Determinantal wave function	$\hat{L}_z$, $\hat{S}_z$	Φ_1 through Φ_6; *e.g.*, $\lvert\Phi_1(^1\Sigma_g\text{: }\sigma_g^2)\rangle = \lvert\varphi_+, \bar{\varphi}_+\rvert$	6
True wave function	$\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, $\hat{S}_z$	Ψ_1 through Ψ_6	6

When the spin-orbit coupling is ignored, the orbital and spin angular momenta are independent of each other and the second requirement is to be obeyed individually for the $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$ operators.

In this section we will introduce several kinds of wave functions which we will handle later. These are compiled in Table 4 and their short discussion follows.

a) Two 1s-*atomic orbitals* ψ_A and ψ_B centered at the atom A and B; each of them is a solution of the *Schrödinger* equation for the hydrogen atom and they have the form shown in Eqs. (50) and (51).

$$\psi_A = (a^3/\pi)^{1/2} \mathrm{e}^{-ar_A} \tag{50}$$

$$\psi_B = (a^3/\pi)^{1/2} \mathrm{e}^{-ar_B} \tag{51}$$

The orbital exponent α scales the atomic orbital: it expands when $\alpha > 1$ and compresses when $\alpha < 1$.

b) Two *molecular orbitals* φ_+ and φ_- that are linear combinations of atomic orbitals; they are linear combinations of the atomic orbitals (Eq. (52)) and since the centers are equivalent the only parameter is the normalization constant $N_\pm$ which can be easily determined from the normalization condition.

$$\begin{aligned}\varphi_\pm(i) &= c_\pm\psi_A(i) + c'_\pm\psi_B(i) = N_\pm[\psi_A(i) \pm \psi_B(i)] \\ &= (2 \pm 2S_{AB})^{-1/2}[\psi_A(i) \pm \psi_B(i)]\end{aligned} \tag{52}$$

The symbol i specifies that the i-th electron occupies the molecular orbital.

c) Two *spin functions* α and β for the spin-up orientation ($m_s = +1/2$) and spin-down orientation ($m_s = -1/2$). Their actual form need not (and cannot) be specified as only rules for handling with them are known (the orthonormality condition).

d) The two spin functions are used to form four *two-electron spin functions* of the type $\eta(S, M_s)$ (Eqs. (53)–(56))

$$\eta(0,0) = [\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2} \tag{53}$$

$$\eta(1,0) = [\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2} \tag{54}$$

$$\eta(1,+1) = \alpha(1)\alpha(2) \tag{55}$$

$$\eta(1,-1) = \beta(1)\beta(2) \tag{56}$$

While the first function for the spin singlet $(S = 0)$ is antisymmetric with respect to interchange of the electrons, the remaining functions for the spin triplet $(S = 1)$ are symmetric in this respect.

The transformation of the local-spin wave functions to the molecular-spin ones can be performed with the help of the transformation matrix $\mathbf{U}$ for coupling of two spins $s_1 = s_2 = 1/2$ (Eqs. (57) or (58)).

$$|S, M_S\rangle = \mathbf{U}|(s_1, s_2), m_1, m_2\rangle \tag{57}$$

$$\begin{pmatrix} |0,0\rangle \\ |1,-1\rangle \\ |1,0\rangle \\ |1,+1\rangle \end{pmatrix} = \begin{pmatrix} 0 & -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} |-1/2,-1/2\rangle \\ |-1/2,+1/2\rangle \\ |+1/2,-1/2\rangle \\ |+1/2,+1/2\rangle \end{pmatrix} \tag{58}$$

The members of the unitary matrix $\mathbf{U}$ are nothing but the *Clebsch-Gordan* coefficients $\langle s_1, s_2, m_1, m_2 | SM\rangle$ for the addition of the angular momenta.

e) Four molecular *spinorbitals* are formed by combining the two molecular orbitals and two spin functions, namely $\phi_1(i) = \varphi_+(i)\alpha(i)$, $\phi_2(i) = \varphi_+(i)\beta(i)$, $\phi_3(i) = \varphi_-(i)\alpha(i)$, and $\phi_4(i) = \varphi_-(i)\beta(i)$. These still are one-electron wave functions and a shortened notation for them used to be applied: $\phi_1 = \varphi_+$, $\phi_2 = \bar{\varphi}_+$, $\phi_3 = \varphi_-$, and $\phi_4 = \bar{\varphi}_-$.

f) Six *determinantal wave functions* can be created form four molecular spinorbitals and two electrons: Φ_1 through Φ_6. This number matches the number of combinations (Eq. (59) and Fig. 2).

$$n = \begin{pmatrix} \text{spinorbitals} \\ \text{electrons} \end{pmatrix} = \begin{pmatrix} 4 \\ 2 \end{pmatrix} = 6 \tag{59}$$

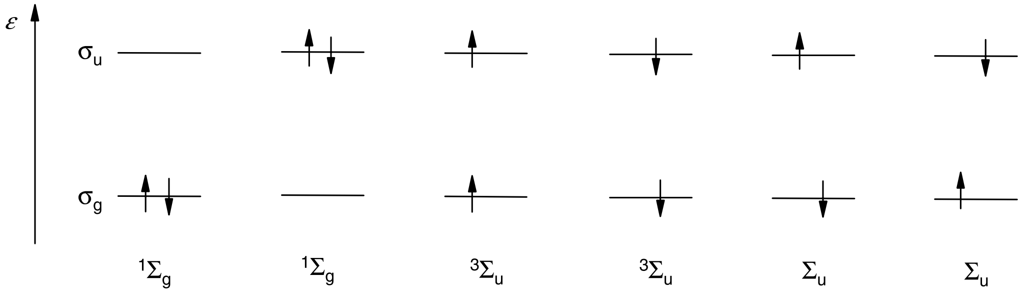


Fig. 2. Six electron configurations of the H_2 molecule

Each *Slater determinant* refers to a definite electron configuration (Fig. 2) and guarantees the antisymmetry condition (Eqs. (60)–(65)).

$$|\Phi_1(^1\Sigma_g : \sigma_g^2)\rangle = |\varphi_+, \bar{\varphi}_+| \tag{60}$$

$$|\Phi_2(^1\Sigma_g : \sigma_u^2)\rangle = |\varphi_-, \bar{\varphi}_-| \tag{61}$$

$$|\Phi_3(^3\Sigma_u : \sigma_g^\uparrow\sigma_u^\uparrow)\rangle = |\varphi_+, \varphi_-| \tag{62}$$

$$|\Phi_4(^3\Sigma_u : \sigma_g^\downarrow\sigma_u^\downarrow)\rangle = |\bar{\varphi}_+, \bar{\varphi}_-| \tag{63}$$

$$|\Phi_5(\Sigma_u : \sigma_g^\downarrow\sigma_u^\uparrow)\rangle = |\bar{\varphi}_+, \varphi_-| \tag{64}$$

$$|\Phi_6(\Sigma_u : \sigma_g^\uparrow\sigma_u^\downarrow)\rangle = |\varphi_+, \bar{\varphi}_-| \tag{65}$$

For instance one of the *Slater* determinants is given by Eq. (66) and when the electrons 1 and 2 are interchanged, then the resulting wave function alters its sign as shown by Eq. (67).

$$\begin{aligned}|\varphi_-, \bar{\varphi}_-| &= (2)^{-1/2}[\varphi_-(1)\alpha(1)\varphi_-(2)\beta(2) - \varphi_-(2)\alpha(2)\varphi_-(1)\beta(1)]\\ &= [\varphi_-(1)\varphi_-(2)](1/\sqrt{2})[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned} \tag{66}$$

$$\begin{aligned}|\bar{\varphi}_-, \varphi_-| &= (2)^{-1/2}[\varphi_-(1)\beta(1)\varphi_-(2)\alpha(2) - \varphi_-(2)\beta(2)\varphi_-(1)\alpha(1)]\\ &= [\varphi_-(1)\varphi_-(2)](1/\sqrt{2})[-\alpha(1)\beta(2) + \beta(1)\alpha(2)] = -|\varphi_-, \bar{\varphi}_-|\end{aligned} \tag{67}$$

Remember that a single *Slater* determinant guarantees that this is an eigenfunction of the projections of the orbital $\hat{L}_z$ and spin $\hat{S}_z$ angular momenta operators. However, this is not an eigenfunction of the total angular momentum operators $\hat{L}^2$ and $\hat{S}^2$ in general.

g) Six *true wave functions* Ψ_1 through Ψ_6 guarantee that the true state vectors $|S, M_S\rangle$ are the eigenfunctions of all angular momenta operators, $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$; this is provided by an eventual linear combination of *Slater* determinants (functions Ψ_5 and Ψ_6) (Eqs. (68)–(73)).

$$\begin{aligned}|\Psi_1(^1\Sigma_g, 0, 0)\rangle &= |\Phi_1(^1\Sigma_g : \sigma_g^2)\rangle\\ &= [\varphi_+(1)\varphi_+(2)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned} \tag{68}$$

$$\begin{aligned}|\Psi_2(^1\Sigma_g, 0, 0)\rangle &= |\Phi_2(^1\Sigma_g : \sigma_u^2)\rangle\\ &= [\varphi_-(1)\varphi_-(2)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned} \tag{69}$$

$$\begin{aligned}|\Psi_3(^3\Sigma_u, 1, +1)\rangle &= |\Phi_3(^3\Sigma_u : \sigma_g^\uparrow\sigma_u^\uparrow)\rangle\\ &= \frac{1}{\sqrt{2}}[\varphi_+(1)\varphi_-(2) - \varphi_+(2)\varphi_-(1)]\alpha(1)\alpha(2)\end{aligned} \tag{70}$$

$$\begin{aligned}|\Psi_4(^3\Sigma_u, 1, -1)\rangle &= |\Phi_4(^3\Sigma_u : \sigma_g^\downarrow\sigma_u^\downarrow)\rangle\\ &= \frac{1}{\sqrt{2}}[\varphi_+(1)\varphi_-(2) - \varphi_+(2)\varphi_-(1)]\beta(1)\beta(2)\end{aligned} \tag{71}$$

$$\begin{aligned}|\Psi_5(^3\Sigma_u, 1, 0)\rangle &= \frac{1}{\sqrt{2}}[|\Phi_5(\Sigma_u : \sigma_g^{\downarrow}\sigma_u^{\uparrow})\rangle + |\Phi_6(\Sigma_u : \sigma_g^{\uparrow}\sigma_u^{\downarrow})\rangle] \\ &= \frac{1}{\sqrt{2}}[\varphi_+(1)\varphi_-(2) - \varphi_+(2)\varphi_-(1)] \\ &\quad \times \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{aligned} \tag{72}$$

$$\begin{aligned}|\Psi_6(^1\Sigma_u, 0, 0)\rangle &= \frac{1}{\sqrt{2}}[|\Phi_5(\Sigma_u : \sigma_g^{\downarrow}\sigma_u^{\uparrow})\rangle - |\Phi_6(\Sigma_u : \sigma_g^{\uparrow}\sigma_u^{\downarrow})\rangle] \\ &= \frac{1}{\sqrt{2}}[\varphi_+(1)\varphi_-(2) + \varphi_+(2)\varphi_-(1)] \\ &\quad \times \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \end{aligned} \tag{73}$$

h) Four different *spatial wave functions* can be identified in the MO method:

1) for the ground singlet state $^1\Sigma_g(\sigma_g^2)$ (symmetric function) (Eq. (74));

$$\begin{aligned}\Theta_+ = \Theta_1(^1\Sigma_g) = \varphi_+(1)\varphi_+(2) = (2 + 2S_{AB})^{-1} \\ \times\{[\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)] + [\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)]\}\end{aligned} \tag{74}$$

2) for the excited singlet state $^1\Sigma_g(\sigma_u^2)$ (symmetric function) (Eq. (75));

$$\begin{aligned}\Theta_- = \Theta_2(^1\Sigma_g) = \varphi_-(1)\varphi_-(2) = (2 - 2S_{AB})^{-1} \\ \times\{[\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)] - [\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)]\}\end{aligned} \tag{75}$$

3) for the triplet spin state $^3\Sigma_u(\sigma_g^1\sigma_u^1)$ (antisymmetric function) (Eq. (76));

$$\begin{aligned}\Theta_3(^3\Sigma_u) = \Theta_4(^3\Sigma_u) = \Theta_5(^3\Sigma_u) &= \frac{1}{\sqrt{2}}[\varphi_+(1)\varphi_-(2) - \varphi_+(2)\varphi_-(1)] \\ &= 2^{-1/2}(2 + 2S_{AB})^{-1/2}(2 - 2S_{AB})^{-1/2}2[\psi_B(1)\psi_A(2) \\ &\quad - \psi_A(1)\psi_B(2)] \\ &= -[2(1 - S_{AB}^2)]^{-1/2}[\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)]\end{aligned} \tag{76}$$

4) for the singlet state $^1\Sigma_u(\sigma_g^1\sigma_u^1)$ (symmetric function) (Eq. (77)).

$$\begin{aligned}\Theta_6(^1\Sigma_u) &= \frac{1}{\sqrt{2}}[\varphi_+(1)\varphi_-(2) + \varphi_+(2)\varphi_-(1)] \\ &= 2^{-1/2}(2 + 2S_{AB})^{-1/2}(2 - 2S_{AB})^{-1/2}2[\psi_A(1)\psi_A(2) \\ &\quad - \psi_B(1)\psi_B(2)] \\ &= [2(1 - S_{AB}^2)]^{-1/2}[\psi_A(1)\psi_A(2) - \psi_B(1)\psi_B(2)]\end{aligned} \tag{77}$$

i) Four different product functions can be created for the VB method

1) the two "valence structures" (Eqs. (78) and (79));

$$\Omega_1 = \psi_A(1)\psi_B(2) \tag{78}$$

$$\Omega_2 = \psi_A(2)\psi_B(1) \tag{79}$$

2) the two "ionic structures" (Eqs. (80) and (81)).

$$\Omega_3 = \psi_A(1)\psi_A(2) \tag{80}$$

$$\Omega_4 = \psi_B(1)\psi_B(2) \tag{81}$$

j) Symmetry adapted VB-functions are given by Eqs. (82)–(85).

$$\Theta_1^{\mathrm{VB}}(^1\Sigma_{\mathrm{g}}) = [2(1+s^2)]^{-1/2}(\Omega_1 + \Omega_2) \tag{82}$$

$$\Theta_3^{\mathrm{VB}}(^3\Sigma_{\mathrm{u}}) = [2(1-s^2)]^{-1/2}(\Omega_1 - \Omega_2) \tag{83}$$

$$\Theta_2^{\mathrm{VB}}(^1\Sigma_{\mathrm{g}}) = [2(1+s^2)]^{-1/2}(\Omega_3 + \Omega_4) \tag{84}$$

$$\Theta_4^{\mathrm{VB}}(^1\Sigma_{\mathrm{u}}) = [2(1-s^2)]^{-1/2}(\Omega_3 - \Omega_4) \tag{85}$$

The relationship between the spatial functions in the MO and VB methods can be easily proven by Eqs. (86)–(89).

$$\Theta_1^{\mathrm{MO}}(^1\Sigma_{\mathrm{g}}) = [2(1+s)]^{-1}[(\Omega_1 + \Omega_2) + (\Omega_3 + \Omega_4)] = N_1(\Theta_1^{\mathrm{VB}} + \Theta_3^{\mathrm{VB}}) \tag{86}$$

$$\Theta_2^{\mathrm{MO}}(^1\Sigma_{\mathrm{g}}) = [2(1-s)]^{-1}[(\Omega_1 + \Omega_2) - (\Omega_3 + \Omega_4)] = N_2(\Theta_1^{\mathrm{VB}} - \Theta_3^{\mathrm{VB}}) \tag{87}$$

$$\Theta_3^{\mathrm{MO}}(^3\Sigma_{\mathrm{u}}) = -[2(1-s^2)]^{-1/2}[\Omega_1 - \Omega_2] = -\Theta_2^{\mathrm{VB}} \tag{88}$$

$$\Theta_6^{\mathrm{MO}}(^1\Sigma_{\mathrm{u}}) = [2(1-s^2)]^{-1/2}[\Omega_3 - \Omega_4] = \Theta_4^{\mathrm{VB}} \tag{89}$$

Now we can compare the spatial wave functions of the $^1\Sigma_{\mathrm{g}}$ symmetry according to the VB method and the MO method: the MO method includes the "ionic structures" as well but with the same weight as the "covalent structures". Apparently this overestimation of the "ionic structures" is an intrinsic defect of the MO method that is improved through the configuration interaction.

We have not considered the Hamiltonian so far. The above wave functions are common for the hydrogen molecule and a joint helium atom with the exception of the symmetry labels, since the hydrogen molecule spans the point group of symmetry $\boldsymbol{D}_{\infty\mathbf{h}}$ whereas the helium atom belongs to the rotational group $\boldsymbol{R}_3$.

Table 5. Molecular integrals in the H_2^+, H_2, and H_2^-diatomics

Integral	Symbol	Expression
overlap	$s = S_{AB}$	$\langle\psi_A(1)\vert\psi_B(1)\rangle$
one-center kinetic	$t_0 = T_{AA}$	$\langle\psi_A(1)\vert\hat{T}_1\vert\psi_A(1)\rangle = \langle\psi_B(1)\vert\hat{T}_1\vert\psi_B(1)\rangle$
kinetic	$t = T_{AB}$	$\langle\psi_A(1)\vert\hat{T}_1\vert\psi_B(1)\rangle = \langle\psi_B(1)\vert\hat{T}_1\vert\psi_A(1)\rangle$
one-center *Coulomb*	$\alpha_0 = J_{AA}$	$\langle\psi_A(1)\vert\hat{V}_{A1}\vert\psi_A(1)\rangle = \langle\psi_B(1)\vert\hat{V}_{B1}\vert\psi_B(1)\rangle$
one-electron *Coulomb*	$\alpha = J_{AB}$	$\langle\psi_A(1)\vert\hat{V}_{B1}\vert\psi_A(1)\rangle = \langle\psi_B(1)\vert\hat{V}_{A1}\vert\psi_B(1)\rangle$
resonance	$\beta = K_{AB}$	$\langle\psi_A(1)\vert\hat{V}_{B1}\vert\psi_B(1)\rangle = \langle\psi_B(1)\vert\hat{V}_{A1}\vert\psi_A(1)\rangle$ $= \langle\psi_A(1)\vert\hat{V}_{A1}\vert\psi_B(1)\rangle = \langle\psi_B(1)\vert\hat{V}_{B1}\vert\psi_A(1)\rangle$
two-electron *Coulomb*	$j = J_{AABB}$	$\langle\psi_A(1)\psi_B(2)\vert\hat{V}_{12}\vert\psi_A(1)\psi_B(2)\rangle$
one-center two-electron *Coulomb*	$j_0 = J_{AAAA}$	$\langle\psi_A(1)\psi_A(2)\vert\hat{V}_{12}\vert\psi_A(1)\psi_A(2)\rangle$
two-electron exchange	$k = K_{ABAB}$	$\langle\psi_A(1)\psi_B(2)\vert\hat{V}_{12}\vert\psi_A(2)\psi_B(1)\rangle$
two-electron hybrid	$h = H_{ABBB}$	$\langle\psi_A(1)\psi_B(2)\vert\hat{V}_{12}\vert\psi_B(2)\psi_B(1)\rangle$ $= \langle\psi_A(1)\psi_A(2)\vert\hat{V}_{12}\vert\psi_A(2)\psi_B(1)\rangle$

Molecular Integrals

In treating the $H_2{}^+$, H_2, and $H_2{}^-$ diatomics the same basis set will be considered: it consists of two 1s atomic orbitals centered at A and B, respectively. These functions are contained within expressions for molecular integrals. The full set is listed in Table 5. By using either polar or elliptic coordinates, all these integrals can be expressed as functions of the orbital exponent a and the internuclear distance R (Table 6).

It can be seen from Fig. 3 that on increasing R all the integrals vanish, and:

a) the overlap integral decreases from the value of 1.0;
b) the kinetic integral decreases from the value of 0.5;

Table 6. Expressions for molecular integrals over 1s atomic orbitals

Integral	Unit reduction	Reduced integral[a]
Kinetic	$T_{AB} = (\hbar^2/m_e)T'_{AB}$	$T'_{AB} = (a^2/2)\mathrm{e}^{-aR}(1 + aR - a^2R^2/3)$
Resonance	$K_{AB} = -(e^2/4\pi\varepsilon_0)K'_{AB}$	$K'_{AB} = (1/R)\mathrm{e}^{-aR}(aR + a^2R^2)$
Coulomb attraction	$J_{AB} = -(e^2/4\pi\varepsilon_0)J'_{AB}$	$J'_{AB} = (1/R)[1 - \mathrm{e}^{-2aR}(1 + aR)]$
Overlap		$S_{AB} = \mathrm{e}^{-aR}(1 + aR + a^2R^2/3)$
2e-*Coulomb*	$J_{AABB} = (e^2/4\pi\varepsilon_0)J'_{AABB}$	$J'_{AABB} = (1/R)\{1 - \mathrm{e}^{-2c}[1 + (11/8)c$ $+(3/4)c^2 + (1/6)c^3]\}$
2e-hybrid	$H_{ABBB} = (e^2/4\pi\varepsilon_0)H'_{ABBB}$	$H'_{ABBB} = (1/R)\{\mathrm{e}^{-c}[(5/16) + (1/8)c + c^2]$ $-\mathrm{e}^{-3c}[(5/16) + (1/8)c]\}$
2e-exchange	$K_{ABAB} = (e^2/4\pi\varepsilon_0)K'_{ABAB}$	$K'_{ABAB} = (1/R)\{\mathrm{e}^{-2c}[(5/8)c - (23/20)c^2$ $-(3/5)c^3 - (1/15)c^4] + (6/5)[(C_0 + \ln c)S_c^2$ $-2S_cS_{-c}E_{-2c} + S_{-c}^2E_{-4c}]\}$ with $S_x = \mathrm{e}^{-x}(1 + x + x^2/3)$, *Euler* constant $C_0 = 0.5772156649$, integral exponential function $E_{-x} = -\int_x^\infty (\mathrm{e}^{-t}/t)\mathrm{d}t$
2e-one-center	$J_{AAAA} = (e^2/4\pi\varepsilon_0)J'_{AAAA}$	$J'_{AAAA} = (5/8)a$

[a] $c = aR$; a – orbital exponent, R – internuclear distance

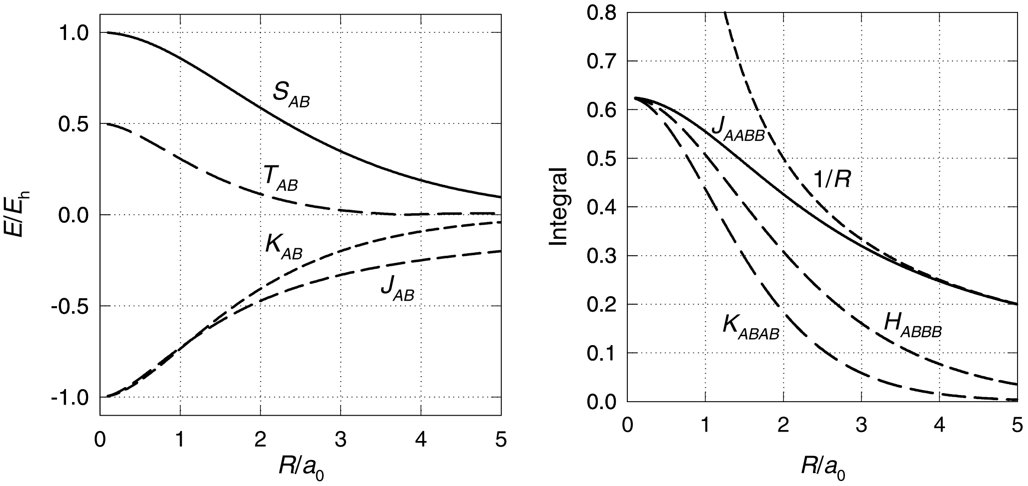
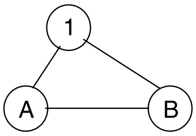


Fig. 3. Molecular integrals as functions of the internuclear distance R; the orbital exponent of 1s functions is $a = 1.0$; left: one-electron integrals; right: two-electron integrals

c) the *Coulomb* attraction integral increases from the value of -1.0;
d) the resonance integral behaves analogously but it increases more rapidly than the *Coulomb* integral;
e) the two-electron integrals adopt the same value of $(5/8)$ for $R=0$. On increasing R, they vanish but with different rate: K_{ABAB} more rapidly than H_{ABBB} and this one more rapidly than J_{AABB}. Above $R=4a_0$ the two-center *Coulomb* integral behaves practically the same as the $1/R$ function.

The Chemical Bond in Dihydrogen Cation by the MO Method

The molecular ion ${H_2}^+$ is the simplest system bound by the chemical bond. Constituents of the ${H_2}^+$ are two nuclei (protons A and B) and a single electron (abbreviated as 1).



The complete molecular Hamiltonian is given by Eq. (90).

$$\hat{H} = \hat{T} + \hat{V} = |\cancel{\hat{T}_A} + \cancel{\hat{T}_B}| + \hat{T}_1 + \hat{V}_{A1} + \hat{V}_{B1} + \hat{V}_{AB} \tag{90}$$

Within the *Born–Oppenheimer* approximation the kinetic energy of the nuclei $\hat{T}_A$ and $\hat{T}_B$ is omitted.

The number of electron configurations is given by Eq. (91).

$$n = \binom{\text{spinorbitals}}{\text{electrons}} = \binom{4}{1} = 4 \tag{91}$$

The trial wave function will be represented by a single molecular spinorbital (Eq. (92)).

$$\Phi_1(1) = \phi_1(1) = \varphi_+(1)\alpha(1) \tag{92}$$

The two molecular orbitals are expressed in the form of a linear combination of atomic orbitals (1s functions centered at A and B) (Eq. (93)).

$$\varphi_\pm = c_A\psi_A \pm c_B\psi_B \tag{93}$$

The normalization constant is determined as follows (Eq. (94)) so that we have Eq. (95).

$$\langle\varphi_\pm|\varphi_\pm\rangle = N_\pm^2\langle\psi_A \pm \psi_B|\psi_A \pm \psi_B\rangle = N_\pm^2(2 \pm 2\langle\psi_A|\psi_b\rangle) = 1 \tag{94}$$

$$N_\pm = (2 \pm 2S_{AB})^{-1/2} \tag{95}$$

The atomic orbitals have been normalized (Eq. (96)).

$$S_{AA} = S_{BB} = 1 \tag{96}$$

Normally, the combination coefficients should be determined by the linear variation method, *i.e.* by solving Eq. (97) where the overlap integrals are given by Eq. (98) and the matrix elements of the Hamiltonian are described by Eq. (99).

$$\begin{pmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - ES_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0 \tag{97}$$

$$S_{AB} = \langle \psi_A | \psi_B \rangle \tag{98}$$

$$H_{AB} = \langle \psi_A | \hat{H} | \psi_B \rangle \tag{99}$$

However, owing to the symmetry, the coefficients are equivalent, $|c_A| = |c_B|$, so that the two solutions can be written as shown by Eq. (100).

$$\varphi_\pm = N_\pm (\psi_A \pm \psi_B) = (2 \pm 2S_{AB})^{-1/2} (\psi_A \pm \psi_B) \tag{100}$$

Since the wave function is known, the mean value of the molecular energy can be evaluated as given by Eq. (101).

$$\begin{aligned} E_\pm &= \langle \varphi_\pm | \hat{H} | \varphi_\pm \rangle \cdot \langle \alpha(1) | \alpha(1) \rangle = N_\pm^2 \langle \psi_A \pm \psi_B | \hat{T}_1 + \hat{V}_{A1} + \hat{V}_{B1} + \hat{V}_{AB} | \psi_A \pm \psi_B \rangle \\ &= N_\pm^2 \left(\langle \psi_A | \hat{T}_1 | \psi_A \rangle + \langle \psi_B | \hat{T}_1 | \psi_B \rangle \pm 2 \langle \psi_A | \hat{T}_1 | \psi_B \rangle + \langle \psi_A | \hat{V}_{A1} | \psi_A \rangle \right. \\ &\quad + \langle \psi_B | \hat{V}_{A1} | \psi_B \rangle \pm 2 \langle \psi_A | \hat{V}_{A1} | \psi_B \rangle \\ &\quad + \langle \psi_A | \hat{V}_{B1} | \psi_A \rangle + \langle \psi_B | \hat{V}_{B1} | \psi_B \rangle \pm 2 \langle \psi_A | \hat{V}_{B1} | \psi_B \rangle + \langle \psi_A | \hat{V}_{AB} | \psi_A \rangle \\ &\quad \left. + \langle \psi_B | \hat{V}_{AB} | \psi_B \rangle \pm 2 \langle \psi_A | \hat{V}_{AB} | \psi_B \rangle \right) \end{aligned} \tag{101}$$

Here we are left with a set of molecular integrals composed of atomic orbitals. Using a simplified notation for molecular integrals (Table 5), the mean value of the molecular energy for H_2^+ becomes Eq. (102) and making use of the normalization constant we obtain the following energy expression (Eq. (103)).

$$E_\pm = 2N_\pm^2 \left[(t_0 \pm t + \alpha_0 + \alpha \pm 2\beta) + V_{AB}(1 \pm s) \right] \tag{102}$$

$$E_\pm = V_{AB} + (t_0 \pm t + \alpha_0 + \alpha \pm 2\beta)/(1 \pm s) \tag{103}$$

When the atomic orbitals in use are eigenfunctions of the hydrogen atom, then the energy of the free hydrogen atoms is given by Eq. (104) and furthermore Eq. (105) holds true.

$$t_0 + \alpha_0 = \langle \psi_A | \hat{T}_1 + \hat{V}_{B1} | \psi_A \rangle = E_0 \langle \psi_A | \psi_A \rangle = E_0 \tag{104}$$

$$t + \beta = \langle \psi_A | \hat{T}_1 + \hat{V}_{B1} | \psi_B \rangle = E_0 \langle \psi_A | \psi_B \rangle = E_0 s \tag{105}$$

Using these assumptions the molecular energy can be simplified to Eq. (106).

$$E_\pm = E_0 + V_{AB} + \frac{\alpha \pm \beta}{1 \pm s} \tag{106}$$

However, this simplified relationship is not generally valid.

In atomic units, $E_0/E_h = -1/2$ has a constant value and $V_{AB}/E_h = 1/R$ (the internuclear repulsion) is always positive. The remaining integrals are smooth functions of the internuclear distance and the orbital exponent (a) of the basis set 1s functions (Table 6).

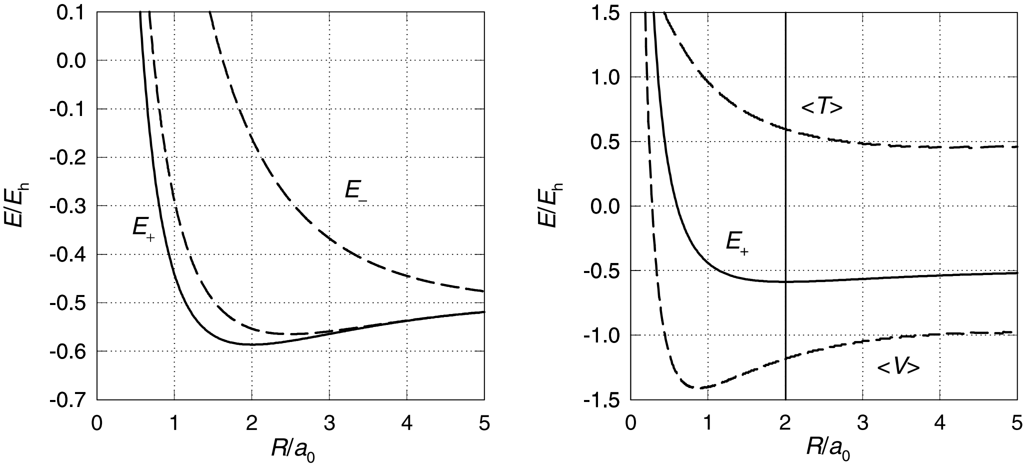


Fig. 4. Energy of the $H_2{}^+$ ion by the MO method; left: dashed – for orbital exponent $a = 1.0$; solid – a optimized for each R; right: energy terms using a optimized for each R

On lowering R the molecular energy abbreviated as E_+ passes through a minimum, which means that a stabilization (binding) energy E_b (relative to the energy of the hydrogen atom E_0) is liberated. This amount should be comparable with the experimental determination of the dissociation energy D_e. The position of the energy minimum corresponds to an equilibrium distance R_0 (Fig. 4). On the contrary, the second solution E_- is always increasing which indicates that no chemical bond is formed in this molecular state. The difference between the energies $E_\pm$ lies in the sign of the resonance and overlap integrals.

Using the orbital exponent $a = 1.0$ the calculated molecular energy is $E_+/E_h = -0.565$ at $R_0/a_0 = 2.495$. These values are much improved when the orbital exponent is subjected to variation (Table 7): the final energy value is not too far from the experimentally determined value.

The optimum orbital exponent a_{opt} secures not only lowering of the energy but also satisfaction of the virial theorem. The individual energy terms behave with varying R as shown in Fig. 4. The optimization of the orbital exponent should be done individually for each internuclear distance. The virial ratio $v = -2$ is obtained only at the equilibrium distance R_0 when the energy gradient vanishes.

Frequently it is claimed that the chemical bond appears as a result of occurrence of the resonance integral. Such an understanding, however, is mistaken. The physical nature of the chemical bond is given by the virial theorem: an increase in the kinetic energy accompanied by a decrease of the potential energy. The appear-

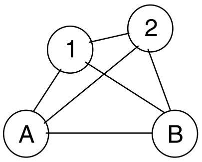
Table 7. Calculated bonding characteristics for $H_2{}^+$

Method	E_+/E_h	R_0/a_0	$\langle T\rangle$	$\langle V\rangle$	$\langle V\rangle/\langle T\rangle$
$a = 1.0$	−0.56483	2.495	0.38271	−0.94753	−2.47592
$a = 1.238$	−0.58651	2.003	0.58648	−1.17299	−2.00005
Experiment	−0.60263				

ance of the resonance integral originates in the molecular orbital approach and thus it should be considered as a descriptive parameter only. If a more rigorous approach is applied the resonance integral can disappear completely but the chemical bond exists irrespective of appearance of resonance integrals.

The MO Method for the Dihydrogen Molecule

The molecule H_2 contains two nuclei (protons A and B) and two electrons (1 and 2).



The complete molecular Hamiltonian is given by Eq. (107).

$$\hat{H} = \hat{T} + \hat{V} = |\cancel{\hat{T}_A} + \cancel{\hat{T}_B}| + \hat{T}_1 + \hat{T}_2 + \hat{V}_{A1} + \hat{V}_{B1} + \hat{V}_{A2} + \hat{V}_{B2} + \hat{V}_{12} + \hat{V}_{AB} \tag{107}$$

Within the *Born–Oppenheimer* approximation the kinetic energy of the nuclei $\hat{T}_A$ and $\hat{T}_B$ is omitted. The Hamiltonian for the H_2 molecule, which is a two-electron system, can be rewritten as Eq. (108).

$$\hat{H} = V_{AB} + 2(\hat{T}_1 + \hat{V}_{A1} + \hat{V}_{B1}) + \hat{V}_{12} = \hat{h}_0 + \hat{h}(1) + \hat{h}(2) + \hat{g}(1,2) \tag{108}$$

The two-electron antisymmetrized wave function is constructed in the form of a spatial part $\Theta(1,2)$ and a spin part $\eta(S, M_S)$ as explained above (Eq. (109)).

$$\Psi(1,2) = \Theta(1,2) \cdot \eta(S, M_S) \tag{109}$$

The total molecular wave function is antisymmetric with respect to interchange of the two electrons.

The molecular energy will be evaluated under four different approximations:

a) within the MO (Molecular Orbital) method,
b) by the CI (Configuration Interaction) applied after the MO method;
c) according to the limited VB (Valence Bond) method that considers only the "valence structures";
d) according to the complete VB method that includes also the "ionic structures".

The MO Method

The construction of the wave function in the MO method follows the following procedure:

a) In the basis set of 1s atomic orbitals two molecular orbitals can be constructed *via* LCAO (Eq. (110)).

$$\varphi_{\pm}(i) = (2 \pm 2S_{AB})^{-1/2}[\psi_A(i) \pm \psi_B(i)] \tag{110}$$

b) By adding the spin functions, the MOs form four molecular spinorbitals: $\phi_1 = \varphi_+$, $\phi_2 = \bar{\varphi}_+$, $\phi_3 = \varphi_-$, and $\phi_4 = \bar{\varphi}_-$. Their different occupation by two electrons defines six electron configurations.

c) Each electron configuration is characterized by a *Slater* determinant so that one can construct six determinantal wave functions Φ_1 through Φ_6 (A single *Slater* determinant guarantees that this is an eigenfunction of the projections of the orbital and spin angular momenta operators; however, this is not an eigenfunction of the total angular momentum operators, in general).

d) The true state vectors $|S, M_S\rangle$, which are the eigenfunctions of the spin operators $\hat{S}^2$ and $\hat{S}_z$, are given by the eventual linear combinations of *Slater* determinants (In fact only the two last determinantal functions need to be linearly combined to yield the proper molecular-state wave functions).

There are only four distinguishable spatial wave functions in these formulae, namely:

1. for the ground singlet state ${}^1\Sigma_g(\sigma_g^2)$, $\Theta_+ = \Theta_1({}^1\Sigma_g) = \varphi_+(1)\varphi_+(2)$ which is a symmetric function;
2. for the excited singlet state ${}^1\Sigma_g(\sigma_u^2)$, $\Theta_- = \Theta_2({}^1\Sigma_g) = \varphi_-(1)\varphi_-(2)$ which is a symmetric function also;
3. for the triplet spin state ${}^3\Sigma_u(\sigma_g^1\sigma_u^1)$, $\Theta_3({}^3\Sigma_u) = [\varphi_+(1)\varphi_-(2) - \varphi_+(2)\varphi_-(1)]/\sqrt{2}$ which is an antisymmetric function common for the spin multiplet $\Theta_3({}^3\Sigma_u) = \Theta_4({}^3\Sigma_u) = \Theta_5({}^3\Sigma_u)$;
4. for the singlet state ${}^1\Sigma_u(\sigma_g^1\sigma_u^1)$, $\Theta_6({}^1\Sigma_u) = [\varphi_+(1)\varphi_-(2) + \varphi_+(2)\varphi_-(1)]/\sqrt{2}$ which is a symmetric function.

The feature that the spatial part of the ground-state wave function in the MO method is a combination of the "valence structures" and "ionic structures" with equal weights will be identified later as the main drawback of the simple MO method.

The mean value of the molecular energy for the states ${}^1\Sigma_g$ is described by Eq. (111).

$$\begin{aligned} E_\pm({}^1\Sigma_g) &= \langle \Psi_\pm|\hat{H}|\Psi_\pm\rangle = \langle \Theta_\pm|\hat{H}|\Theta_\pm\rangle\langle\eta|\eta\rangle \\ &= \langle \varphi_\pm(1)\varphi_\pm(2)|\hat{H}|\varphi_\pm(1)\varphi_\pm(2)\rangle \end{aligned} \tag{111}$$

The evaluation in this form is rather tedious since there are 4 (wave function terms) × 8 (Hamiltonian components) × 4 (wave function terms) = 128 terms contributing to the molecular energy. A more transparent derivation is obtained when the *Slater rules* for matrix elements are applied. According to the first *Slater* rule E is given by Eq. (112).

$$E = h_0 + \sum_i h_{ii} + \sum_i \sum_{j<i} (J_{ij} - K_{ij}) \tag{112}$$

For the ground-state antisymmetrized wave function (a *Slater* determinant) the Hamiltonian matrix element, according to the first *Slater* rule, is described by

Eq. (113) which is rewritten as Eq. (114).

$$
\begin{aligned}
E_+(^1\Sigma_g) = \langle {}^1\Psi_+|\hat{H}|{}^1\Psi_+\rangle = h_0 &+ \langle\varphi_+(1)|\hat{h}(1)|\varphi_+(1)\rangle + \langle\varphi_+(2)|\hat{h}(2)|\varphi_+(2)\rangle \\
&+ \langle\varphi_+(1)\varphi_+(2)|\hat{g}(1,2)|\varphi_+(1)\varphi_+(2)\rangle\langle\alpha(1)|\alpha(1)\rangle\langle\beta(2)|\beta(2)\rangle \\
&- \langle\varphi_+(1)\varphi_+(2)|\hat{g}(1,2)|\varphi_+(2)\varphi_+(1)\rangle\cancel{\langle\alpha(1)|\beta(1)\rangle}\cancel{\langle\alpha(2)|\beta(2)}\rangle
\end{aligned}
\tag{113}
$$

$$
E_+(^1\Sigma_g) = h_0 + h_{11} + h_{22} + J_{12} \tag{114}
$$

Here, in addition to one-electron integrals the *Coulomb* integrals over MOs appear. The exchange integral between MOs disappears, $K_{12} = 0$, owing to the orthogonality of the spin functions. The one-electron terms are specified as shown by Eq. (115).

$$
\begin{aligned}
h_{11} = h_{22} &= N_+^2\langle\psi_A(1) + \psi_B(1)|\hat{T}_1 + \hat{V}_{A1} + \hat{V}_{B1}|\psi_A(1) + \psi_B(1)\rangle \\
&= N_+^2[(T_{AA} + 2T_{AB} + T_{BB}) + (J_{AA} + 2K_{AB} + J_{AB}) + (J_{AB} + 2K_{AB} + J_{BB})] \\
&= [2t_0 + 2t + 2\alpha_0 + 2\alpha + 4\beta]/(2 \pm 2s)
\end{aligned}
\tag{115}
$$

The *Coulomb* integral over MOs is expanded as given by Eq. (116) and finally J_{12} is described by Eq. (117).

$$
\begin{aligned}
J_{12} &= N_+^4\langle[\psi_A(1) + \psi_B(1)][\psi_A(2) + \psi_B(2)]|\hat{V}_{12}|[\psi_A(1) + \psi_B(1)][\psi_A(2) + \psi_B(2)]\rangle \\
&= N_+^4[J_{AAAA} + H_{AAAB} + H_{AAAB} + K_{ABAB} + H_{AAAB} + J_{AABB} + K_{ABAB} + H_{AAAB} \\
&\quad + H_{AAAB} + K_{ABAB} + J_{AABB} + H_{AAAB} + K_{ABAB} + H_{AAAB} + H_{AAAB} + J_{AAAA}] \\
&= (J_{AAAA} + J_{AABB} + 2K_{ABAB} + 4H_{AAAB})/[2(1 + S_{AB})^2]
\end{aligned}
\tag{116}
$$

$$
J_{12} = (j_0 + j + 2k + 4h)/[2(1 + s^2)] \tag{117}
$$

In these formulae the two-electron integrals over the basis-set atomic orbitals occur. The normalization constant was already evaluated as $N_\pm = (2 \pm 2S_{AB})^{-1/2}$.

Then, using a simplified notation, the total molecular energies for the two singlet spin states, $E_\pm(^1\Sigma_g)$, become expressed as Eq. (118).

$$
E_\pm(^1\Sigma_g) = V_{AB} + 2\frac{t_0 + \alpha_0 \pm (t + \beta)}{1 \pm s} + 2\frac{\alpha \pm \beta}{1 \pm s} + \frac{j_0 + j + 2k \pm 4h}{2(1 \pm s)^2} \tag{118}
$$

Making use of the identities Eqs. (119) and (120), fulfilled for the 1s orbitals (with $a = 1$) as eigenfunctions of the hydrogen atom, we get a simplification for this particular case (Eq. (121)).

$$
t_0 + \alpha = \langle\psi_A(1)|\hat{T}_1 + \hat{V}_{A1}|\psi_A(1)\rangle = E_0 \tag{119}
$$

$$
t + \beta = \langle\psi_A(1)|\hat{T}_1 + \hat{V}_{B1}|\psi_B(1)\rangle = E_0 s \tag{120}
$$

$$
E_\pm(^1\Sigma_g) = 2E_0 + V_{AB} + 2\frac{\alpha \pm \beta}{1 \pm s} + \frac{j_0 + j + 2k \pm 4h}{2(1 \pm s)^2} \tag{121}
$$

Table 8. Expressions for the integrals over the molecular spinorbitals[a]

One-electron integrals	Two-electron integrals
$h_{gg} = h_{11} = h_{22} = [t_0 + \alpha_0 + \alpha + (t + 2\beta)]/(1+s)$	$J_{gg} = J_{12} = [j_0 + j + 2k + 4h]/[2(1+s)^2]$
$h_{uu} = h_{33} = h_{44} = [t_0 + \alpha_0 + \alpha - (t + 2\beta)]/(1-s)$	$J_{uu} = J_{34} = [j_0 + j + 2k - 4h]/[2(1-s)^2]$
	$J_{gu} = J_{13} = J_{23} = [j_0 + j - 2k]/[2(1-s^2)]$
	$K_{gu} = K_{13} = [j_0 - j]/[2(1-s^2)]$

[a] The spinorbitals are labeled according to $\phi_1 = \varphi_+,\ \phi_2 = \bar{\varphi}_+,\ \phi_3 = \varphi_-,\ \phi_4 = \bar{\varphi}_-$

The one-electron and two-electron integrals over the molecular spinorbitals are collected in Table 8. They allow evaluation of the energy of the triplet state, (Eq. (122)), hence yielding Eq. (123).

$$\begin{aligned} E_3({}^3\Sigma_u) &= \langle \Psi_3 | \hat{H} | \Psi_3 \rangle = \langle \Phi_3 | \hat{H} | \Phi_3 \rangle \\ &= h_0 + h_{11} + h_{33} + J_{13} - K_{13} = h_0 + h_{gg} + h_{uu} + J_{gu} - K_{gu} \end{aligned} \tag{122}$$

$$E_3({}^3\Sigma_u) = V_{AB} + \frac{t_0 + \alpha_0 + (t+\beta)}{1+s} + 2\frac{\alpha+\beta}{1+s} + \frac{t_0 + \alpha_0 - (t+\beta)}{1-s} + \frac{\alpha-\beta}{1-s} + \frac{j-k}{1-s^2} \tag{123}$$

Now it is evident that eventual stabilization of the electronic state involves no two-electron exchange integrals as often claimed erroneously. For the singlet states the hybrid integral has opposite sign and this integral disappears in the triplet spin state.

The energy of the remaining singlet state is given through the combination of *Slater* determinants (Eq. (124)) and after the application of the *Slater* rules it becomes expressed over the molecular spinorbitals as Eq. (125) which simplifies to Eq. (126).

$$\begin{aligned} E_6({}^1\Sigma_u) &= \langle \Psi_6 | \hat{H} | \Psi_6 \rangle = \frac{1}{2}[\langle \Phi_5 - \Phi_6 | \hat{H} | \Phi_5 - \Phi_6 \rangle] \\ &= \frac{1}{2}[\langle \Phi_5 | \hat{H} | \Phi_5 \rangle + \langle \Phi_6 | \hat{H} | \Phi_6 \rangle - 2\langle \Phi_5 | \hat{H} | \Phi_6 \rangle] \end{aligned} \tag{124}$$

$$\begin{aligned} E_6({}^1\Sigma_u) = \frac{1}{2}&[(h_0 + h_{22} + h_{33} + J_{23}) + (h_0 + h_{11} + h_{44} + J_{14}) \\ &- 2(\langle 23|\hat{g}|14\rangle \cancel{\langle\beta|\alpha\rangle}\cancel{\langle\alpha|\beta\rangle} - \langle 23|\hat{g}|41\rangle\langle\beta|\beta\rangle\langle\alpha|\alpha\rangle)] \end{aligned} \tag{125}$$

$$E_6({}^1\Sigma_u) = h_0 + h_{gg} + h_{uu} + J_{gu} + K_{gu} \tag{126}$$

The expansion into the basis set of the atomic orbitals yields finally Eq. (127).

$$E_6({}^1\Sigma_u) = V_{AB} + \frac{t_0 + \alpha_0 + (t+\beta)}{1+s} + \frac{\alpha+\beta}{1+s} + \frac{t_0 + \alpha_0 - (t+\beta)}{1-s} + \frac{\alpha-\beta}{1-s} + \frac{j_0-k}{1-s^2} \tag{127}$$

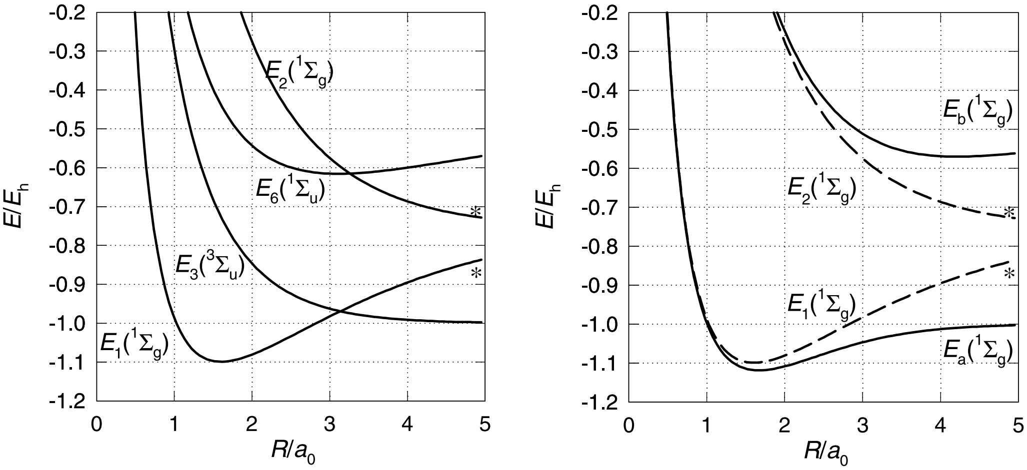


Fig. 5. Energy of the lowest molecular states by the simple MO method; orbital exponent $a = 1.0$; an asterisk indicates an improper limiting behaviour; right: energy of the molecular $^1\Sigma_g$ states by the MO + CI method; orbital exponent $a = 1.0$; dashed – simple MO, solid – MO + CI

Table 9. Calculated bonding characteristics for H_2 molecule by the MO method

Method		E_0/E_h	R_0/a_0	$\langle V\rangle/\langle T\rangle$
1. MO	$a = 1.0$	-1.09908	1.602	-2.37954
	$a_{opt} = 1.193$	-1.12823	1.385	-1.99674
2. MO + CI	$a = 1.0$	-1.11865	1.670	
	$a_{opt} = 1.194$	-1.14794	1.430	
3. Experimental		-1.17447	1.401	

Having the molecular integrals at our disposal makes the plot of the molecular energy possible (Fig. 5). The calculated bonding characteristics are collected in Table 9. In can be seen that although the MO wave functions describe the chemical bond qualitatively well, they behave incorrectly at the dissociation limit (Eq. (128)), *i.e.*, the energy of separated atoms is erroneously higher by $j_0/2 = (5/16)a$ in units of E_h.

$$\lim_{R\to\infty} E_+(^1\Sigma_g) = 2E_0 + j_0/2 \tag{128}$$

Configuration Interaction

The configuration interaction (CI method) mixes the *Slater* determinants of the same symmetry. In the minimum basis set of 1s functions we have two electron configurations, $1\sigma_g{}^2$ and $1\sigma_u{}^2$, of the same symmetry $^1\Sigma_g$. A more flexible wave function is a linear combination of the corresponding *Slater* determinants (Eq. (129)).

$$\Psi^{CI}(1,2) = C_1 \cdot {}^1\Psi_+^{MO} + C_2 \cdot {}^1\Psi_-^{MO} \tag{129}$$

Application of the variation method implies the fulfillment of the secular Eq. (130)

$$\det\begin{pmatrix} H_{11}-E & H_{12}-ES_{12} \\ H_{12}-ES_{12} & H_{22}-E \end{pmatrix} = 0 \tag{130}$$

Since the respective *Slater* determinants are orthogonal, $S_{12} = 0$ holds true. Thus an explicit solution of the quadratic Eq. (131) exists (Eq. (132)).

$$(H_{11}-E)(H_{22}-E) - H_{12}^2 = 0 \tag{131}$$

$$E_{a,b} = (H_{11}+H_{22})/2 \pm \{[(H_{11}-H_{22})/2]^2 + H_{12}^2\}^{1/2} \tag{132}$$

The diagonal matrix elements of the Hamiltonian are $H_{11} = {}^1E_+$ and $H_{22} = {}^1E_-$. In evaluating the off-diagonal matrix element H_{12} the *Slater* rules are helpful. Since the two *Slater* determinants differ in two pairs of spin-orbitals, the one-electron term vanishes and the only non-zero contribution is given by the electron repulsion (Eq. (133)) which becomes Eq. (134).

$$\begin{aligned} H_{12} = \langle {}^1\Psi_+|\hat{H}|{}^1\Psi_-\rangle &= \langle \varphi_+(1)\varphi_+(2)|\hat{V}_{12}|\varphi_-(1)\varphi_-(2)\rangle \\ &= N_+^2N_-^2\langle \psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2) + \psi_A(1)\psi_A(2) \\ &\quad + \psi_B(1)\psi_B(2)|\hat{V}_{12}|\psi_A(1)\psi_B(2) \\ &\quad + \psi_B(1)\psi_A(2) - \psi_A(1)\psi_A(2) - \psi_B(1)\psi_B(2)\rangle \end{aligned} \tag{133}$$

$$\begin{aligned} H_{12} &= [2(1+s)2(1-s)]^{-1} \\ &\quad \times [j+k+h+h+k+j+h+h-(h+h+j_0+k+h+h+k+j_0)] \\ &= (j-j_0)/[2(1-s^2)] \end{aligned} \tag{134}$$

In the limit of infinite internuclear distance we obtain Eq. (135) and the roots of the secular equation are shown by Eq. (136).

$$\lim_{R\to\infty} H_{12} = -j_0/2 \tag{135}$$

$$E_{a,b}^{\mathrm{CI}}(R\to\infty) = (2E_0 + j_0/2) \pm |j_0/2| \tag{136}$$

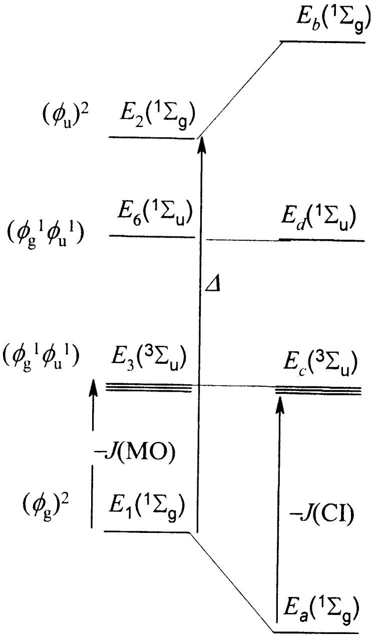
The lower energy solution is given by Eq. (137) whereas the higher energy solution is described by Eq. (138) and now they behave correctly in the limit of infinite internuclear separation. As a correct limiting behaviour of the energy on the dissociation is obtained, the configuration interaction removes the intrinsic defects of the MO method (of the one-electron approximation).

$$E_a^{\mathrm{CI}}(R\to\infty) = 2E_0 \tag{137}$$

$$E_b^{\mathrm{CI}}(R\to\infty) = 2E_0 + j_0 \tag{138}$$

The quantitative results obtained by the MO + CI method are involved in Table 9 and visualized in Fig. 5. The molecular states $E(^3\Sigma_u)$ and $E(^1\Sigma_u)$ are unaffected by

Table 10. Survey of the MO formulae for the H_2 molecule

Molecular orbitals (LCAO)	$\varphi_g(i) = (2+2s)^{-1/2}[\psi_A(i) + \psi_B(i)]$ $\varphi_u(i) = (2-2s)^{-1/2}[\psi_A(i) - \psi_B(i)]$
Energies in terms of MO and AO integrals  	$E_1 = V_{AB} + 2h_{gg} + J_{gg}$ $= 2\frac{t_0+\alpha_0+(t+\beta)}{1+s} + 2\frac{\alpha+\beta}{1+s} + \frac{j_0+j+2k+4h}{2(1+s)^2}$ $E_2 = V_{AB} + 2h_{uu} + J_{uu}$ $= 2\frac{t_0+\alpha_0-(t+\beta)}{1-s} + 2\frac{\alpha-\beta}{1-s} + \frac{j_0+j+2k-4h}{2(1-s)^2}$ $E_3 = V_{AB} + h_{gg} + h_{uu} + J_{gu} - K_{gu}$ $= \frac{t_0+\alpha_0+t+\beta}{1+s} + \frac{\alpha+\beta}{1+s} + \frac{t_0+\alpha_0-(t+\beta)}{1-s}$ $+ \frac{\alpha-\beta}{1-s} + \frac{j-k}{(1+s)(1-s)}$ $E_6 = V_{AB} + h_{gg} + h_{uu} + J_{gu} + K_{gu}$ $= \frac{t_0+\alpha_0+t+\beta}{1+s} + \frac{\alpha+\beta}{1+s} + \frac{t_0+\alpha_0-(t+\beta)}{1-s}$ $+ \frac{\alpha-\beta}{1-s} + \frac{j_0-k}{(1+s)(1-s)}$
Interaction matrix elements	$H_{ij} = \langle\Theta_i\|\hat{H}\|\Theta_j\rangle$; $H_{12} = K_{gu} = \frac{j_0-j}{2(1-s^2)}$; $S_{12} = 0$

the CI method since they have no symmetry-matching counterpart within the minimum basis set of the 1s functions.

The survey of the MO formulae is presented in Table 10.

Amplitudes of Molecular Orbitals

The molecular orbitals are completely known in the form of Eq. (139).

$$\varphi_\pm(i) = (2 \pm 2S_{AB})^{-1/2}[\psi_A(i) \pm \psi_B(i)] \tag{139}$$

The 1s functions being described by Eqs. (140) and (141) and the overlap integral is a function of $c = aR_{AB}$, namely $S_{AB} = \mathrm{e}^{-c}(1 + c + c^2/3)$.

$$\psi_A(i) = (a^3/\pi)^{1/2}\mathrm{e}^{-ar_{Ai}} \tag{140}$$

$$\psi_B(i) = (a^3/\pi)^{1/2}\mathrm{e}^{-ar_{Bi}} \tag{141}$$

This information is sufficient in constructing and visualisation of the amplitudes of molecular orbitals.

Since the whole molecule has a cylindrical shape the problem can be visualized in cylindrical coordinates (Fig. 6). These are defined by three variables: the radius

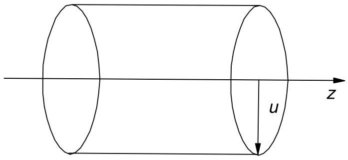


Fig. 6. Definition of the cylindrical coordinates

$u = \sqrt{x^2 + y^2}$ varies from $u = 0$ to ∞; the angle of rotation $\phi = 0$ to 2π; the height of the cylinder ranges between $z = -\infty$ and $+\infty$. The volume element is $\mathrm{d}V = u\mathrm{d}u\,\mathrm{d}z\,\mathrm{d}\phi$. The usual normalization in spherical coordinates yields Eq. (142) where the factor 4π arises from integration over the polar angles ϑ_1 and ϕ_1. Now the following normalization holds true in cylindrical coordinates (Eq. (143)) where the factor 2π results from integration over the remaining coordinate ϕ_1.

$$I = \int_V [\psi_A(r_1, \vartheta_1, \phi_1)]^2\,\mathrm{d}V = (a^3/\pi)(4\pi)\int_{r_1=0}^{\infty} \exp(-2ar_1)r_1^2\,\mathrm{d}r_1 = 1 \tag{142}$$

$$I = (a^3/\pi)^{1/2}(2\pi)\int_{z_1=-\infty}^{+\infty}\int_{u_1=0}^{\infty} \exp\{-2a[u_1^2 + (z_1 - z_A)^2]^{1/2}\}\,u_1\mathrm{d}u_1\,\mathrm{d}z_1 = 1 \tag{143}$$

The cylindrical coordinates are probably not suitable for analytic integration. However, a numerical integration in cylindrical coordinates causes no problem. One should define a dense network of grids: the coordinate z ranges from $-r_{\max}$ to $+r_{\max}$ by a small step Δz; the coordinate u varies from 0 to $+r_{\max}$ by a step Δu. The semi-integral of the function $F(u, z)$ can be integrated as a sum multiplied by the step (Eq. (144)) and the full integral becomes Eq. (145).

$$F(z) = \int_{u=0}^{\infty} F(u, z)\,u\,\mathrm{d}u\int_0^{2\pi}\mathrm{d}\phi = (2\pi)(\Delta u)\cdot\sum_{u_i=0}^{+r_{\max}} F(u_i, z_j)\,u_i \tag{144}$$

$$F = \int_{z=-\infty}^{+\infty} F(z)\,\mathrm{d}z = (\Delta z)\cdot\sum_{z_j=-r_{\max}}^{+r_{\max}} F(z_j) \tag{145}$$

The molecular orbitals are the one-electron wave functions (common for ${H_2}^+$, H_2, and ${H_2}^-$ systems), which can be displayed along the z-coordinate passing through the atomic nuclei A–B. We need to set the internuclear distance (say $R_{AB} = 1.4a_0$) and the radius of the plot $r_{\max}$. Then the center of the molecule is set to zero, the position of the first center is at $z_A = -R_{AB}/2$ and that of the second center at $z_B = +R_{AB}/2$. The electron coordinate z_1 ranges from $-r_{\max}$ to $+r_{\max}$.

In the cylindrical coordinate system the atomic orbitals become expressed as shown by Eqs. (146) and (147).

$$\psi_A = (a^3/\pi)^{1/2}\exp\{-a[u_1^2 + (z_1 - z_A)^2]^{1/2}\} \tag{146}$$

$$\psi_B = (a^3/\pi)^{1/2}\exp\{-a[u_1^2 + (z_1 - z_B)^2]^{1/2}\} \tag{147}$$

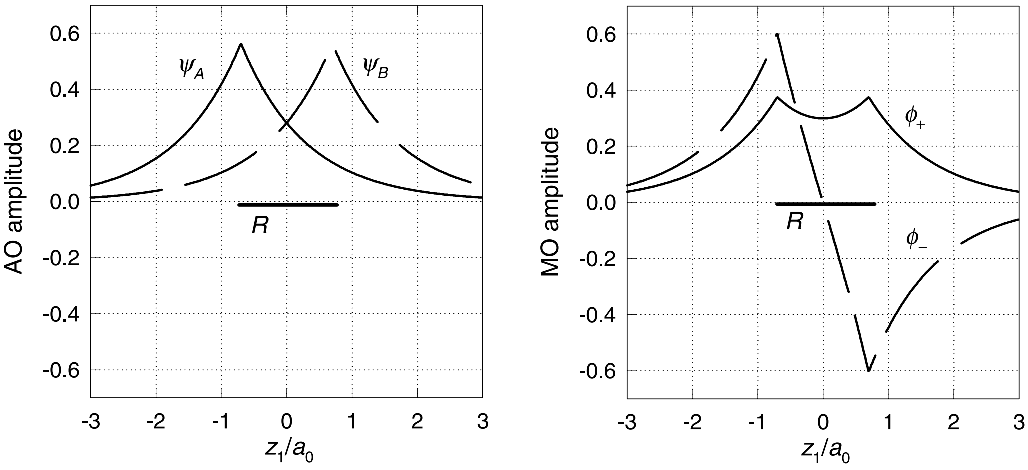


Fig. 7. Amplidutes of atomic 1s orbitals (left) and molecular orbitals (right) in H_2 molecule along the internuclear linkage ($u = 0$, ϕ – arbitrary)

The addition and/or subtraction of atomic orbitals along with the proper normalization constant $N_\pm$ reveals the amplitudes of molecular orbitals (Eq. (148)).

$$\varphi_\pm(z_1) = [\psi_A(z_1) \pm \psi_B(z_1)]N_\pm = [\psi_A(z_1) \pm \psi_B(z_1)](2 \pm 2S_{AB})^{-1/2} \tag{148}$$

The amplitudes of molecular orbitals are visualized in Fig. 7. It can be seen that the bonding molecular orbital possesses an amplitude increase in the internuclear region. Unlikely, the antibonding molecular orbital alters the sign just in the center of the molecule where its amplitude vanishes.

The true difference between MOs of $H_2{}^+$, H_2, and $H_2{}^-$ systems appears as an effect of different orbital exponent (the scaling factor) a, and a different equilibrium internuclear distance R_{AB} in these systems.

The probability of finding the electron in the volume element dV_1 is given by Eq. (149).

$$P_\pm = |\varphi\pm(x_1, y_1, z_1)|^2\,dV_1 = |\varphi\pm(z_1, u_1, \phi_1)|^2\,u_1 du_1\,dz_1\,d\phi_1 \tag{149}$$

In generating the probability functions for the MOs we have Eq. (150).

$$P_\pm(u_1, z_1, \phi_1) = |\varphi_\pm(u_1, z_1, \phi_1)|^2\,dV_1 = N_\pm^2\,[\psi_A(u_1, z_1, \phi_1) \pm \psi_B(u_1, z_1, \phi_1)]^2\,dV_1 \tag{150}$$

Let us introduce the *atomic charge density* (Eq. (151)) which can be semi-integrated along the coordinate ϕ_1 to give Eq. (152) as well as along the coordinate u_1 to yield Eq. (153) or fully integrated to give Eq. (154).

$$\begin{aligned} P_A^{ch}(u_1, z_1, \phi_1) &= [\psi_A(u_1, z_1, \phi_1)]^2\,u_1 du_1\,dz_1\,d\phi_1 \\ &= (a^3/\pi)\exp\{-2a[u_1^2 + (z_1 - z_A)^2]^{1/2}\}\,u_1 du_1\,dz_1\,d\phi_1 \end{aligned} \tag{151}$$

$$P_A^{ch}(z_1, u_1) = (a^3/\pi)(2\pi)\exp\{-2a[u_1^2 + (z_1 - z_A)^2]^{1/2}\}\,u_1 du_1\,dz_1 \tag{152}$$

$$P_A^{\mathrm{ch}}(z_1) = (a^3/\pi)(2\pi)\left[\int_{u_1=0}^{\infty} \exp\{-2a[u_1^2 + (z_1 - z_A)^2]^{1/2}\}\, u_1 \mathrm{d}u_1\right]\mathrm{d}z_1 \tag{153}$$

$$P_A^{\mathrm{ch}} = \int_{z_1=-\infty}^{+\infty} P_A^{\mathrm{ch}}(z_1)\,\mathrm{d}z_1 = 1 \tag{154}$$

Analogous expressions hold true for $P_B^{\mathrm{ch}}(u_1, z_1, \phi_1)$, $P_B^{\mathrm{ch}}(u_1, z_1)$, $P_B^{\mathrm{ch}}(z_1)$, and $P_B^{\mathrm{ch}} = 1$. The *overlap density* is introduced as shown by Eq. (155) and it is semi-integrated to yield Eqs. (156) and (157).

$$P_{AB}^{\mathrm{ov}}(u_1, z_1, \phi_1) = \psi_A(u_1, z_1, \phi_1)\psi_B(u_1, z_1, \phi_1)\, u_1 \mathrm{d}u_1\, \mathrm{d}z_1\, \mathrm{d}\phi_1 \tag{155}$$

$$\begin{aligned} P_{AB}^{\mathrm{ov}}(u_1, z_1) = (a^3/\pi)(2\pi) &\exp\{-a[u_1^2 + (z_1 - z_A)^2]^{1/2}\} \\ &\times \exp\{-a[u_1^2 + (z_1 - z_B)^2]^{1/2}\}\, u_1 \mathrm{d}u_1\, \mathrm{d}z_1 \end{aligned} \tag{156}$$

$$\begin{aligned} P_{AB}^{\mathrm{ov}}(z_1) = (a^3/\pi)(2\pi)\Bigg[\int_{u_1=0}^{\infty} &\exp\{-a[u_1^2 + (z_1 - z_A)^2]^{1/2}\} \\ &\times \exp\{-a[u_1^2 + (z_1 - z_B)^2]^{1/2}\}\, u_1 \mathrm{d}u_1\Bigg]\mathrm{d}z_1 \end{aligned} \tag{157}$$

The complete integral done numerically should converge to the value of the overlap integral (Eq. (158)).

$$P_{AB}^{\mathrm{ov}} = \int_{z_1=-\infty}^{+\infty} P_{AB}^{\mathrm{ov}}(z_1)\,\mathrm{d}z_1 = S_{AB} = f(a, R) \tag{158}$$

The charge density and the overlap density functions are plotted in Fig. 8.

It can be seen that the charge density $P_A^{\mathrm{ch}}(z_1, u_1)$ exhibits a maximum at the position of the atomic nucleus ($z_1 = -R/2$) and 1 *bohr* apart from the nucleus ($u_1/a_0 = 1.0$). The charge density at the nucleus is exactly zero: $P_A^{\mathrm{ch}}(z_1 = -R/2, u_1 = 0) = 0$. This quantity matches the monoatomic density function when placed at the position $\{z_1 = -R/2, u_1 = 0, \phi_1 = 0\}$. A similar property exhibits the second charge density $P_B^{\mathrm{ch}}(z_1, u_1)$. The overlap density is a constant in the internuclear region and escapes progressively outside the nuclei.

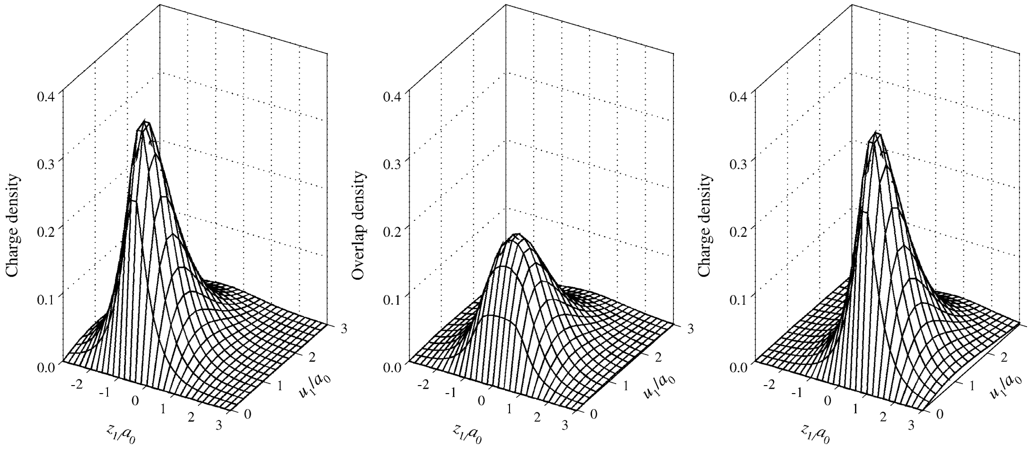


Fig. 8. The charge and overlap densities, $P_A^{\mathrm{ch}}(z_1, u_1)$, $P_{AB}^{\mathrm{ov}}(z_1, u_1)$, and $P_B^{\mathrm{ch}}(z_1, u_1)$, in the H_2 molecule semi-integrated over the angle ϕ_1

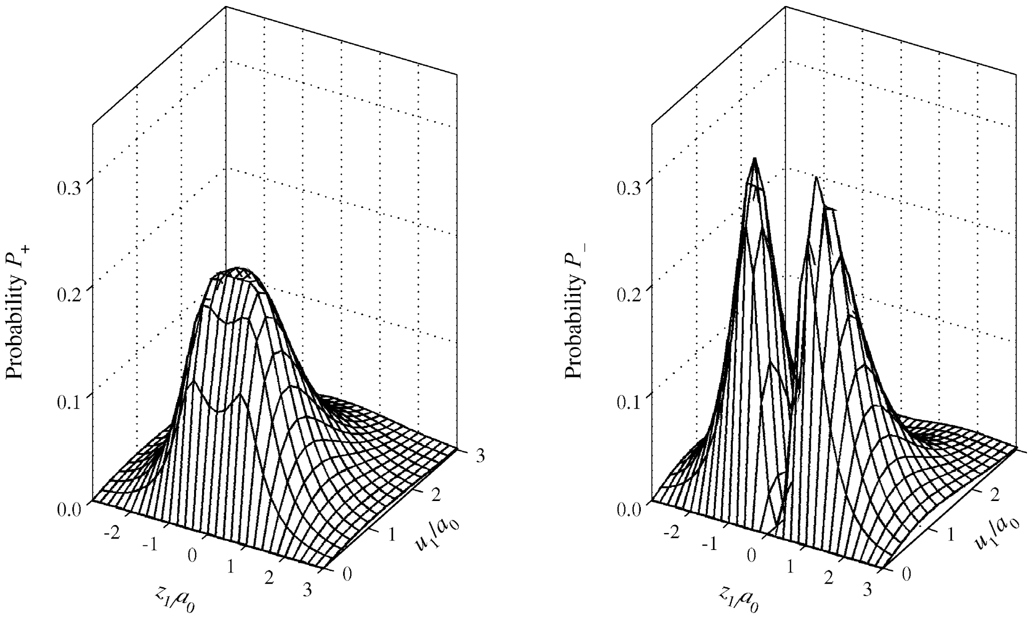


Fig. 9. The MO probability functions, $P_+(z_1, u_1)$ and $P_-(z_1, u_1)$, in the H_2 molecule semi-integrated over the angle ϕ_1

The MO probability functions can be rewritten into the semi-integrated form (Eq. (159)) and they are displayed in Fig. 9. Analogously, Eq. (160) is obtained.

$$P_\pm(z_1, u_1) = [P_A^{\mathrm{ch}}(z_1, u_1) + P_B^{\mathrm{ch}}(z_1, u_1) \pm P_{AB}^{\mathrm{ov}}(z_1, u_1)]/[2(1 \pm S_{AB})] \tag{159}$$

$$P_\pm(z_1) = [P_A^{\mathrm{ch}}(z_1) + P_B^{\mathrm{ch}}(z_1) \pm P_{AB}^{\mathrm{ov}}(z_1)]/[2(1 \pm S_{AB})] \tag{160}$$

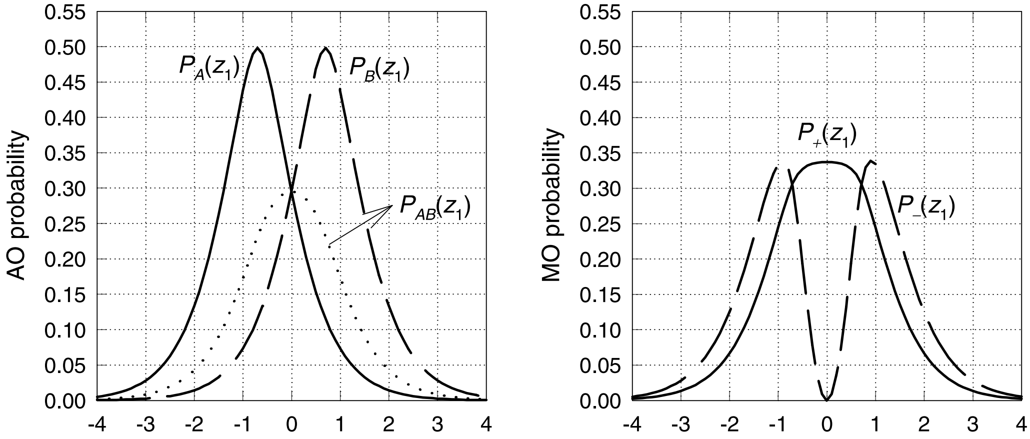


Fig. 10. Semi-integrated atomic and molecular probability functions; left – atomic orbital probabilities for two isolated H atoms placed at the positions ± $0.7a_0$ (area under the solid and dashed functions equals to 1.0); the overlap probability function – dotted; right – molecular orbital probabilities for H_2 molecule with internuclear separation $1.4a_0$; solid – for bonding MO, dashed – for antibonding MO

The individual monoatomic components $P_A^{\mathrm{ch}}(z_1)$, $P_B^{\mathrm{ch}}(z_1)$, and the diatomic $P_{AB}^{\mathrm{ov}}(z_1)$ component are shown in Fig. 10 – left. The MO probability functions $P_\pm(z_1)$ are displayed in Fig. 10 – right.

Amplitudes of State Functions

The molecular state (wave) functions in the H_2 molecule depend upon the coordinates of two electrons, so that we need to map the two-dimensional functions $\Theta(r_1, r_2)$. Let us recapitulate the expressions for the spatial parts of the molecular wave functions (state functions) (Eqs. (161)–(164)).

$$\Theta_1\{{}^1\Sigma_\mathrm{g}(\sigma_\mathrm{g}^2)\} = \varphi_+(r_1)\varphi_+(r_2) \tag{161}$$

$$\Theta_2\{{}^1\Sigma_\mathrm{g}(\sigma_\mathrm{u}^2)\} = \varphi_-(r_1)\varphi_-(r_2) \tag{162}$$

$$\Theta_3\{{}^3\Sigma_\mathrm{u}(\sigma_\mathrm{g}^\uparrow\sigma_\mathrm{u}^\uparrow)\} = [\varphi_+(r_1)\varphi_-(r_2) - \varphi_+(r_2)\varphi_-(r_1)]/\sqrt{2} \tag{163}$$

$$\Theta_6\{{}^1\Sigma_\mathrm{u}(\sigma_\mathrm{g}^\downarrow\sigma_\mathrm{u}^\uparrow; \sigma_\mathrm{g}^\uparrow\sigma_\mathrm{u}^\downarrow)\} = [\varphi_+(r_1)\varphi_-(r_2) + \varphi_+(r_2)\varphi_-(r_1)]/\sqrt{2} \tag{164}$$

Using the results of the previous paragraph we can start mapping these functions in one dimension, $\Theta(z_1, z_2 = z_1)$. This is permitted for electrons having opposite spin (electron correlation is not included in the MO method). The results are visualized in Fig. 11.

It can be seen that the ground state ${}^1\Sigma_\mathrm{g}(\sigma_\mathrm{g}^2)$, in which two electrons of an opposite spin occupy the bonding molecular orbital, is bonding in nature: there exists a concentration of electron charge density in the internuclear region. The excited state ${}^1\Sigma_\mathrm{g}(\sigma_\mathrm{u}^2)$, in which two electrons occupy the antibonding MO, is antibonding at the internuclear distance of $R_{AB} = 1.4a_0$. Analogously, the excited state ${}^1\Sigma_\mathrm{u}(\sigma_\mathrm{g}^\uparrow\sigma_\mathrm{u}^\downarrow; \sigma_\mathrm{u}^\uparrow\sigma_\mathrm{g}^\downarrow)$ is antibonding; the subscript *u* means that the wave function is an odd function of space coordinates and thus alters its sign at the center of

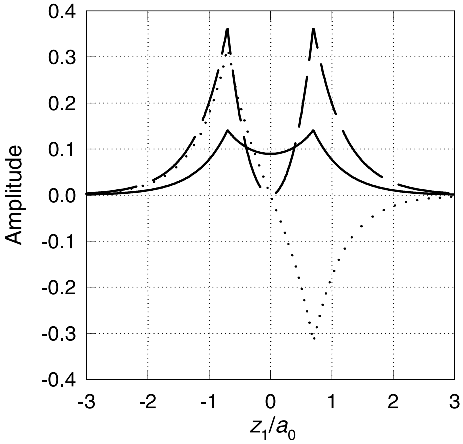
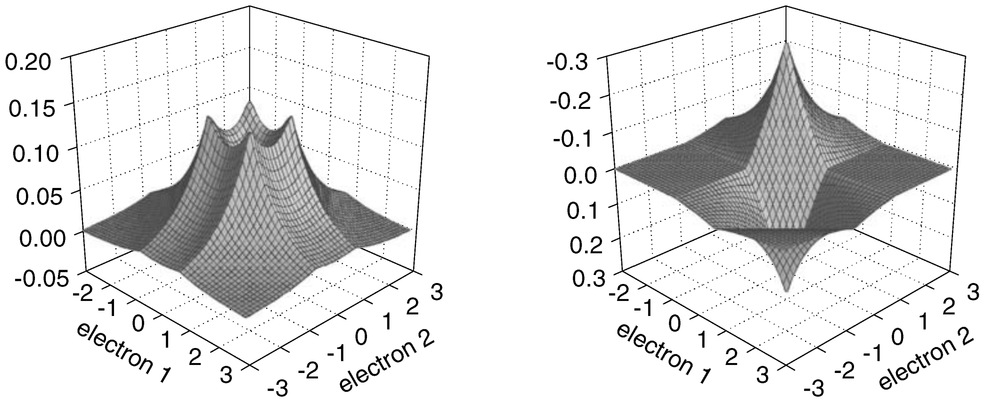


Fig. 11. The amplitude of the wave function for H_2 along the coordinate $z_1 = z_2$ ($u = \phi = 0$): solid – ${}^1\Sigma_\mathrm{g}(\sigma_\mathrm{g}^2)$; dashed – ${}^1\Sigma_\mathrm{g}(\sigma_\mathrm{u}^2)$; dotted – ${}^1\Sigma_\mathrm{u}(\sigma_\mathrm{g}^\uparrow\sigma_\mathrm{u}^\downarrow; \sigma_\mathrm{u}^\uparrow\sigma_\mathrm{g}^\downarrow)$; zero – ${}^3\Sigma_\mathrm{u}$

the molecule. The last wave function ${}^3\Sigma_u(\sigma_g^\uparrow\sigma_u^\uparrow)$ vanishes exactly along the path $\Theta(z_1, z_2 = z_1)$ in accordance with the *Pauli* principle: the occurrence of two electrons having the same spin at the same point in space is not allowed.

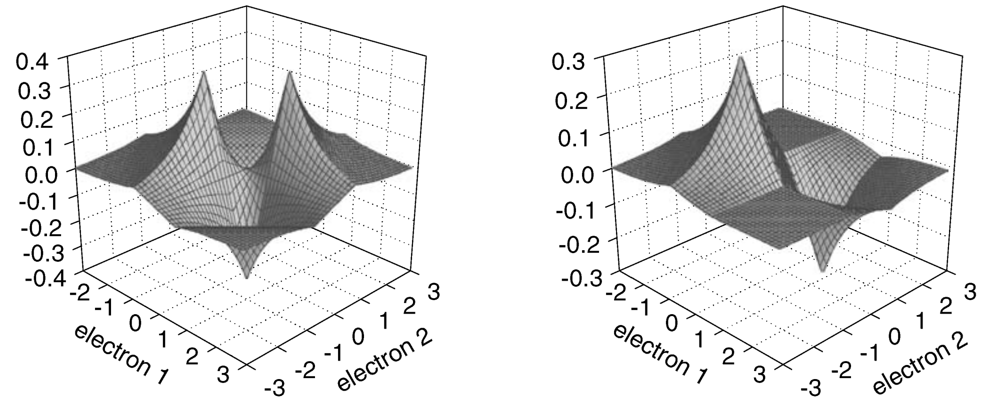
Changing to a three-dimensional graphic brings more information about the properties of the molecular wave functions. The wave functions are mapped as $\Theta(z_1, z_2)$ for $u_1 = u_2 = \phi_1 = \phi_2 = 0$ and displayed in Fig. 12.

The wave function of the ground state ${}^1\Sigma_g(\sigma_g^2)$ is symmetric with respect to the interchange of coordinates of electrons: $\Theta_1(z_1, z_2) = \Theta_1(z_2, z_1)$. Its cross-section



spatial function $\Theta_1\{{}^1\Sigma_g(\sigma_g^2)\}$;
symmetric, as $\Theta_1(1,2) = +\Theta_1(2,1)$;
non-correlated (the maximum occurs at $z_1 = z_2$)

spatial function $\Theta_3\{{}^3\Sigma_u(\sigma_g^\uparrow\sigma_u^\uparrow)\}$;
antisymmetric, as $\Theta_3(1,2) = -\Theta_3(2,1)$;
correlated (the maximum occurs at $z_1 \neq z_2$)



spatial function $\Theta_2\{{}^1\Sigma_g(\sigma_u^2)\}$;
symmetric, as $\Theta_2(1,2) = +\Theta_2(2,1)$;
non-correlated (the maximum occurs at $z_1 = z_2$)

spatial function $\Theta_6\{{}^1\Sigma_u(\sigma_g^\downarrow\sigma_u^\uparrow;\sigma_g^\uparrow\sigma_u^\downarrow)\}$;
symmetric, as $\Theta_6(1,2) = +\Theta_6(2,1)$;
non-correlated (the maximum occurs at $z_1 = z_2$)

Fig. 12. Amplitudes of the wave functions for H_2 along the z-coordinates of two electrons according to the MO method

for $z_1 = z_2$ is identical with the function displayed in Fig. 11. The required antisymmetry of the total molecular wave function is provided by its spin part. The same symmetry properties exhibit the remaining spatial wave functions for the singlet states. On the contrary, the spatial wave function for the triplet state is antisymmetric with respect to the electron coordinate: $\Theta_3(z_1, z_2) = -\Theta_3(z_2, z_1)$. The corresponding spin function is symmetric.

The MO Method for the Dihydrogen Anion

The molecular ion H_2^- contains two nuclei (*A* and *B*) and three electrons (1 to 3). Its Hamiltonian is written as follows (Eq. (165)).

$$\begin{aligned}\hat{H} &= \hat{V}_{AB} + \sum_{i=1}^{3} \hat{T}_i + \sum_{i=1}^{3}\sum_{A=1}^{2} \hat{V}_{iA} + \sum_{i=1}^{3}\sum_{j>i}^{3} \hat{V}_{ij} \\ &= \hat{h}_0 + \hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \hat{V}_{12} + \hat{V}_{13} + \hat{V}_{23} \end{aligned} \tag{165}$$

The number of electron configurations is given by the formula $n = \binom{4}{3} = 4$. The three-electron wave function is constructed in the form of a *Slater* determinant containing three occupied molecular spinorbitals (Eq. (166)) where only two molecular orbitals, φ_1 and φ_2, are involved.

$$\Psi_1(1,2,3) = \hat{A}\{\varphi_1(1)\alpha(1) \cdot \varphi_1(2)\beta(2) \cdot \varphi_2(3)\alpha(3)\} \tag{166}$$

These are constructed *via* LCAO of a pair of 1s basis set functions and they have the symmetry σ_g and σ_u, respectively (Eqs. (167) and (168)).

$$\varphi_1(\sigma_g) = N_1(\psi_A + \psi_B) = (2 + 2S_{AB})^{-1/2}(\psi_A + \psi_B) \tag{167}$$

$$\varphi_2(\sigma_u) = N_2(\psi_A - \psi_B) = (2 - 2S_{AB})^{-1/2}(\psi_A - \psi_B) \tag{168}$$

The symmetry of the ground-state wave function Ψ_1 is $^2\Sigma_u$ and for the excited-state wave function Ψ_2 it is $^2\Sigma_g$ (see Fig. 13). Each wave function is (spin) doubly degenerate. The symmetry of the ground-state wave function follows from the direct products of the irreducible representations of the molecular spinorbitals contained in the electron configuration $\sigma \otimes \sigma \otimes \sigma = \Sigma$. For the ground state there is $\sigma_g^2\sigma_u^1$ and therefore $g \otimes g \otimes u = u$. The electron configuration of the first excited state is $\sigma_g^1\sigma_u^2$ and thus $g \otimes u \otimes u = g$.

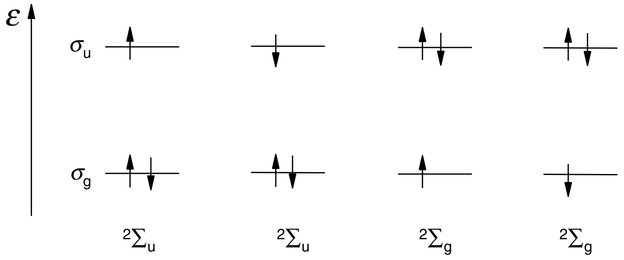


Fig. 13. Four electron configurations of the H_2^- system

The *Slater* rules can be used for the expression of the total molecular energy (Eq. (169)) where η_i is the spin function (α or β) for the i-th molecular orbital φ_i. Using this formula the energy of the electron configuration $\sigma_g^1\sigma_u^2$ is given by Eq. (170) and for the electron configuration $\sigma_g^1\sigma_u^2$ by Eq. (171).

$$\begin{aligned}
E &= h_0 + \sum_{i=1}^{3}\langle\varphi_i(1)|\hat{h}_1|\varphi_i(1)\rangle + \sum_{i=1}^{3}\sum_{j>i}^{3}[\langle\varphi_i(1)\varphi_j(2)|\hat{g}_{12}|\varphi_i(1)\varphi_j(2)\rangle \\
&\quad - \langle\varphi_i(1)\varphi_j(2)|\hat{g}_{12}|\varphi_i(2)\varphi_j(1)\rangle\langle\eta_i(1)|\eta_j(1)\rangle\langle\eta_i(1)|\eta_j(1)\rangle] \\
&= h_0 + \sum_{i=1}^{3} h_{ii} + \sum_{i=1}^{3}\sum_{j<i}^{3}(J_{ij} - K_{ij}\delta_{si,sj})
\end{aligned} \tag{169}$$

$$\begin{aligned}
E_1(^2\Sigma_u) &= h_0 + h_{11} + h_{22} + h_{33} + J_{12} - K_{12}\cancel{\langle\alpha|\beta\rangle}\,\cancel{\langle\alpha|\beta\rangle} \\
&\quad + J_{13} - K_{13}\langle\alpha|\alpha\rangle\langle\alpha|\alpha\rangle + J_{23} - K_{23}\cancel{\langle\beta|\alpha\rangle}\,\cancel{\langle\alpha|\beta\rangle} \\
&= h_0 + 2h_{11} + h_{33} + J_{12} + 2J_{13} - K_{13}
\end{aligned} \tag{170}$$

$$\begin{aligned}
E_2(^2\Sigma_g) &= h_0 + h_{11} + h_{33} + h_{44} + J_{13} - K_{13}\langle\alpha|\alpha\rangle\langle\alpha|\alpha\rangle \\
&\quad + J_{14} - K_{14}\cancel{\langle\alpha|\beta\rangle}\,\cancel{\langle\beta|\alpha\rangle} + J_{34} - K_{34}\cancel{\langle\alpha|\beta\rangle}\,\cancel{\langle\beta|\alpha\rangle} \\
&= h_0 + h_{11} + 2h_{33} + 2J_{13} - K_{13} + J_{34}
\end{aligned} \tag{171}$$

The one-electron and the relevant two-electron integrals among molecular orbitals we already met in the problem of the H_2 molecule. Thus the final energy formulae become Eqs. (172) and (173)

$$\begin{aligned}
E_1(^2\Sigma_u) &= V_{AB} \\
&\quad + 2\frac{t_0 + \alpha_0 + (t + \beta)}{1 + s} + 2\frac{\alpha + \beta}{1 + s} + \frac{t_0 + \alpha_0 - (t + \beta)}{1 - s} + \frac{\alpha - \beta}{1 - s} \\
&\quad + \frac{j_0 + j + 2k + 4h}{2(1 + s)^2} + 2\frac{j_0 + j - 2k}{2(1 + s)(1 - s)} - \frac{j_0 - j}{2(1 + s)(1 - s)}
\end{aligned} \tag{172}$$

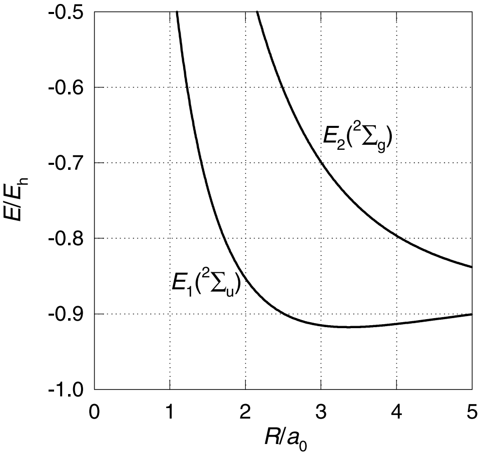


Fig. 14. Energy of lowest states for H_2^- by the MO method

Table 11. Calculated bonding characteristics for H_2^- ion by the MO method

Method		E_0/E_h	R_0/a_0	$\langle V\rangle/\langle T\rangle$
MO	$a = 1.0$	-0.91760	3.365	-1.62088
	$a_{opt} = 0.796$	-0.97411	3.472	-1.99985

$$E_2(^2\Sigma_g) = V_{AB} + \frac{t_0+\alpha_0+(t+\beta)}{1+s} + \frac{\alpha+\beta}{1+s} + 2\frac{t_0+\alpha_0-(t+\beta)}{1-s} + 2\frac{\alpha-\beta}{1-s} + \frac{j_0+j+2k-4h}{2(1-s)^2} + 2\frac{j_0+j-2k}{2(1+s)(1-s)} - \frac{j_0-j}{2(1+s)(1-s)} \tag{173}$$

The plot of energies E_1 and E_2 as functions of the internuclear distance is shown in Fig. 14 and the calculated equilibrium data are listed in Table 11.

The VB Method for the Dihydrogen Molecule

Limited VB Method

Within the valence bond method the spatial part of the electronic wave function is approximated by the linear combination of two product functions (Eq. (174)) where each of them is represented by a "covalent structure" describing the ground state of the hydrogen atom (Eqs. (175) and (176)).

$$\Theta(1,2) = C_1\Omega_1 + C_2\Omega_2 \tag{174}$$

$$\Omega_1 = \psi_A(1)\psi_B(2) \tag{175}$$

$$\Omega_2 = \psi_A(2)\psi_B(1) \tag{176}$$

The coefficients C_1 and C_2 can be determined by the linear variation method. However, the product function Φ_1 and Φ_2 should be equivalent (as an effect of the symmetry) and thus $|C_1| = |C_2|$ holds true. For the spatial part of the VB functions Eqs. (177) and (178) can be directly written where the overlap integral of atomic orbitals is $S_{AB} \equiv \langle\psi_A(1)|\psi_B(1)\rangle$. The normalization constant is to be determined from $\langle\Theta_\pm|\Theta_\pm\rangle = 1$ yielding $N_\pm = [2(1 \pm S_{AB}^2)]^{-1/2}$.

$$\Theta_+ \equiv \Theta_1(^1\Sigma_g) = N_+(\Omega_1 + \Omega_2) = [2(1 + S_{AB}^2)]^{-1/2}(\Omega_1 + \Omega_2) \tag{177}$$

$$\Theta_- \equiv \Theta_2(^3\Sigma_u) = N_-(\Omega_1 - \Omega_2) = [2(1 - S_{AB}^2)]^{-1/2}(\Omega_1 - \Omega_2) \tag{178}$$

The mean value of the total energy is given by Eq. (179).

$$\begin{aligned} E_\pm &= \langle\Psi_\pm|\hat{H}|\Psi_\pm\rangle = \langle\Theta_\pm|\hat{H}|\Theta_\pm\rangle\langle\eta|\eta\rangle = [2(1 \pm S_{AB}^2)]^{-1}\langle\Omega_1 \pm \Omega_2|\hat{H}|\Omega_1 \pm \Omega_2\rangle \\ &= [2(1 \pm S_{AB}^2)]^{-1}[\langle\Omega_1|\hat{H}|\Omega_1\rangle + \langle\Omega_2|\hat{H}|\Omega_2\rangle \pm 2\langle\Omega_1|\hat{H}|\Omega_2\rangle] \\ &= (1 \pm S_{AB}^2)^{-1}[\langle\psi_A(1)\psi_B(2)|\hat{H}|\psi_A(1)\psi_B(2)\rangle \pm \langle\psi_A(1)\psi_B(2)|\hat{H}|\psi_A(2)\psi_B(1)\rangle] \end{aligned} \tag{179}$$

Using the explicit form of the Hamiltonian we have Eq. (180) and these 16 terms are rewritten as shown by Eq. (181).

$$\begin{aligned}E_\pm = (1 \pm S_{AB}^2)^{-1}[&\langle\psi_A(1)\psi_B(2)|\hat{T}_1 + \hat{T}_2 + \hat{V}_{A1} + \hat{V}_{A2} + \hat{V}_{B1} + \hat{V}_{B2} + \hat{V}_{12}\\ &+ \hat{V}_{AB}|\psi_A(1)\psi_B(2)\rangle\\ &\pm \langle\psi_A(1)\psi_B(2)|\hat{T}_1 + \hat{T}_2 + \hat{V}_{A1} + \hat{V}_{A2} + \hat{V}_{B1} + \hat{V}_{B2} + \hat{V}_{12} + \hat{V}_{AB}|\psi_A(2)\psi_B(1)\rangle]\end{aligned} \tag{180}$$

$$\begin{aligned}E_\pm = (1 \pm S_{AB}^2)^{-1}[&T_{AA}S_{BB} + T_{BB}S_{AA} + J_{AA}S_{BB} + J_{AB}S_{AA} + J_{AB}S_{BB} + J_{BB}S_{AA}\\ &+ J_{AABB} + V_{AB}S_{AA}S_{BB} \pm (2T_{AB}S_{AB} + 4K_{AB}S_{AB} + K_{ABAB} + V_{AB}S_{AB}^2)]\end{aligned} \tag{181}$$

The energy formula becomes more transparent when the simplified notation is used for the molecular integrals according to Table 5 (Eq. (182)).

$$E_\pm = V_{AB} + \frac{[2(t_0 + \alpha_0) \pm 2(t + \beta)s] + 2(\alpha \pm \beta s) + j \pm k}{1 \pm s^2} \tag{182}$$

If we apply exactly the hydrogen atom 1s orbitals (with the orbital exponent $a = 1$) then the following identities are fulfilled (Eqs. (183) and (184)).

$$t_0 + \alpha = \langle\psi_A(1)|\hat{T}_1 + \hat{V}_{A1}|\psi_A(1)\rangle = E_0 \tag{183}$$

$$t + \beta = \langle\psi_A(1)|\hat{T}_1 + \hat{V}_{B1}|\psi_B(1)\rangle = E_0 s \tag{184}$$

Consequently the energies of the two molecular states simplify to Eq. (185).

$$E_\pm = 2E_0 + V_{AB} + \frac{2(\alpha \pm \beta s) + j \pm k}{1 \pm s^2} \tag{185}$$

Having the molecular integrals at our disposal, the plot of the molecular energy is possible (Fig. 15). On lowering R the molecular energy E_+ passes through a

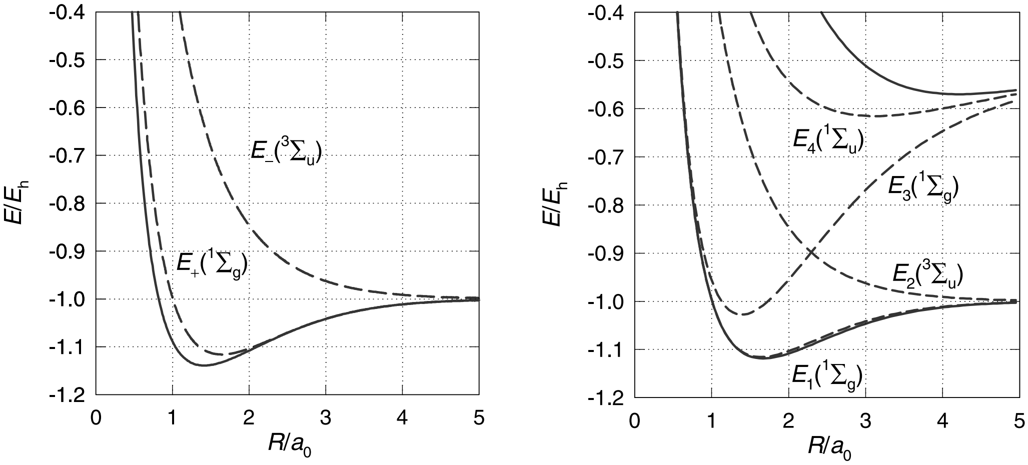


Fig. 15. Left: energy of the H_2 molecule by the LVB method; dashed – orbital exponent $a = 1.0$, solid – a optimized for each R; right: comparison of the LVB (dashed) and CVB methods for H_2; $a = 1$, solid – $E_a(^1\Sigma_g)$ and $E_c(^1\Sigma_g)$ states according to the CVB method

Table 12. Calculated bonding characteristics for H_2 molecule

Method		E_0/E_h	R_0/a_0	$\langle V\rangle/\langle T\rangle$
1. LVB	$a = 1.0$	-1.11597	1.644	-2.33216
	$a_{opt} = 1.166$	-1.13908	1.415	-2.00022
2. CVB	$a = 1.0$	-1.11865	1.669	
	$a_{opt} = 1.195$	-1.14794	1.430	
3. Experimental		-1.17447	1.401	

minimum that corresponds to the equilibrium state. The second solution E_-, on the contrary, describes a non-bonding state whose energy is always above $2E_0 = -E_h$. The two solutions differ from each other in the sign of the β, k, and s integrals in the energy formula.

The calculated bonding characteristics are collected in Table 12. It can be seen that the variation of the orbital exponent leads to lowering of the energy and also satisfies the virial theorem at the equilibrium distance. The existence of the chemical bond, however, is determined by the increase of the kinetic energy and decrease of the potential energy, as it follows from the virial theorem. It is not associated with the presence of the resonance and exchange integrals.

Complete VB Method

The VB method can be improved by including more terms, *i.e.* "structures" into the molecular wave function. Within the basis set of 1s functions, in addition to "covalent structures", also the "ionic structures" can be considered (Eqs. (186) and (187)).

$$\Omega_3 = \psi_A(1)\psi_A(2) \tag{186}$$

$$\Omega_4 = \psi_B(1)\psi_B(2) \tag{187}$$

The ionic structures refer to a situation when both electrons would be situated on one atom. The molecular wave function is more flexible as it is expanded over four product functions (Eq. (188)).

$$\Theta(1,2) = C_1\Omega_1 + C_2\Omega_2 + C_3\Omega_3 + C_4\Omega_4 \tag{188}$$

The linear variation method implies that the following secular Eq. (189) is to be obeyed.

$$\det\begin{pmatrix} h_{11} - E & h_{12} - Es^2 & h_{13} - Es & h_{13} - Es \\ h_{12} - Es^2 & h_{11} - E & h_{13} - Es & h_{13} - Es \\ h_{13} - Es & h_{13} - Es & h_{33} - E & h_{34} - Es^2 \\ h_{13} - Es & h_{13} - Es & h_{34} - Es^2 & h_{33} - E \end{pmatrix} = 0 \tag{189}$$

Using the symmetry considerations, according to which $|C_1| = |C_2|$ and $|C_3| = |C_4|$, it can be rewritten as Eq. (190) where only one independent parameter λ occurs.

$$\begin{aligned} \Theta(1,2) &= N[(\Omega_1 + \Omega_2) + \lambda(\Omega_3 + \Omega_4)] \\ &= N\{[\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)] + \lambda[\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)]\} \end{aligned} \tag{190}$$

Because of the symmetry arguments, only $\Theta_a(^1\Sigma_g)$ and $\Theta_c(^1\Sigma_g)$ arise from the mixing of the configurations (Eqs. (191)–(194)).

$$\Theta_a(^1\Sigma_g) = N_a[(\Omega_1 + \Omega_2) + \lambda_a(\Omega_3 + \Omega_4)] \tag{191}$$

$$\Theta_b(^3\Sigma_u) = \Theta_2(^3\Sigma_u) = N_b(\Omega_1 - \Omega_2) = (\Omega_1 - \Omega_2)[2(1 - s^2)]^{-1/2} \tag{192}$$

$$\Theta_c(^1\Sigma_g) = N_c[(\Omega_1 + \Omega_2) + \lambda_c(\Omega_3 + \Omega_4)] \tag{193}$$

$$\Theta_d(^1\Sigma_u) = \Theta_4(^1\Sigma_u) = N_c[(\Omega_3 - \Omega_4)] = (\Omega_3 - \Omega_4)[2(1 - s^2)]^{-1/2} \tag{194}$$

The constant N can be determined from the normalization condition.

The matrix elements h_{11}, h_{22}, and h_{12} are already known from the LVB; the remaining matrix elements among the product functions are given by Eqs. (195)–(197).

$$h_{33} = \langle \Omega_3|\hat{H}|\Omega_3\rangle = \langle \Omega_4|\hat{H}|\Omega_4\rangle = 2(t_0 + \alpha_0) + 2\alpha + j_0 + V_{AB} \tag{195}$$

$$h_{34} = \langle \Omega_3|\hat{H}|\Omega_4\rangle = 2ts + 4\beta s + k + V_{AB}s^2 \tag{196}$$

$$\begin{aligned} h_{13} &= \langle \Omega_1|\hat{H}|\Omega_3\rangle = \langle \Omega_2|\hat{H}|\Omega_3\rangle = \langle \Omega_1|\hat{H}|\Omega_4\rangle = \langle \Omega_2|\hat{H}|\Omega_4\rangle \\ &= 2(t_0 + \alpha_0)s + t + \beta + \alpha s + \beta + h + V_{AB}s \end{aligned} \tag{197}$$

A truncated problem within the "ionic structures" (Eq. (198)) has the solutions shown by Eq. (199) and explicitly by Eq. (200).

$$\det\begin{pmatrix} h_{33} - E & h_{34} - Es^2 \\ h_{34} - Es^2 & h_{33} - E \end{pmatrix} = 0 \tag{198}$$

$$E_{3,4} = \frac{h_{33} \pm h_{34}}{1 \pm s^2} \tag{199}$$

$$E_3(^1\Sigma_g) = V_{AB} + 2\frac{t_0 + \alpha_0 + (t + \beta)s}{1 + s^2} + \frac{2\alpha + j_0 + 2\beta s + k}{1 + s^2} \tag{200}$$

$$E_4(^1\Sigma_u) = V_{AB} + 2\frac{t_0 + \alpha_0 - (t + \beta)s}{1 - s^2} + \frac{2\alpha + j_0 - 2\beta s - k}{1 - s^2} \tag{201}$$

Then the energy separation of the two $^1\Sigma_g$ states before their "interaction" or mixing is given by Eq. (202).

$$\Delta = E_3 - E_1 = \frac{j_0 - j}{1 + s^2} > 0 \tag{202}$$

The off-diagonal matrix element connecting these states can be evaluated with the help of the wave functions (Eqs. (203) and (204)) as follows from Eq. (205) and the non-orthogonality integral is given by Eq. (206).

$$\Theta_1(^1\Sigma_g) = (\Omega_1 + \Omega_2)[2(1 + s^2)]^{-1/2} \tag{203}$$

$$\Theta_3(^1\Sigma_g) = (\Omega_3 + \Omega_4)[2(1 + s^2)]^{-1/2} \tag{204}$$

$$H_{13} = \langle \Theta_1 | \hat{H} | \Theta_3 \rangle = 4h_{13}[2(1+s^2)]^{-1} \tag{205}$$

$$S_{13} = \langle \Theta_1 | \Theta_3 \rangle = 4s[2(1+s^2)]^{-1} \tag{206}$$

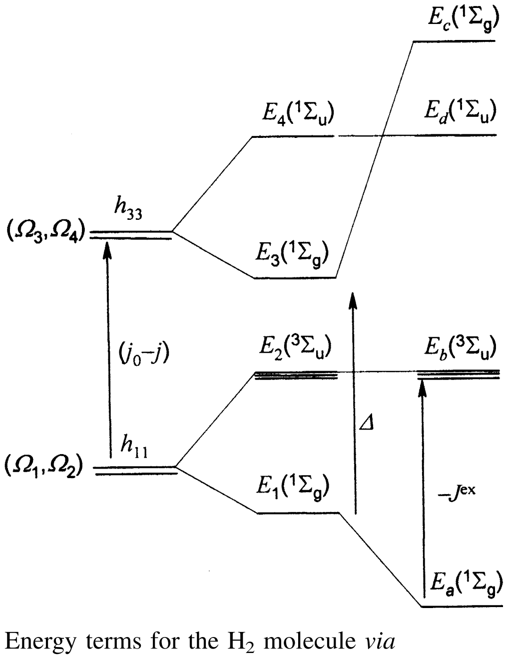
The secular equation in the new basis set of the symmetry adapted VB-functions Θ_1, Θ_2, Θ_3, and Θ_4 is shown by Eq. (207) and hence the quadratic Eq. (208) determines the two energies of the ${}^1\Sigma_g$ states (Eq. (209)).

$$\det \begin{pmatrix} E_1 - E & 0 & H_{13} - S_{13}E & 0 \\ 0 & E_2 - E & 0 & 0 \\ H_{13} - S_{13}E & 0 & E_3 - E & 0 \\ 0 & 0 & 0 & E_4 - E \end{pmatrix} = 0 \tag{207}$$

$$(E_1 - E)(E_3 - E) - (H_{13} - S_{13}E)^2 = 0 \tag{208}$$

$$E_{a,c} = \frac{E_3 + E_1 - 2H_{13}S_{13} \pm \sqrt{(E_3 - E_1)^2 + 4(H_{13} - S_{13}E_3)(H_{13} - S_{13}E_1)}}{2(1 - S_{13}^2)} \tag{209}$$

Table 13. Survey of the VB formulae for the H_2 molecule



Energy terms for the H_2 molecule *via* the VB method

Limited VB	Complete VB
Product functions	
$\Omega_1 = \psi_A(1)\psi_B(2)$ $\Omega_2 = \psi_B(1)\psi_A(2)$	$\Omega_3 = \psi_A(1)\psi_A(2)$ $\Omega_4 = \psi_B(1)\psi_B(2)$
Matrix elements $h_{ij} = \langle \Phi_i \vert \hat{H} \vert \Phi_j \rangle$	
$h_{11} = h_{22}$ $= 2(t_0 + \alpha_0) + 2\alpha + j + V_{AB}$ $h_{12} = 2ts + 4\beta s + k + V_{AB}s^2$	$h_{33} = h_{44}$ $= 2(t_0 + \alpha_0) + 2\alpha + j_0 + V_{AB}$ $h_{34} = 2ts + 4\beta s + k + V_{AB}s^2$
Symmetry adapted functions	
${}^1\Sigma_g, {}^3\Sigma_u$: $\Theta_{1,2} = [2(1 \pm s^2)]^{-1/2} \times (\Omega_1 \pm \Omega_2)$	${}^1\Sigma_g, {}^1\Sigma_u$: $\Theta_{3,4} = [2(1 \pm s^2)]^{-1/2} \times (\Omega_3 \pm \Omega_4)$
VB energies	
$E_{1,2} = \frac{h_{11} \pm h_{12}}{1 \pm s^2} = V_{AB} + 2\frac{t_0 + \alpha_0 \pm (t+\beta)s}{1 \pm s^2} + \frac{2\alpha + j \pm 2\beta s \pm k}{1 \pm s^2}$	$E_{3,4} = \frac{h_{33} \pm h_{34}}{1 \pm s^2} = V_{AB} + 2\frac{t_0 + \alpha_0 \pm (t+\beta)s}{1 \pm s^2} + \frac{2\alpha + j_0 \pm 2\beta s \pm k}{1 \pm s^2}$
Interaction matrix elements $H_{ij} = \langle \Theta_i \vert \hat{H} \vert \Theta_j \rangle$	
	$H_{13} = \frac{2h_{13}}{1+s^2}; S_{13} = \frac{2s}{1+s^2}$ $h_{13} = (t_0 + \alpha_0)s + t + \alpha s + 2\beta + h + V_{AB}s$

The survey of the LVB and CVB formulae is presented in Table 13. The corresponding energies are plotted in Fig. 15. It can be seen that the CVB method improves the LVB approximation only insignificantly for the ground state. This means that the LVB function already includes a substantial part of the correlation energy.

Amplitude of the Wave Function

Let us visualize the amplitudes of the molecular state functions for the H_2 molecule constructed on the basis of the LVB method. The spatial wave functions in the MO method expressed in terms of the LVB functions are given by Eqs. (210)–(213).

$$\Theta_1^{\mathrm{MO}}(^1\Sigma_{\mathrm{g}}) = [2(1+s)]^{-1}[(\Omega_1+\Omega_2)+(\Omega_3+\Omega_4)] = N_1(\Theta_1^{\mathrm{VB}}+\Theta_3^{\mathrm{VB}}) \tag{210}$$

$$\Theta_2^{\mathrm{MO}}(^1\Sigma_{\mathrm{g}}) = [2(1-s)]^{-1}[(\Omega_1+\Omega_2)-(\Omega_3+\Omega_4)] = N_2(\Theta_1^{\mathrm{VB}}-\Theta_3^{\mathrm{VB}}) \tag{211}$$

$$\Theta_3^{\mathrm{MO}}(^3\Sigma_{\mathrm{u}}) = -[2(1-s^2)]^{-1/2}[\Omega_1-\Omega_2] = -\Theta_2^{\mathrm{VB}} \tag{212}$$

$$\Theta_6^{\mathrm{MO}}(^1\Sigma_{\mathrm{u}}) = [2(1-s^2)]^{-1/2}[\Omega_3-\Omega_4] = \Theta_4^{\mathrm{VB}} \tag{213}$$

Now we can compare the spatial wave functions of the $^1\Sigma_{\mathrm{g}}$ symmetry according to the LVB method and the MO method: the MO method includes the "ionic structures" as well but with the same weight as the "covalent structures" Apparently this overestimation of the "ionic structures" is an intrinsic defect of the MO method that is improved through CI.

The LVB wave functions in the H_2 molecule are given through combinations (Eqs. (214)–(217)) where the product functions $\Omega_1(r_1,r_2)=\psi_A(r_1)\psi_B(r_2)$, $\Omega_2(r_1,r_2)=\psi_A(r_2)\psi_B(r_1)$, $\Omega_3(r_1,r_2)=\psi_A(r_1)\psi_A(r_2)$, and $\Omega_4(r_1,r_2)=\psi_B(r_1)\psi_B(r_2)$ depend upon the coordinates of two electrons.

$$\Theta_1\{^1\Sigma_{\mathrm{g}}(\Omega_1,\Omega_2)\} = [\Omega_1(r_1,r_2)+\Omega_2(r_1,r_2)]/[2(1+s^2)]^{1/2} \tag{214}$$

$$\Theta_2\{^1\Sigma_{\mathrm{g}}(\Omega_3,\Omega_4)\} = [\Omega_3(r_1,r_2)+\Omega_4(r_1,r_2)]/[2(1+s^2)]^{1/2} \tag{215}$$

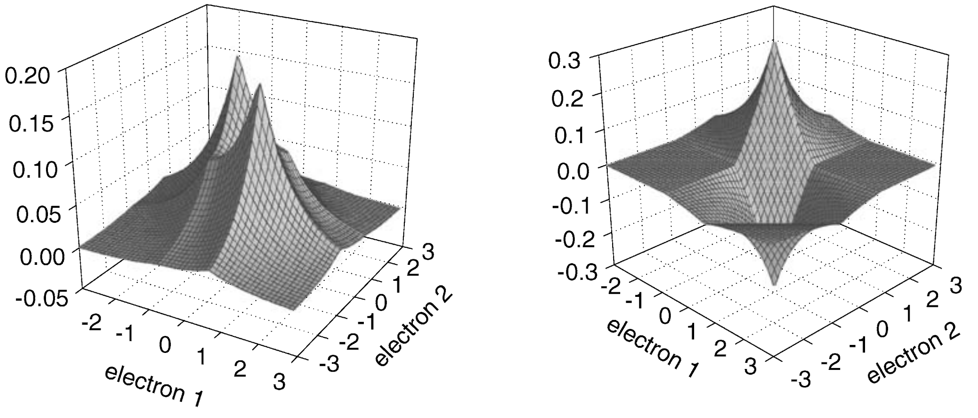
$$\Theta_3\{^3\Sigma_{\mathrm{u}}(\Omega_1,\Omega_2)\} = [\Omega_1(r_1,r_2)-\Omega_2(r_1,r_2)]/[2(1-s^2)]^{1/2} \tag{216}$$

$$\Theta_4\{^1\Sigma_{\mathrm{u}}(\Omega_3,\Omega_4)\} = [\Omega_3(r_1,r_2)-\Omega_4(r_1,r_2)]/[2(1-s^2)]^{1/2} \tag{217}$$

The mapping of the spatial functions along a pair of coordinates $\{z_1,z_2\}$ for fixed $\{u_1=u_2=\phi_1=\phi_2=0\}$ is shown in Fig. 16. The spatial wave functions for the singlet states are symmetric with respect to the electron coordinate interchange, whereas that for the triplet state is antisymmetric.

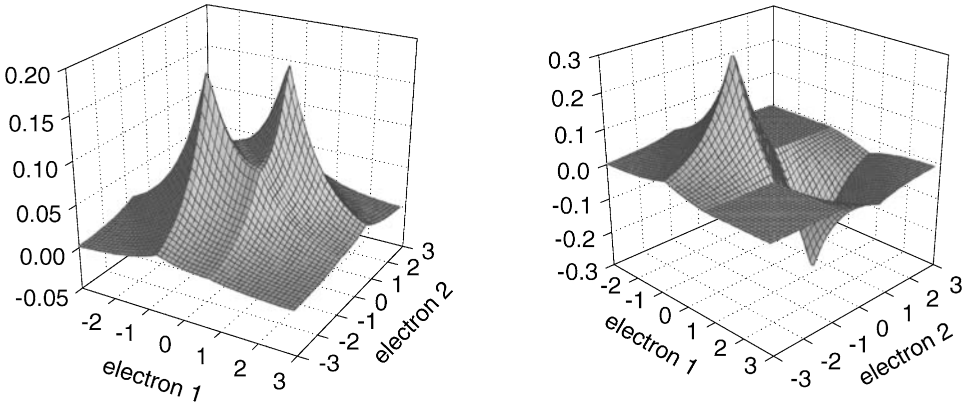
Except the irrelevant sign, the wave function $\Theta_3^{\mathrm{VB}}\{^3\Sigma_{\mathrm{u}}(\Omega_1,\Omega_2)\}$ matches exactly its MO counterpart $\Theta_3^{\mathrm{MO}}\{^3\Sigma_{\mathrm{u}}(\sigma_{\mathrm{g}}^{\uparrow}\sigma_{\mathrm{u}}^{\uparrow})\}$. Analogously, the wave function $\Theta_4^{\mathrm{VB}}\{^1\Sigma_{\mathrm{u}}(\Omega_3,\Omega_4)\}$ equals its MO counterpart $\Theta_6^{\mathrm{MO}}\{^1\Sigma_{\mathrm{u}}(\sigma_{\mathrm{g}}^{\downarrow}\sigma_{\mathrm{u}}^{\uparrow};\sigma_{\mathrm{g}}^{\uparrow}\sigma_{\mathrm{u}}^{\downarrow})\}$.

The ground-state wave function $\Theta_1\{^1\Sigma_{\mathrm{g}}(\Omega_1,\Omega_2)\}$ is constant in the internuclear region along $z_1=z_2$. Notice, just this wave function includes a part of the correlation energy. This is the reason why its amplitude increases when the electrons depart from each other: the maximum of the molecular wave function occurs for $z_1 \neq z_2$.



spatial function $\Theta_1\{{}^1\Sigma_g(\Omega_1,\Omega_2)\}$;
symmetric, as $\Theta_1(1,2) = +\Theta_1(2,1)$;
correlated (the maximum occurs at $z_1 \neq z_2$)

spatial function $\Theta_3\{{}^3\Sigma_u(\Omega_1,\Omega_2)\}$;
antisymmetric, as $\Theta_3(1,2) = -\Theta_3(2,1)$;
correlated (the maximum occurs at $z_1 \neq z_2$)



spatial function $\Theta_2\{{}^1\Sigma_g(\Omega_3,\Omega_4)\}$;
symmetric, as $\Theta_2(1,2) = +\Theta_2(2,1)$;
non-correlated (the maximum occurs at $z_1 = z_2$)

spatial function $\Theta_4\{{}^1\Sigma_u(\Omega_3,\Omega_4)\}$;
symmetric, as $\Theta_4(1,2) = +\Theta_4(2,1)$;
non-correlated (the maximum occurs at $z_1 = z_2$)

Fig. 16. Amplitudes of the wave functions for H_2 along the z-coordinates of two electrons according to the LVB method

In the next stage the configuration interaction can be applied. We need the CI mixing coefficients of the expansion (Eq. (218)) or the CVB coefficients mixing the covalent and ionic structures (Eq. (219)).

$$\Theta_a(1,2) = C_1 \cdot \Theta_1^{\mathrm{MO}} + C_2 \cdot \Theta_2^{\mathrm{MO}} \tag{218}$$

$$\Theta_a(1,2) = C_1 \cdot \Theta_1^{\mathrm{VB}} + C_3 \cdot \Theta_3^{\mathrm{VB}} = N_a[(\Omega_1 + \Omega_2) + \lambda_a(\Omega_3 + \Omega_4)] \tag{219}$$

The linear variation method with orthogonal MO functions yields Eq. (220) and the solution of the secular equation is given by Eq. (221).

$$\begin{pmatrix} H_{11} - E_a & H_{12} \\ H_{12} & H_{22} - E_a \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0 \tag{220}$$

$$E_a = (H_{11} + H_{22})/2 - \{[(H_{11} - H_{22})/2]^2 + H_{12}^2\}^{1/2} \tag{221}$$

We have two unknown mixing coefficients and the energy but only two equations. The third equation is given by the normalization. In order to determine the mixing coefficients we need to exploit the additional Eq. (222).

$$C_2 = \sqrt{1 - C_1^2} \tag{222}$$

Then we get the first independent Eq. (223).

$$(H_{11} - E_a)C_1 + H_{12}\sqrt{1 - C_1^2} = 0 \tag{223}$$

By rearrangement we obtain Eq. (224).

$$|C_1| = \frac{H_{12}}{\sqrt{(H_{11} - E_a)^2 + H_{12}^2}} \tag{224}$$

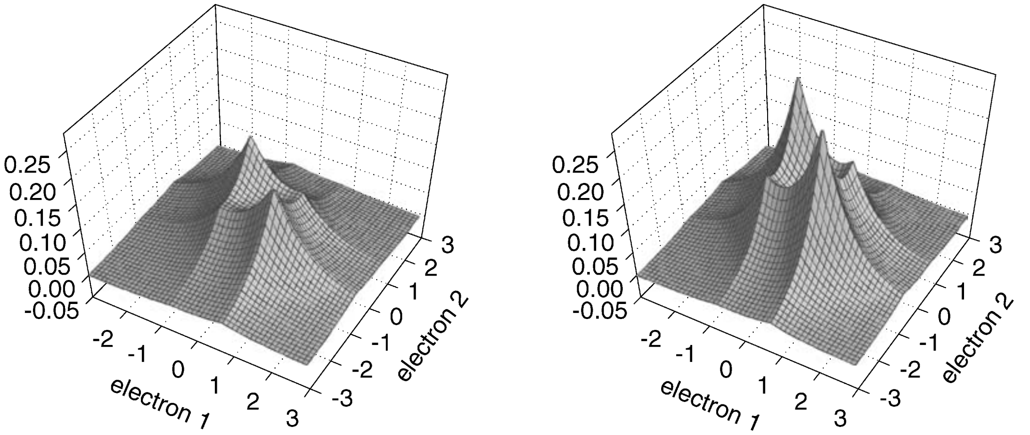
The second Eq. (225) finally yields Eq. (226).

$$H_{12}C_1 + (H_{22} - E_a)C_2 = 0 \tag{225}$$

$$C_2 = -C_1 \frac{H_{12}}{H_{22} - E_a} \tag{226}$$

The phase of the wave functions cannot be determined so that both mixing coefficient can alter their signs without influencing the molecular properties.

The computer program returns the CI mixing coefficients (at $R = 1.44\ a_0$, $a_{\mathrm{opt}} = 1.194$): $C_1 = 0.9933$ and $C_2 = -0.1153$. The amplitude of the molecular wave function is shown in Fig. 17 and it is analysed in Table 14.



Spatial function $\Theta_a\{^1\Sigma_g\}$; $a = 1.0$

Spatial function $\Theta_a\{^1\Sigma_g\}$; $a = 1.195$; CI mixing coefficients 0.9933 and –0.1153

Fig. 17. Amplitudes of the wave functions for H_2 along the z-coordinates of two electrons according to either MO + CI or the CVB methods

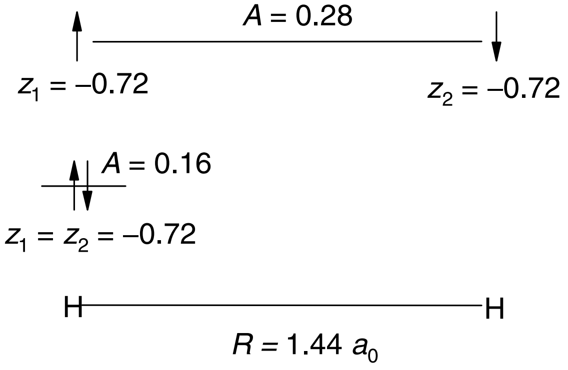


Fig. 18. Electron positions for which the amplitude (A) of the ground-state molecular wave function is maximum

Table 14. Principal features of the ground-state molecular wave function for the H_2 molecule

Function	Feature	Drawback
MO, Θ_1^{MO} Fig. 12	The function is maximum when both electrons are either at the same centre or at the opposite centres.	No electron correlation; two electrons (of opposite spin) can occupy the same space. The "ionic structures" are included with the same weight as the "covalent structures".
VB, Θ_1^{VB} Fig. 16	Dominant part of the electron correlation is included: the function is maximum when both electrons are apart from each other (being at opposite centres).	The wave function is constant in the internuclear region for $z_1 = z_2$. This is an overestimation of the covalent structures.
CI, Θ_a^{CI}, or CVB, Θ_a^{CVB}, Fig. 17	Electron correlation is included: the function is maximum when both electrons are apart from each other (being at opposite centres) – Fig. 18. The wave function is non-constant in the internuclear region.	

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