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QUANTUM MECHANICS OF MANY-ELECTRON SYSTEMS

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1) OBJECTIVE

Obtain solutions of the time-independente Schrödinger equation for polyelectronic systems: atoms containing N electrons,

$$H\Psi\ (1,2,\ldots N;) = E\Psi\ (1,2,\ldots N)$$

and molecules containing N electrons and M nuclei :

$$H\Psi\ (1,2,\ldots N;\ A,B,C,\ldots M) = E\Psi\ (1,2,\ldots N;\ A,B,C,\ldots M)$$

Problem: Analytical solutions are only possible for one-electron atoms and for the H_2^+ molecule within the Born-Oppenheimer approximation.

IS THERE AN ALTERNATIVE TO SOLVING S. E. ?

Yes! Use the variational principle for the S.E.

To find $|\Psi>$ such that the functional

$$E = < \Psi \,|\, H \,|\Psi >$$

is stationary, is absolutely equivalent to solving Schrödinger's equation,

$$H \,|\Psi > = E \,|\Psi >$$

Obs: Stationary meaning that for any infinitesimal variation on the wavefunction, $\delta|\Psi >$, one has $\delta E = 0$

How to make good use of <u>this variational principle?</u>

Guess an approximate form to the exact $|\Psi>$ and use it to calculate the energy, according to the variational principle:

$$E_{ap} = < \Psi_{ap} \mid H \mid \Psi_{ap} >$$

How do we know if $|\Psi_{ap} >$ is a good approximation?

The <u>variational method</u> tells us that for any well behaved function, the computed energy E_{ap} will be greater or equal to the exact energy for the ground-state, E_o, of the system:

$$E_{ap} \geq E_o$$

This method is extremely useful but one must not forget that it derives from a variational principle. Therefore, no matter how approximate $|\Psi_{ap}>$ is, it must satisfy the same conditions imposed to the acceptable solutions of the Schrödinger equation!

What conditions?

a) $|\Psi_{ap}>$ must be well behaved

b) what else ?

2) THE MANY-ELECTRON HAMILTONIAN AND ITS SYMMETRIES

A) Point-group symmetry:

For certain molecules, it is possible to define an operation $\hat{O}$ which exchanges the position of some of the nuclei leaving the hamiltionan unchanged , thus

$$[H, \hat{O}\ ] = 0.$$

The energy of the system is then invariant to this operation and as a consequence, $|\Psi>$, solution of $H\,|\Psi> = E\,|\Psi>$, or $|\Psi_{ap}>$ determined through the variational principle, **must** reflect this symmetry:

$$E_{ap} = <\Psi_{ap} \mid H \mid \Psi_{ap}> \ = \ < \hat{O}\Psi_{ap} \mid H \mid \hat{O}\,\Psi_{ap}>$$

$$H\,\hat{O}|\Psi> = E\,\hat{O}|\Psi>$$

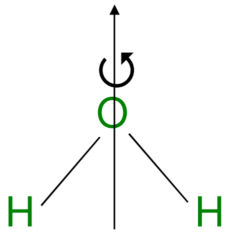
If $|\Psi>$, and consequently $|\Psi_{ap}>$, represents a non-degenerate state of the system, thus one necessarily has:

$$\hat{O}|\Psi> \; = \; \pm |\Psi>$$

and

$$\hat{O}|\Psi_{ap}> \; = \pm |\Psi_{ap}>$$

Ex: H_2O



$E, C_2 , \sigma_v , \sigma_v'$

Because $[H,C_2] = [H,\sigma_v] = [H, \sigma_v'] = 0$, the exact wavefunction, or any approximation to the exact wavefunction representing anyof the electronic states of H_2O, MUST transform like one of the irreducible representations (A_1, A_2, B_1, B_2) of the C_{2v} point group.

Point-group symmetry can be very useful, however, only a very small number of molecules (< 10% of the presently known molecules) exhibit this kind of symmetry.

Is there another type of symmetry ?

YES! There is another type of symmetry which is present in any hamiltonian of a many-electron system, ATOM or MOLECULE!

B) Permutation symmetry

Define P_{ij} as the operator which exchanges electrons *i* and *j* in the hamiltonian of a many-electron system (atom or molecule).

Since electrons are indistinguishable, the permutation leaves the hamiltonian invariant :

$$[H, P_{ij}] = 0 \quad \text{for} \ \forall \ i, j$$

As in the case of the point-group symmetry, the permutation symmetry must also impose some conditions on the wavefunctions describing the many-electron system.

WHICH CONDITIONS ?

The energy must be invariant and therefore :

$$< P_{ij} \Psi |H| P_{ij} \Psi> = E$$

implying that $P_{ij} |\Psi> = \pm |\Psi>$

For a *n*-fold degenerate state, there will be *n* linearly independent wave functions, Ψ_i (r), of the SE with the same eigenvalue as well as a linear combination of such wave functions. Therefore, the action of any such operator $\widehat{P_{ij}}$ can be written as:

$$\widehat{P_{ij}}\,\Psi_i(r) = \sum_{k=1}^{n} \Gamma_{ki}\left(\widehat{P_{ij}}\right) \Psi_k(r) = \Phi\,(r)$$

The permutation operators $\widehat{P_{ij}}$ together with the identity operator, $\hat{E}$, form the symmetric or permutation group. As the invariance of the Hamiltonian requires its eigenvalue equation to be preserved, $\Phi\,(r)$ **must be symmetric or anti-symmetric.**

Remember that if we are using the variational principle, which is absolutely equivalent to solving the S.E., regardless of how approximate the solution to the exact wavefunction is, it MUST satisfy the same conditions of the exact wavefunction.

$$\widehat{P_{ij}}\,|\Psi_{ap}> \;=\pm\,|\Psi_{ap}>$$

IMPORTANT CONCLUSION:

For a quantum system of identical particles, the only acceptable wave functions are those which are symmetric or anti-symmetric under the permutation of any two identical particles of the system.

Heisenberg (1926) and Wigner (1926)

IF THE HAMILTONIAN EXHIBITS

A) Point-group symmetry

The wave functions MUST transform like one of the IR of the point-group, *or*, to be a basis for one of the IR of the group.

B) Permutation symmetry (always present for a many-electron system)

The wave functions MUST transform like the totally symmetric or the totally anti-symmetric IR of the symmetric group, *or*, form a basis for these IRs.

BUT ATTENTION!!!

The results obtained so far, derived from the symmetry properties of a hamiltonian which does not contain spin, apply only to the SPATIAL PART of any wave function representing a many-electron system.

But, what about the spin ?

3) Introducing the electron spin in a non-relativistic formulation of quantum mechanics

Experimental facts:

- Electrons have a spin angular momentum

- They all have the same value of spin: $\sqrt{3}/_2\,\hbar$

- Only two values are allowed for its projection along any direction in space: $\pm\left(1/_2\right)\hbar$ ($m_s = \pm ½$)

- There is no classical counterpart to this property of the electron.

Theoretical fact: **If the electron spin is not included in the non-relativistic formulation of QM, nothing works.**

- *Spin* is some kind of angular momentum.
- Invent a *spin* angular momentum operator, $\hat{s}$, with componentes $\hat{s}_x$, $\hat{s}_y$ and $\hat{s}_z$, such that:

$$[\hat{s}_x , \hat{s}_y] = i\hbar\, \hat{s}_z \qquad [\hat{s}_y , \hat{s}_z] = i\, \hbar\, \hat{s}_x \qquad [\hat{s}_z , \hat{s}_x] = i\, \hbar\, \hat{s}_y$$

- Introduce two *spin*-eigenfunctions, α and β, such that:

$$\begin{cases} \hat{s}_z\, \alpha = m_s\, \hbar\, \alpha = (1/2)\, \hbar\, \alpha \\ \hat{s}_z\, \beta = -\, m_s \hbar\, \beta = -\, (1/2)\, \hbar\, \beta \end{cases}$$

- For any angular momentum operator:

$-s \leq m_s \leq s \Rightarrow s = 1$ (*spin* quantum number)

$\hat{s}^2\, \alpha = s(s+1)\, \hbar^2\, \alpha$ and $\hat{s}^2\, \beta = s(s+1)\, \hbar^2\, \beta$

$\hat{s}^2\, \alpha = (3/4)\, \hbar^2\, \alpha$ and $\hat{s}^2\, \beta = (3/4)\, \hbar^2\, \beta$

HOW TO PROCEED FOR *N*-ELECTRONS SYSTEMS ?

In an analogous way:

Invent an operador $\hat{S}$, for the total *spin* of the system, with components $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$, satisfying the commutation rules:

$$[\hat{S}_x , \hat{S}_y] = i\hbar \hat{S}_z \qquad [\hat{S}_y , \hat{S}_z] = i\hbar \hat{S}_x \qquad [\hat{S}_z, \hat{S}_x] = i\hbar \hat{S}_y$$

VERY IMPORTANT:

The non-relativistic many-electrons Hamiltonian does not contain *spin* coordinates. Therefore:

$$[H, \hat{S}^2] = [H, \hat{S}_x] = [H, \hat{S}_y] = [H, \hat{S}_z] = 0$$

IMPORTANT CONSEQUENCE OF THE LAST RESULT:

The total *spin* as well as its projection in any direction of space are "constants of the motion", *i.e.,* they have very well defined values for any many-electrons-system.

WHAT ABOUT THE SPIN-EIGENFUNCTION FOR A MANY-ELECTRONS SYSTEM?

- Must be a function of the *spin* of all the electrons:

$$|\chi\,(s_1, s_2, ..\ s_N)>$$

such that the result of $\hat{S}^2$ operating on $|\chi>$ gives the total *spin* value, S, of the many-electrons system:

$$\hat{S}^2\,\chi \;= S\,(S+1)\;\hbar^2\,\chi$$

WHAT ELSE ?

- Electrons are indistinguishable and they all have the same *spin*

- The total *spin*, *S*, cannot change its value if one exchanges the *spin* of any two electrons of the system. Therefore:

$$[\hat{S}^2, \widehat{P_{ij}}] = 0$$

$$\widehat{P_{ij}}\,\hat{S}^2\,\chi = \hat{S}^2\,(\widehat{P_{ij}}\,\chi) = S\,(S+1)\,\hbar^2\,\widehat{P_{ij}}(\,\chi)$$

-The many-electron *spin* functions MUST also be invariant to the permutation of the *spin* of any two electrons. The many-electrons *spin* functions MUST also transform like totally symmetric or anti-symmetric representations of S_N:

$$\widehat{P_{ij}}\,|\chi\,(s_1, s_2, .. s_N)> \;= \pm\,|\chi\,(s_1, s_2, .. s_N)>$$

4) Incorporating the *spin* wave function in the description of a many-electron system (atom or molecule)

H does not contain *spin* variables. Thus, the solution of the many-electron problem, either through Schrödinger equation

$$H\,|\Psi> = E\,|\Psi>$$

or its equivalent, the variational principle;

$$E = <\Psi|H|\Psi> \quad ,$$

will furnish wave functions which depend only on the spatial coordinates of the electrons and the nuclei:

$\psi(r_1, r_2\, r_3 \ldots r_N; \xi)$, where ξ stands for the set

of the nuclear coordinates (in the B.O. approximation).

However, once this solution is known, it can be multiplied by another function, of other variables, not present in H, *spin* for example, and the product function will satisfy Schrödinger equation, although not being a solution to S.E. of the spinless hamiltonian.

$$\Psi(r_1, r_2\, r_3 \,..\, r_N\,,\, s_1\, s_2 \,..\, s_N\,;\xi) = \psi(r_1, r_2\, r_3 \,..\, r_N; \xi)\,\chi(s_1\, s_2 \,..\, s_N)$$

total wave function — spatial part — spin part

THIS IS NOT AN APPROXIMATION!

THIS IS THE <u>EXACT</u> ANALYTICAL FORM OF THE TOTAL WAVE FUNCTION FOR ANY NON-RELATIVISTIC MANY-ELECTRON SYSTEM, ATOM OR MOLECULE!

5) THE ANTISYMMETRY PRINCIPLE

The antisymmetry principle requires the *total wave function (including spin) to be antisymmetric with respect to the interchange of any pair of electrons*.

But now we know that the only acceptable way of including the spin in a non-relativistic formulation is to multiply the spatial part of the wave function by a spin function corresponding to a given value of *S*, the total spin of the system.

Two ways of generating total wave functions satisfying the antisymmetry principle :

$$\Psi(r_1, r_2\, r_3 .. r_N\, , s_1\, s_2 .. s_N\, ;\xi) = \psi(r_1, r_2\, r_3 .. r_N; \xi)\, \chi(s_1\, s_2 ... s_N)$$

S x A

A x S

Once the *spin* state is defined, the symmetry of the spin function is automatically defined and, because of the antisymmetry principle, the spatial part of the wave function will have its symmetry perfectly determined.

Thus, in the non-relativistic formulation the spin is just an *indicator* of the symmetry that the spatial wave function MUST have so that the total wave function obeys the antisymmetry principle.

In non-relativistic quantum mechanics, the electronic spin is only an "indicator"

Van Vleck and Sherman (1935)

CONCLUSIONS:

- the indistinguishability of the electrons;
- the antisymmetry principle;
- the fact that for a non-relativistic system, the **spatial** and ***spin*** coordinates are independent of each other.

OBLIGES:

a) the exact function to be a **product** of a spatial and of a *spin* function.

b) both the **spatial** and ***spin*** parts of the wave function to be symmetric or antisymmetric under the exchange of **either** the spatial or the *spin* coordinates of any two electrons of the system;

c) the **total wave function** to be antisymmetric

6) INDEPENDENT PARTICLE MODELS

BASIC IDEA:

REPLACE THE PROBLEM OF FINDING THE WAVE FUNCTION WHICH DESCRIBES THE COLLECTIVE MOTION OF THE *N* ELECTRONS OF AN ATOM OR MOLECULE BY THE ONE OF FINDING *N* OCCUPIED ORBITAIS WHICH DESCRIBE THE INDIVIDUAL MOTION OF EACH ELECTRON OF THE SYSTEM, ATOM OR MOLECULE:

$$\Psi_{el}\,(i,j,k,\ldots N) \longrightarrow \{\varphi_i\}_{i=1,\,N}$$ **atomic orbitals**

$$\Psi_{el}\,(i,j,k,\ldots N;\,A,B\ldots M) \longrightarrow \{\phi_i\}_{i=1,\,N}$$ **molecular orbitals**

ONCE THE *N* ORBITALS ARE DETERMINED,

$\{\varphi_i\}_{i=1, N}$ atomic orbitals or $\{\phi_i\}_{i=1, N}$ molecular orbitals

ONE MUST CONSTRUCT THE TOTAL WAVE FUNCTION,

Ψ_{el} (i,j,k,...N) or Ψ_{el} (i,j,k,...N; ξ),

IT IS FROM TOTAL WF THAT THE PROPERTIES OF THE SYSTEM ARE DETERMINED.

ATTENTION! Ψ_{el} HAS TO BE:

$$\left\{ \begin{array}{l} \text{WELL BEHAVED} \\ \text{ANTISYMMETRIC} \end{array} \right.$$

CONSTRUCTING ANTISYMMETRIC WAVE FUNCTIONS FROM A SET OF ORBITALS $\{\varphi_i\}_{i=1, N}$

A) Heisenberg (1926) and Wigner (1926)

$$\Psi_H = \mathcal{A}\,[\varphi_1(1)\varphi_2(2)\varphi_3(3)\ \ldots\ \varphi_N(N)\ \chi\,(1,2\ldots N)]\ ,$$

$\mathcal{A} = (1/N!)\ \Sigma_P\, \delta_P\, P$ is the antisymmetrizer operator

$\chi\ (1,2\ldots N)$ eigenfunction of $\widehat{S^2}$ and $\widehat{S_z}$

$$\widehat{S^2}\chi = S\,(S+1)\,\chi \qquad \widehat{S_z}\,\chi = M_S\chi$$

Example: He	S	M_S
$\psi_{H1} = [\varphi_1(1)\,\varphi_2(2) + \varphi_2(1)\varphi_1(2)]\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$	0	0
$\psi_{H2} = [\varphi_1(1)\,\varphi_2(2) - \varphi_2(1)\,\varphi_1(2)]\ [\alpha(1)\alpha(2)]$	1	1
$\psi_{H3} = [\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)]\,[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$	1	0
$\psi_{H4} = [\varphi_1(1)\,\varphi_2(2) - \varphi_2(1)\,\varphi_1(2)]\ [\beta(1)\beta(2)]$	1	-1

B) SLATER (1927) Spin-orbital : $\Phi(r,\sigma)$

$\Psi(1,2) = \Phi_1(1)\,\Phi_2(2)$ neither symmetric nor antisymmetric, BUT

$\Psi_S(1,2) = \Phi_1(1)\,\Phi_2(2) - \Phi_1(2)\,\Phi_2(1)$

$\widehat{P_{12}}\,\Psi_S(1,2) = -\Psi_S(1,2)$ **Conclusion:** $\Psi_S(1,2)$ is antisymmetric

Notice that $\Psi_S(1,2)$ can be written as a 2 x 2 determinant:

$$\Psi_S(1,2) = \begin{vmatrix} \Phi_1(1) & \Phi_1(2) \\ \Phi_2(1) & \Phi_2(2) \end{vmatrix}$$

VERY PRACTICAL, BUT WHAT IS A SPIN-ORBITAL?

HOW DOES IT LOOK LIKE?

A) Slater wave function for 2-e systems with S=0

$u_1 = \phi_1\alpha$ and $u_2 = \phi_2\beta$

$\Psi_{S1} = \sqrt{\frac{1}{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(2)\alpha(2) \\ \phi_2(1)\beta(1) & \phi_2(2)\beta(2) \end{vmatrix}$ $\widehat{P_{12}}\, \Psi_{S1} = -\Psi_{S1}$ **OK!**

$\widehat{S_z}\, \Psi_{S1} = 0\, \Psi_{S1}$ **BUT** $\widehat{S^2}\, \Psi_{S1} \neq (const)\Psi_{S1}$

Ψ_{S1} DOES NOT REPRESENT A STATE WITH DEFINED SPIN !!!

$\Psi_{S2} = \sqrt{\frac{1}{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_2(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix}$

$\widehat{S_z}\, \Psi_{S2} = 0\, \Psi_{S2}$ and $\widehat{S^2}\, \Psi_{S2} = 0\, \Psi_{S2}$

BUT $\widehat{P_{12}}\, \Psi_{S2} \neq -\Psi_{S2}$ **NOT OK!**

NOT ANTISYMMETRIC !!!

THIRD ATTEMPT:

Take the same spatial part for both spin-orbitals

$u_1 = \phi\,\alpha$ and $u_2 = \phi\,\beta$ BUT WHY ?

$$\Psi_{S3} = \sqrt{\frac{1}{2}}\begin{vmatrix} \phi(1)\alpha(1) & \phi(1)\beta(1) \\ \phi(2)\alpha(2) & \phi(2)\beta(2) \end{vmatrix}$$

$\widehat{S_z}\,\Psi_{S3} = 0\,\Psi_{S3}$ and $\widehat{S^2}\,\Psi_{S3} = 0\,\Psi_{S3}$ AND $\widehat{P_{12}}\,\Psi_{S3} = -\,\Psi_{S3}$ OK!

IT WORKS !!!

GREAT, BUT THE DOUBLE OCCUPANCY IS A RESTRICTION! THERE IS NO PHYSICAL REASON FOR ATTRIBUTING THE SAME SPATIAL PART FOR THE TWO SPINORBITALS.
AFTER ALL, WE WANT TO DEVELOP A GENERAL METHOD TO CONSTRUCT INDEPENDENT PARTICLES WAVE FUNCTIONS!

7) COMBINIG THE IDEA OF INDEPENDENT PARTICLES WITH THE VARIATIONAL PRINCIPLE

INDEPENDENT PARTICLES MODELS

HARTREE-FOCK:

- Atomic orbitals must retain the form of the hydrogenoid (*s, p, d, f* etc.) orbitals and, therefore, must be orthogonal;

- Use orbital double occupation, *i. e.* , two electrons in the same orbital (atomic or molecular) with different *spins*;

- Use Slater-type wave functions to obtain the best orbitals (atomic or molecular) through the variational principle.

GVB (*Generalized Valence Bond*)

- No restrictions imposed to the form of atomic orbitals;

- Singly-occupied atomic orbitals not necessarily orthogonal;

- Use Heisenberg-type wave functions to obtain the best atomic orbitals through the variational principle.

The GVB (*Generalized Valence-Bond*) Model

The GVB wave function, in its most general form, can be written as :

$$\Psi_{GVB} = \mathcal{A}\,[\varphi_1\varphi_2\varphi_3 \dots \varphi_N\, \chi\, (1,2 \dots N)],$$

where $\mathcal{A} = (1/N!)\, \Sigma_P\, \delta_P\, P$ is the antisymmetrizer. The orbitals $\{\varphi_i\}$ are atomic-like, singly occupied and not necessarily orthogonal.

The orbitals $\{\varphi_i\}$ and the spin function χ are simultaneously optimized by requiring the functional $E_{GVB} = <\Psi_{GVB}|H|\Psi_{GVB}>$ to be stationary. No restrictions are imposed to the *spin* function other than requiring χ to be an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$:

$$\hat{S}^2 \chi = S(S+1)\,\chi \qquad \hat{S}_z\, \chi = M_S\, \chi$$

Ex: 4 electrons Singlet

There are two possible spin functions :

χ_1 = $(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)$ "perfect-pairing coupling"

χ_2 = $2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - (\alpha\beta+\alpha\beta)(\alpha\beta+\beta\alpha)$

Thus : $\chi = c_1\,\chi_1 + c_2\,\chi_2$

$$\Psi_{GVB} = c_1\,\mathcal{A}\,[\varphi_1\varphi_2\varphi_3\varphi_4\,\chi_1\,(1,2,3,4)] + c_2\,\mathcal{A}\,[\varphi_1\varphi_2\varphi_3\varphi_4\,\chi_2\,(1,2,3,4)]$$

In general, if a spin function of the type χ_1 is allowed, its coefficient is much larger than the others, and the GVB function can be rewritten as :

$$\Psi_{GVB} \cong \mathcal{A}\,[\varphi_1\varphi_2\varphi_3\varphi_4\,(\alpha\beta-\beta\alpha)\,(\alpha\beta-\beta\alpha)]$$

Experience with this type of wave function also shows that all orbitals, other than the two within a given singlet pair, are orthogonal or nearly orthogonal.

Imposing the "*strong orthogonality constraint*" plus the perfect-pairing coupling scheme, gives rise to the GVB/PP wave function.

Ex: 4e singlet

$$\Psi_{GVB/PP} = \mathcal{A}\,[\varphi_1\varphi_2\varphi_3\varphi_4\,(\alpha\beta-\beta\alpha)\,(\alpha\beta-\beta\alpha)]$$

with $<\varphi_1\varphi_2>$ **and** $<\varphi_3\varphi_4> \neq 0$

but $<\varphi_1\varphi_3> = <\varphi_1\varphi_4> = <\varphi_2\varphi_3> = <\varphi_2\varphi_4> = 0$

ADVANTAGES:

–Ψ_{GVB} is antisymmetric and a basis for S_N. It has all the properties required from a many-electron wave function.

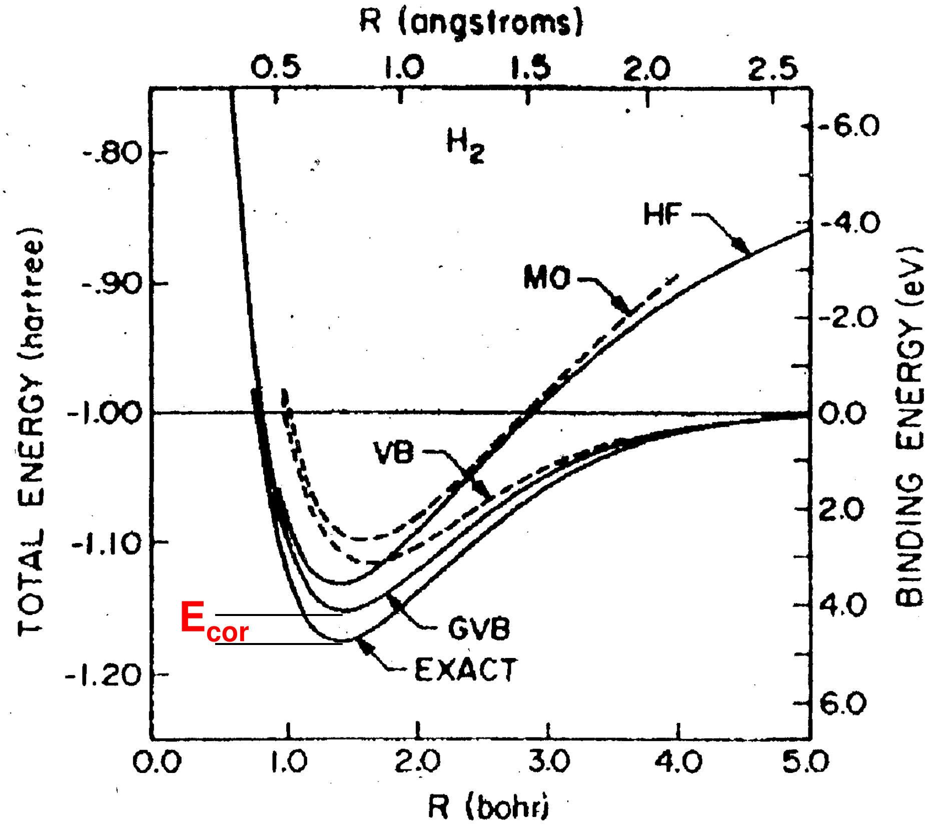
Consequences:

a) ideal reference IPM to compute *real* correlations effects.

$$E_{cor} = E_{exact} - E_{IPM} \quad \text{(Wigner)}$$

$$E_{cor} = E_{FCI} - E_{HF} \quad \text{(Lowdin)}$$

$$\boxed{\text{Proposed : } E_{cor} = E_{exact} - E_{chemical\ structure}}$$


R (angstroms)
0.5
1.0
1.5
2.0
2.5
H2
HF
MO
VB
GVB
EXACT
Ecor
TOTAL ENERGY (hartree)
-.80
-.90
-1.00
-1.10
-1.20
BINDING ENERGY (eV)
-6.0
-4.0
-2.0
0.0
2.0
4.0
6.0
0.0
1.0
2.0
3.0
4.0
5.0
R (bohr)

b) when used as IPM, much less computational effort is needed to recover the *real* correlations effects.

– Ψ_{GVB} , furnishes one-electron states univocally determined within a given basis set

Consequences:

a) one-electron states (orbitals) involved in chemical bonding can be univocally identified;

b) Connectivity among atoms can be precisely identified and, therefore, one can define chemical structures for molecules;

DISADVANTAGES:

- ψ_{GVB} defined in terms of non-orthogonal orbitals;
- $\psi_{GVB/PP}$ much simpler but the orbitals within a singlet-coupled pair are still non-orthogonal.

Consequence:

-Calculation of the one and two-electron integrals requires more computer time.

CAN ONE SIMPLIFY EVEN FURTHER?

He : $1s^2$ $\psi_{HF} = \mathcal{A}\,[1s_{HF}1s_{HF}\,\alpha\beta]$

Li: $1s^2\,2s$ $\psi_{HF} = \mathcal{A}\,[1s_{HF}1s_{HF}2s_{HF}\,\alpha\beta\alpha]$

Both have the wrong form !

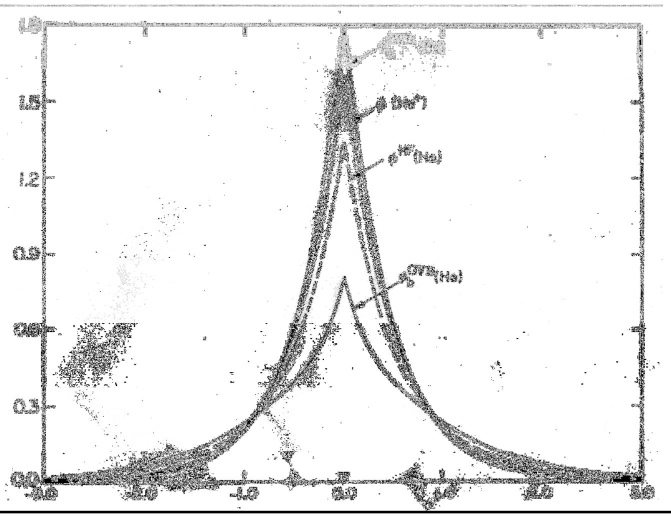
But:

ψ_{GVB} **(He) =** $\mathcal{A}$ **[**$1s_{He}1s'_{He}$ **(**$\alpha\beta - \beta\alpha$**)]**

ψ_{GVB} **(Li) =** $\mathcal{A}$ **[**$1s_{Li}1s'_{Li}2s_{Li}$ **(**$\alpha\beta - \beta\alpha$**)** α**]**

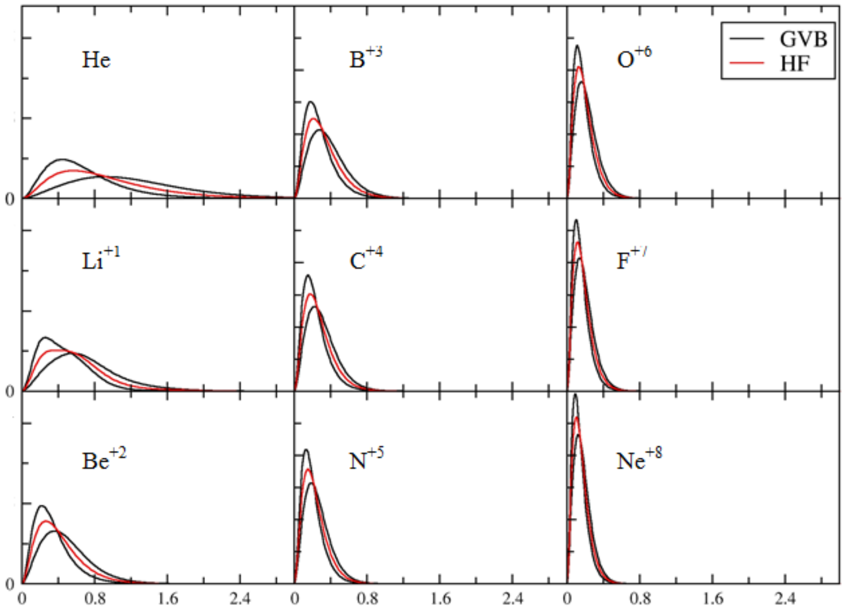
have the right form but orbitals are non orthogonal

How different, for example, the $1s_{HF}$ and $1s_{GVB}$ orbitals of the He atom are?



QUITE DIFFERENT !

WHAT HAPPENS WHEN THE NUCLEAR CHARGE INCREASES ?



Overlap Integral Between the GVB Orbitals.

	H^-	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
S_{12}	0.615	0.879	0.935	0.949	0.960	0.967	0.972	0.976	0.979	0.981

Proposition:

Keep the core electrons in doubly occupied orbitals and the valence ones in singly occupied non-orthogonal orbitals. The wave function will not exhibit permutation symmetry anymore but will be much easier to calculate. However, no artifacts will be produced as long as the core electros are not involved in the process one wants to describe.

Question: Should we keep these doubly occupied orbitals non-orthogonal to the singly occupied ones?

Answer: No! One can take any doubly occupied orbital orthogonal to any singly occupied orbital. THIS IS NOT A RESTRICTION!

SIMPLIFIED FORM OF A GVB/PP WAVE FUNCTION

$$\Psi_{GVB/PP} = \mathcal{A}\,[\ \{\text{core}\}\ \{\text{valence}\}\ \{\text{open shell}\}],$$

where:

{core} : doubly-occupied core orbitals, orthogonal to all the others.

{valence} : GVB orbitals, singly-occupied and non-orthogonal to the open shell orbitals and to the GVB orbital in the same pair.

{open shell} : singly-occupied valence orbitals not involved in chemical bonds.

Attention: The open shell orbitals can be taken orthogonal to the others if ALL the electrons in these orbitals have the SAME SPIN (high spin case). If not, this IS A RESTRICTION !!!

Rewritting the GVB/PP wave function in terms of natural (orthogonal) GVB orbitals.

Suppose:

$$\Psi = c_A \mathcal{A}\,[\psi_A\psi_A\,\alpha\beta] + c_B\,\mathcal{A}\,[\psi_B\psi_B\,\alpha\beta]$$

and $\Psi_{GVB/PP} = \mathcal{A}\,[\varphi_A\varphi_B\,(\alpha\beta - \beta\alpha)]$

with $<\psi_A|\psi_B> = 0$ and $<\varphi_A|\varphi_B> \neq 0$

If ψ_A ,ψ_B , φ_A and φ_B are expanded in the same basis set, it is not difficult to show that:

$$\varphi_A = (a^2 + b^2)^{-1/2}\ (a\,\psi_A + b\,\psi_B)$$
$$\varphi_B = (a^2 + b^{2)-1/2}\ (a\,\psi_A - b\,\psi_B)$$

with $<\varphi_A\,|\varphi_B> = \{a^2 - b^2\}/\ \{a^2 + b^2\}$

Thus, in terms of the orthogonal orbitals ψ_A and $\psi_{B,}$ the GVB/PP wave function can be written as:

$$\Psi_{GVB/PP} = (a^2 + b^{2)-1/2} \left\{ a^2 \mathcal{A} [\psi_A\psi_A\, \alpha\beta] - b^2 \mathcal{A} [\psi_B\psi_B\, \alpha\beta] \right\}$$

ψ_A and ψ_B : doubly-occupied and orthogonal
(GVB natural orbitals)

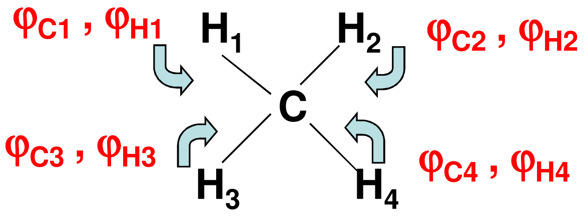
φ_A and φ_B : singly-occupied and non-orthogonal
(GVB orbitals)

VERY IMPORTANT: For each pair of GVB orbitals in the PP wave function there is one unique pair of GVB natural orbitals, and vice-versa:

GVB/PP with n $\varphi_i\ \varphi_j$ pairs $\rightleftarrows$ GVB/PP with 2^n terms $\psi_A\psi_B$

Strategy for Constructing GVB/PP Wave Functions for Molecules

a) Draw the proposed chemical structure of the molecule:



b) Assign to each line connecting two atoms a pair of GVB orbitals, one orbital for each one of the atoms involved in the bond;

c) Keep the core electrons in doubly-occupied orbitals

d) Write the GVB/PP wave function taking into account that each pair of singlet-paired electrons contributes a term of the form $(\varphi_i \varphi_j + \varphi_j \varphi_i)(\alpha\beta - \beta\alpha)$ to the wave function:

$$\Psi_{GVB/PP}(CH_4) = \mathcal{A}[\,1s_C 1s_C (\varphi_{C1}\varphi_{H1}+ \varphi_{H1}\varphi_{C1})(\varphi_{C2}\varphi_{H2}+ \varphi_{H2}\varphi_{C2})(\varphi_{C3}\varphi_{H3}+ \varphi_{H3}\varphi_{C3})(\varphi_{C4}\varphi_{H4}+ \varphi_{H4}\varphi_{C4})\,\alpha\beta\,(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)]$$

e) Transform each pair of GVB singly-occupied non-orthogonal orbitals into the corresponding pair of doubly-occupied orthogonal GVB natural orbitals.

f) Determine the BEST GVB natural orbitals by requiring the functional $E_{GVB/PP} = \langle\Psi_{GVB/PP}\, \mathcal{H}\, \Psi_{GVB/PP}\rangle$ to be an extremum.

g) Transform each pair of GVB natural orbitals back to the corresponding GVB atomic-like, singly-occupied, non-orthogonal orbitals.

What, if more than one equivalent chemical structure can be drawn?

Use the *Generalized Multi-Structural* (GMS) wave function:

(Hollauer and Nascimento, 1993)

$$\Psi_{GMS} = \Sigma_i \; c_i \, \psi_i$$

where ψ_i and c_i are, respectively, the wave function for the i^{th} chemical structure and c_i its weight in Ψ_{GMS}

Two possibilities : ψ_i fixed and c_i variationally determined or

both ψ_i and c_i variationally determined

GENERAL ENERGY EXPRESSION OF A GVB WAVE FUNCTION

$\Psi_{GVB} = \mathcal{A}[\varphi_1\varphi_2\varphi_3 \ldots \varphi_N \chi(1,2\ldots N)]$,

$$E = \sum_{i,j}^{n} D_j^i h_{ij} + \sum_{i,j,k,l}^{n} D_{kl}^{ij} < ik \mid jl >$$

with: $h_{ij} =< \phi_i \mid h \mid \phi_j >$

$$< ik \mid jl >=< \phi_i(1)\phi_j(2) \mid 1/r_{12} \mid \phi_k(1)\phi_l(2) >$$

D_j^i and D_{kl}^{ij} density matrix elements

For GVB/PP wave functions, the general energy expression turns out to be much simpler if the atomic orbitals are expressed in an orthonormal basis:

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

In such a basis, the density matrices D^i_j and D^{ij}_{kl} are diagonal and the only remaining terms different from zero, are:

$$D^i_i = 2f_{ii} \qquad D^{ij}_{ij} = a_{ij} = a_{ji} \qquad D^{ij}_{ji} = b_{ij} = b_{ji}$$

the coefficients f_{ii} , a_{ij} and b_{ij} being independent of $\{\varphi_i\}$

The energy expression of the GVB/PP function becomes:

$$E = 2\sum_{i=1}^{n} f_{ii} h_{ii} + \sum_{i,j=1}^{n} (a_{ij} J_{ij} + b_{ij} K_{ij}) \qquad (1)$$

J_{ij} and K_{ij} being the Coulomb and exchange integrals.

EXAMPLE:

Energy expression of a GVB wave function for 2 electrons, singlet state:

$$E = \frac{h_{11} + h_{22} + 2S_{12}h_{12} + J_{12} + K_{12}}{(1 + S_{12}^{2})} \qquad (2)$$

It does not have the form of (eq. 1) !

NOTE: For 2 electrons singlet state the GVB WF is PP

However, one can express the two GVB non-orthogonal orbitals, φ_1 and φ_2 as a linear combination of two other orthogonal orbitals, ψ_1 and ψ_2 , the natural GVB orbitals:

$$\begin{cases} \varphi_1 = (\sqrt{\sigma_1}\ \psi_1 + \sqrt{\sigma_2}\ \psi_2) / (\sigma_1 + \sigma_2)^{1/2} \\ \varphi_2 = (\sqrt{\sigma_1}\ \psi_1 - \sqrt{\sigma_2}\ \psi_2) / (\sigma_1 + \sigma_2)^{1/2} \end{cases}$$

$$\sigma_1 > 0 \quad ; \quad \sigma_2 > 0 \quad ; \quad \langle \psi_1 | \psi_2 \rangle = 0$$

The GVB wave function expressed in the natural GVB orbitals basis, has the form:

$$\Psi_{GVB} = \sigma_1 \mathcal{A}\,[\psi_1\psi_1\,\alpha\beta\,] - \sigma_2\,\mathcal{A}\,[\psi_2\psi_2\,\alpha\beta\,]$$

whose energy expression is:

$$E = \frac{\sigma_1^2}{\sigma_1^2 + \sigma_2^2}\,(2h_{11} + J_{11}) + \frac{\sigma_2^2}{\sigma_1^2 + \sigma_2^2}\,(2h_{22} + J_{22}) - \frac{2\sigma_1\sigma_2}{\sigma_1^2 + \sigma_2^2}\,K_{12}$$

This energy expression has the form of eq. (1), with one difference: the coefficients { f, a, b }are not fixed anymore, but depend on the coefficients σ_1 and σ_2.

IMPORTANT CONCLUSION:

THE ENERGY OF ANY GVB/PP WAVE FUNCTION CAN BE PUT IN THE FORM OF EQUATION (1)

THE *f* COEFFICIENTS:

$f_i = 1$ *if ψ_i is a core orbital*

$f_i = \sigma_i^2$ *if ψ_i is an orbital of a GVB pair*

$f_i = 1/2$ *if ψ_i is a singly occupied orbital*

THE *a_{ij} and b_{ij}* COEFFICIENTS:

$a_{ij} = 2\, f_i\, f_j$ $b_{ij} = -f_i\, f_j$

Exceptions:

$b_{ij} = -1/2$ *if ψ_i and ψ_j are singly occupied orbitals*

$a_{ii} = f_i$; $b_{ii} = 0$ *if ψ_i is an orbital of a GVB pair*

$a_{ij} = 0$ and $b_{ij} = -\sigma_i\, \sigma_j$ *if ψ_i and ψ_j are orbitals of the same GVB pair*

SOME CONSEQUENCES OF NEGLECTING PERMUTATION SYMMETRY IN THE DESCRIPTION OF MANY-ELECTRON SYSTEMS

INDEPENDENT PARTICLES MODELS

HARTREE-FOCK: (atomic and SCF-MO)

- Use **Slater-type** wave functions to obtain the best orbitals (atomic or molecular) through the **variational principle.**

ST wave functions are not basis for the symmetric group, *i.e.*, do not take into account the permutation symmetry of the many-electron hamiltonian.

GVB (*Generalized Valence Bond*)

- Use **Heisenberg-type** wave functions to obtain the best **atomic** orbitals through the **variational principle.**

GVB wave functions are basis for the symmetric group

A) ORBITAL DOUBLE-OCCUPANCY

WITH ST WFs ONE MUST FORCE DOUBLE OCCUPATION TO GENERATE A WF WITH WELL DEFINED SPIN.

$u_1 = \phi\alpha$ and $u_2 = \phi\beta$

$$\Psi_{S3} = \sqrt{\frac{1}{2}} \begin{vmatrix} \phi(1)\alpha(1) & \phi(1)\beta(1) \\ \phi(2)\alpha(2) & \phi(2)\beta(2) \end{vmatrix}$$

$\widehat{S_z}\Psi_{S3} = 0\ \Psi_{S3}$ and $\widehat{S^2}\ \Psi_{S3} = 0\ \Psi_{S3}$ AND $P_{12}\ \Psi_{S3} = -\Psi_{S3}$ OK!

GREAT, BUT THE DOUBLE OCCUPANCY IS A RESTRICTION! THERE IS NO PHYSICAL REASON FOR ATTRIBUTING THE SAME SPATIAL PART FOR THE TWO SPINORBITALS.

TO AVOID THIS (ARTIFICIAL) PROBLEM ALL WE NEED IS TO CONSTRUCT A WAVE FUNCTION WHICH IS A BASIS FOR THE PERMUTATION GROUP, S_2 :

$$\Psi_H = \{\phi_1(1)\,\phi_2(2) + \phi_1(2)\,\phi_2(1)\}\;[\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]$$

$$\widehat{S_z}\Psi_H = 0\Psi_H \quad \text{and} \quad \widehat{S^2}\,\Psi_H = 0\;\Psi_H \qquad P_{12}\,\Psi_H = -\Psi_H$$

B) THE EXCHANGE INTEGRAL (K_{ij})

Energy of a Slater-type function for any “closed shell” system with *2n* electrons :

$$E = \sum_{i=1}^{n} 2h_{ii} + \sum_{i,j=1}^{n} (2J_{ij} - K_{ij})$$

WHAT IS THE ORIGIN OF K_{ij} ?

ACCORDING TO 99.9% OF THE BOOKS (QUANTUM MECHANICS OR QUANTUM CHEMISTRY) K_{ij} HAS NO CLASSICAL ANALOG. IT ARISES SOLELY AS A CONSEQUENCE OF THE ANTISYMMETRY PRINCIPLE.

REALLY?

Example: He (^1S $1s^2$)

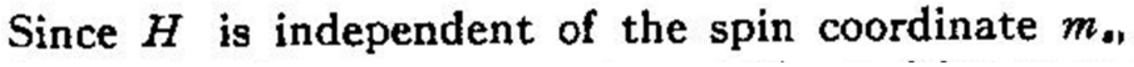
$E\,[\Psi_{S3}\,(1,2)] = h_{11} + h_{22} + J_{12} = 2\,h_{11} + J_{12}$ **WHERE IS K_{12} ?**

BUT, WAIT! K_{ij} EXISTS ONLY FOR ELECTRONS WITH THE SAME SPIN.

RIGHT OR WRONG ?

$E\,[\Psi_{S3}\,(1,2)] = h_{11} + h_{22} + J_{12} = 2\,h_{11} + J_{12} + K_{12}\ \langle\alpha|\beta\rangle$

BUT, according to Slater:



Since H is independent of the spin coordinate m_s,

THE ENERGY SHOULD NOT DEPEND DIRECTLY ON THE SPIN COORDINATES !!!

POSTULATES OF QUANTUM MECHANICS

-THE POSSIBLE RESULTS OF A MEASUREMENT OF ANY DYNAMIC VARIABLE FOR A QUANTUM SYSTEM ARE THE EIGENVALUES OF THE CORRESPONDING OPERATOR.

Example: **Energy** → $H\varphi_n = E_n\varphi_n$ $\{E_n\}$ *eigenvalues*

$$H = -\sum_{A=1}^{M} \frac{1}{2M_A}\nabla_A^2 - \frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{A=1}^{M}\sum_{i=1}^{N}\frac{Z_A}{r_{iA}} + \sum_{i<j}^{N}\frac{1}{r_{ij}} + \sum_{A<B}^{M}\frac{Z_A Z_B}{R_{AB}}$$

BUT, WHAT IN THE HAMILTONIAN – ***THE OPERATOR THAT REPRESENTS THE TOTAL ENERGY OF THE SYSTEM*** **– CAN TELL ELECTRONS WITH SPIN UP FROM THE ONES WITH SPIN DOWN? ABSOLUTELY NOTHING!!!**

ENERGY OF THE HEISENBERG WF CONSIDERING ONLY ITS SPATIAL PART:

$\Psi_{Heisenberg} = \phi_1(1)\,\phi_2(2) + \phi_1(2)\,\phi_2(1)$

THIS IS A SYMMETRIC WF !!!

$$E_{Heisenberg} = \frac{h_{11} + h_{22} + S_{12}\,h_{12} + J_{12} + K_{12}}{1 + S_{12}^2}$$

ENERGY OF THE FULL HEISENBERG WAVE FUNCTION:

$\Psi_H = \{\phi_1(1)\,\phi_2(2) + \phi_1(2)\,\phi_2(1)\}\ [\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]$

THIS IS AN ANTISYMMETRIC WF

$$E_{Heisenberg} = \frac{h_{11} + h_{22} + S_{12}\,h_{12} + J_{12} + K_{12}}{1 + S_{12}^2}$$

CONCLUSION

K_{ij} HAS NOTHING TO DO WITH THE ANTISYMMETRY PRINCIPLE BUT WITH THE PERMUTATION SYMMETRY OF THE HAMILTONIAN AND ITS REFLEXES ON THE WAVE FUNCTIONS.

THERE IS A *K* INTEGRAL FOR EACH PAIR OF ELECTRONS REGARDLESS OF THEIR SPINS.

C) ELECTRONIC CORRELATION ENERGY

$E_{cor} = E_{exact} - E_{MPI}$ Wigner (1934)

$E_{cor} = E_{full\text{-}CI} - E_{HF}$ Lowdin (1959)

Using Löwdin's definition:

$$``E_{exact}" \approx E_{full\text{-}CI} = E_{HF} + E_{cor}$$

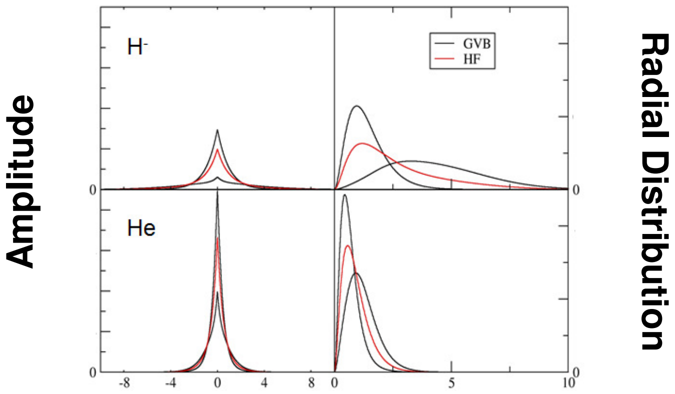
ACCORDING TO THIS LAST EXPRESSION CORRELATION ENERGY IS WHAT IS MISSING IN THE HARTREE-FOCK MODEL TO OBTAIN THE "EXACT" ENERGY OF THE SYSTEM (ATOM OR MOLECULE).

TWO SIMPLE SYSTEMS

$$H^{-}\begin{cases}\psi_{HF} = [1s_{H-}(1)1s_{H-}(2)]\,(\alpha\beta - \beta\alpha)\\ \psi_{GVB} = [1s_{H-}(1)1s'_{H-}(2) + 1s'_{H-}(1)1s_{H-}(2)]\,(\alpha\beta - \beta\alpha)\end{cases}$$

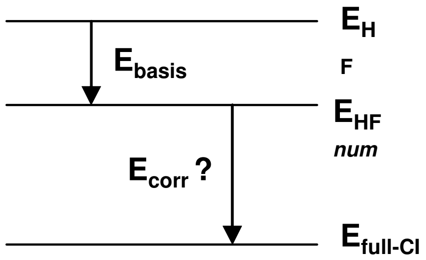
$$He\begin{cases}\psi_{HF} = [1s_{He}(1)1s_{He}(2)]\,(\alpha\beta - \beta\alpha)\\ \psi_{GVB} = [1s_{He}(1)1s'_{He}(2) + 1s'_{He}(1)1s_{He}(2)]\,(\alpha\beta - \beta\alpha)\end{cases}$$

NOTE: A GVB atomic wave function is a Heisenberg-type wave function for which the orbitals are optimized self-consistently. Thus, it has the form of an acceptable WF.



Energy (h)   (10s) Huzinaga’s Basis Set

	Hartree-Fock	GVB
H^-	-0,4877120	-0,5120223
He	-2,8616692	-2,8779850



E_{HF}

E_{basis}

$E_{HF\ num}$

E_{corr} ?

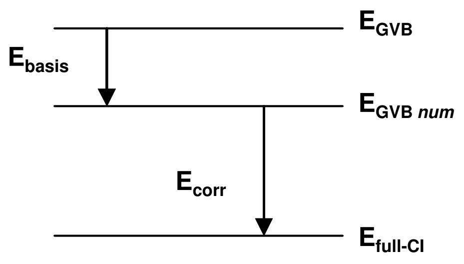
$E_{full\text{-}CI}$

Energy (h). (10s) Huzinaga's basis set

	Hartree-Fock	*Full*-CI	E_{cor}
H^-	-0,4877120	-0,5126604	0,0249484
He	-2,8616692	-2,8790090	0,0173398

THESE RESULTS DO NOT MAKE ANY SENSE !

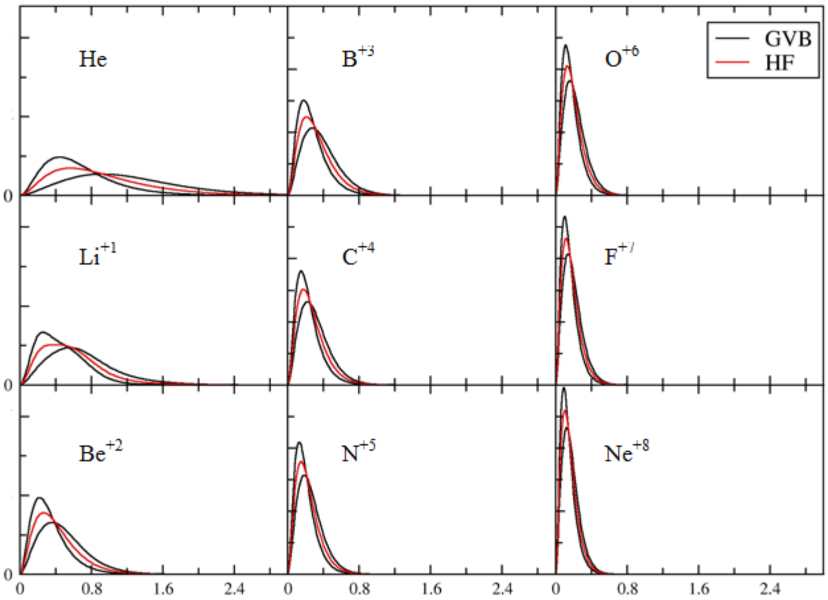
$$E_{cor} = E_{full\text{-}CI} - E_{GVB}$$



	$E_{(HF)}$	$E_{(GVB)}$	$E(_{FullCI})$	$E_{corr}(HF)$	$E_{corr}(GVB)$	$\Delta E_{(HF\text{-}GVB)}$
H-	-0,4877120	-0,5120223	-0,5126604	0,0249484	0,0006381	0,0243104
He	-2,8616692	-2,8779850	-2,8790090	0,0173398	0,0010240	0,0163158

MOST OF THE HF CORRELATION ENERGY IS, IN REALITY, AN ERROR OF FORM ! THE HF WF DOES NOT TAKE INTO ACCOUNT THE PERMUTATION SYMMETRY !!!

WHAT HAPPENS WHEN THE NUCLEAR CHARGE INCREASES ?



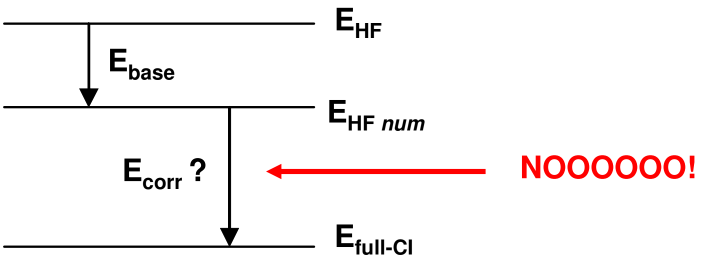
Overlap Integral Between the GVB Orbitals.

	H^-	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
S_{12}	0.615	0.879	0.935	0.949	0.960	0.967	0.972	0.976	0.979	0.981

Energy in hartrees. (10s) Huzinaga's Basis Set

Species	E_{HF}	E_{GVB}	$E_{Full\text{-}CI}$	$E_{corr}(HF)$	$E_{cor}\,(GVB))$	$\Delta E_{HF\text{-}GVB}$
H^-	-0.4877120	-0.5120223	-0.5126604	0.0249484	0.0006381	0.0243104
He	-2.8616692	-2.8779850	-2.8790090	0.0173398	0.0010240	0.0163158
Li^+	-7.1300822	-7.1427386	-7.1438228	0.0137406	0.0010843	0.0126564
Be^{+2}	-13.6109302	-13.6253929	-13.6264590	0.0155289	0.0010661	0.0144627
B^{+3}	-21.9856890	-21.9998624	-22.0009373	0.015248	0.0010749	0.0141734
C^{+4}	-32.3604316	-32.3744235	-32.3755032	0.0150716	0.0010797	0.0139919
N^{+5}	-44.7351638	-44.7490312	-44.7501150	0.0149512	0.0010838	0.0138674
O^{+6}	-59.1098403	-59.1236169	-59.1247031	0.0148628	0.0010862	0.0137766
F^{+7}	-75.4844914	-75.4981990	-75.4992878	0.0147964	0.0010888	0.0137076
Ne^{+8}	-93.8590943	-93.8727474	-93.8738376	0.0147433	0.0010902	0.0136531

CONCLUSIONS OF PART C



(a) $(E_{corr})_{HF}$ = Error of form [$\Delta E_{HF\text{-}GVB}$] + E_{cor} (GVB)

(b) As the nuclear charge increases, double-occupancy for the inner shells seems to be a reasonable approximation, but never for the outer shells.

D) NON-DYNAMIC CORRELATION ENERGY (???)

THE H_2 MOLECULE $({}^1\Sigma_g^+)$

$$|\psi_{HF}> = 1\sigma_g(1)\,1\sigma_g(2)\ [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$|\psi_{GVB}> = [\,\varphi_a(1)\,\varphi_b(2) + \varphi_b(1)\,\varphi_a(2)]\ [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

σ_g : molecular orbitals

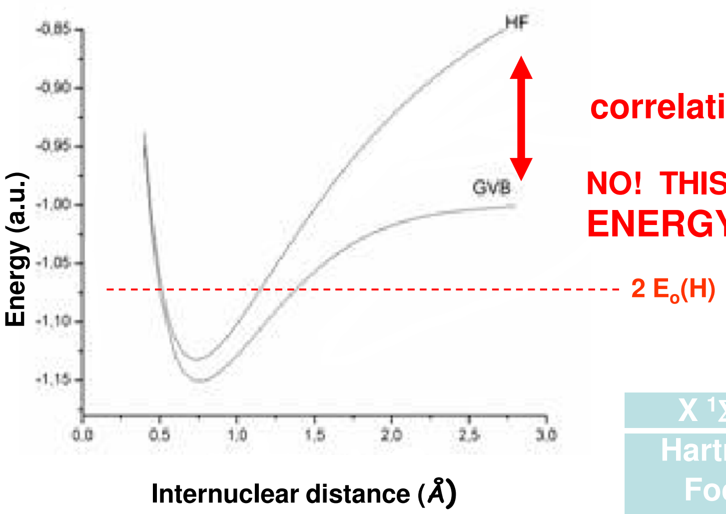
φ_a , φ_b : atomic orbitals

$$|\psi_{HF}> = [\phi_a(1)\,\underbrace{\phi_b(2) + \phi_b(1)\,\phi_a(2)]}_{\text{basis for } S_2}\ [\alpha\beta - \beta\alpha] +$$

ϕ_a , ϕ_b : atomic orbitals

$$+ [\,\phi_a(1)\,\phi_a(2) + \phi_b(1)\,\phi_b(2)]\ [\alpha\beta - \beta\alpha]$$

not a basis for S_2



correlation energy ???

NO! THIS IS NON-DYNAMIC CORRELATION ENERGY !!!!!!!!

X $^1\Sigma_g^+$	R_e (Å)	D_0 (eV)
Hartree-Fock	0.738	------
GVB	0.749	4.06
Kolos and col.	0.74	4.478
Experimental	0.7414	4.478

BACK TO THE POSTULATES OF QUANTUM MECHANICS

- THE POSSIBLE RESULTS OF A MEASUREMENT OF ANY DYNAMIC VARIABLE FOR A QUANTUM SYSTEM ARE THE EIGENVALUES OF THE CORRESPONDING OPERATOR.

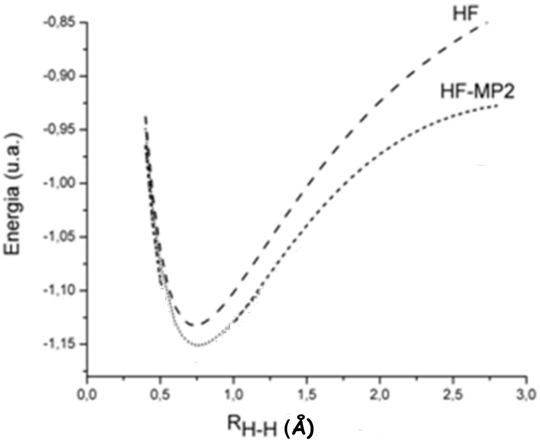
Example: Energy → $H\varphi_n = E_n\varphi_n$ $\{E_n\}$ *eigenvalues*

$$H = -\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{A=1}^{M}\sum_{i=1}^{N}\frac{Z_A}{r_{iA}} + \sum_{i<j}^{N}\frac{1}{r_{ij}} + \sum_{A<B}^{M}\frac{Z_A Z_B}{R_{AB}}$$

BUT, COULD YOU PLEASE TELL ME WHICH TERM OF THE HAMILTONIAN – *THE OPERATOR THAT REPRESENTS THE TOTAL ENERGY OF THE SYSTEM* – IS RESPONSIBLE FOR THIS PART -*NON DYNAMIC CORRELATION ENERGY* – OF THE TOTAL ELECTRONIC ENERGY OF THE SYSTEM???

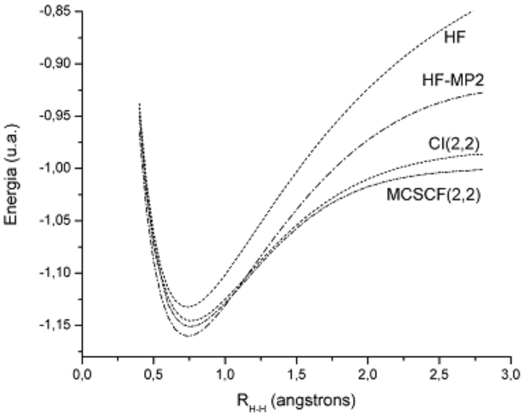
NONE!!! THERE IS NOTHING IN THE HAMILTONIAN THAT COULD ACCOUNT FOR THIS PART OF THE ENERGY OF THE SYSTEM.

Correlation Energy via MP2



WHY MP2 DOES NOT WORK?

Correlation Energy via CI and MCSCF



WHY MCSCF WORKS BETTER THAN CI ?

VERY SIMPLE ANSWER: MP2 DOES NOT CHANGE THE FORM OF THE HF WF WHILE BOTH MCSCF AND CI DO CHANGE THE FORM OF THE HF WF.

SO WHAT? IN WHAT WAY IS THE HF FORM CHANGED?

$\Psi_{MCSCF} = c_1 (1\sigma_g)^2 + c_2 (1\sigma_u)^2$ c_1 , c_2 , $1\sigma_g$ and $1\sigma_u$ variationally determined

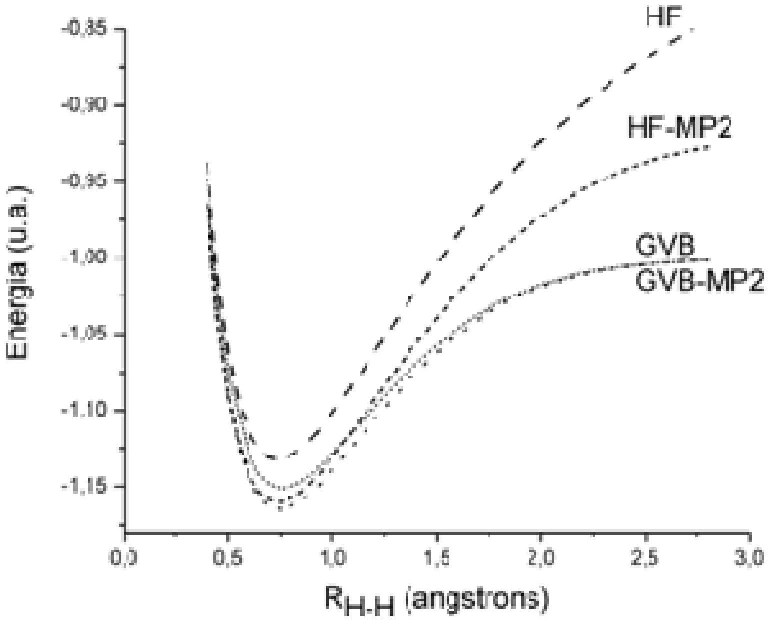
$\Psi_{CI} = c_3 (1\sigma'_g)^2 + c_4 (1\sigma'_u)^2$ only c_3 and c_4 variationally determined

As $R_{H\text{-}H}$ increases: $c_1 \cong - c_2$ e $c_3 \cong - c_4$

$\Psi_{MCSCF} \cong \Psi_{CI} = [1s_a(1)1s_b(2)+1s_a(2)1s_b(1)][\alpha\beta - \beta\alpha]$!!!

BUT THIS IS THE GVB FUNCTION WHICH HAS THE CORRECT FORM!!!

CORRELATION ENERGY FOR THE GVB WAVE FUNCTION



SUMMARY OF THE CONSEQUENCES OF NEGLECTING PERMUTATION SYMMETRY

1- DOUBLE OCCUPANCY OF THE ORBITALS (ATOMIC OR MOLECULAR) INTRODUCED WITHOUT ANY JUSTIFICATION IN ORDER TO GENERATE WF WITH A DEFINED SPIN.

2- WRONG APPROACH TO THE ANTISYMMETRY PRINCIPLE USING THE PROBABILISTIC INTERPRETATION.

THUS

$$|\Psi\,(1,2,3\,\ldots i,\, j,\, \ldots.N;\, t)\,|^2 = |\,\Psi\,(1,2,3,..j,\, i\ldots N;\, t)\,|^2$$

$$\Psi(1,2,3,\,\ldots i,\, j,\, \ldots.N;\, t) = \pm\; \Psi\,(1,2,3,..j,\, i\ldots N;\, t)$$

3- MISINTERPRETATION OF THE EXCHANGE INTEGRAL.

4- ENERGY OF WFs DEPEND DIRECTLY ON THE SPIN COORDINATES DESPITE THE FACT THAT THE OPERATOR WHICH DEFINES THE ENERGY OF THE SYSTEM DOES NOT DEPEND ON SPIN COORDINATES. THIS RESULT VIOLATES TWO QUANTUM MECHANICAL POSTULATES.

4- OVERESTIMATION OF THE TRUE ELECTRONIC CORRELATION ENERGY

5- INTRODUCTION OF THE TOTALLY UNPHYSICAL EFFECT CALLED "*NON-DYNAMIC CORRELATION ENERGY*"

THERE IS NO TERM IN THE HAMILTONIAN WHICH ACCOUNTS FOR SUCH AN "ENERGY"(???)

6- INTRODUCTION OF A TOTALLY ARTIFICIAL "CORRELATION" BETWEEN ELECTRONS WITH THE SAME SPIN.

THERE IS NOTHING IN THE HAMILTONIAN THAT DISTINGUISHES ELECTRONS WITH SPIN UP FROM SPIN DOWN FOR THE SIMPLE REASON THAT THE HAMILTONIAN DOES NOT CONTAIN SPIN COORDINATES.

SOME ADVANTAGES OF USING WAVE FUNCTIONS THAT ACCOUNT FOR THE PERMUTATION SYMMETRY OF THE MANY-ELECTRONS HAMILTONIAN

CAS-GVB : **Much easier interpretation of the results and better convergence**

- S. Clifford, M. J. Bearpark, M. A. Rob, *Chem. Phys. Lett* 1996, *255*, 320.
- L. Blancafort, P. Celani, M. J. Bearpark, M. A. Rob, *Theor. Chem. Acc.* 2003, *110*, 92

GVB-CI : **Computational cheaper and generally as accurate as the post-HF methods**

- J. Cullen, J*. Comput. Chem* 1999, *20*, 999.

GVB-inspired CC theories: **Single-bond and multiple bond dissociation energies for closed and open-shell systems.**

- T. van Voorhis, M. Head-Gordon, *J. Chem. Phys* 2002, *117*, 9190.
- D. W. Small, K. V. Lawler, M. Head-Gordon, *J. Chem. Theor. Comput* 2014, *10*, 2027.
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TD-GVB: Accuracy of the excitation energies superior to those obtained with the TD-HF

K. Chatterjee, K. Pernal, Theor. Chem. Acc. 2015, *134,* 118.

ERPA-GVB: Energy barriers of excellent accuracy and comparable to the ones obtained at the CCSD(T) level, which requires a much higher computational effort.

K. Chatterjee, E. Pastorczak, K. Jawulski, K. Pernal, *J. Chem. Phys* 2016, *144*, 244111

INTERFERENCE ENERGY ANALYSIS: Based on GPF built from GVB-WF, provides a unique way of analysing chemical bonds in different types of molecules exhibitin distinct bonding patterns.

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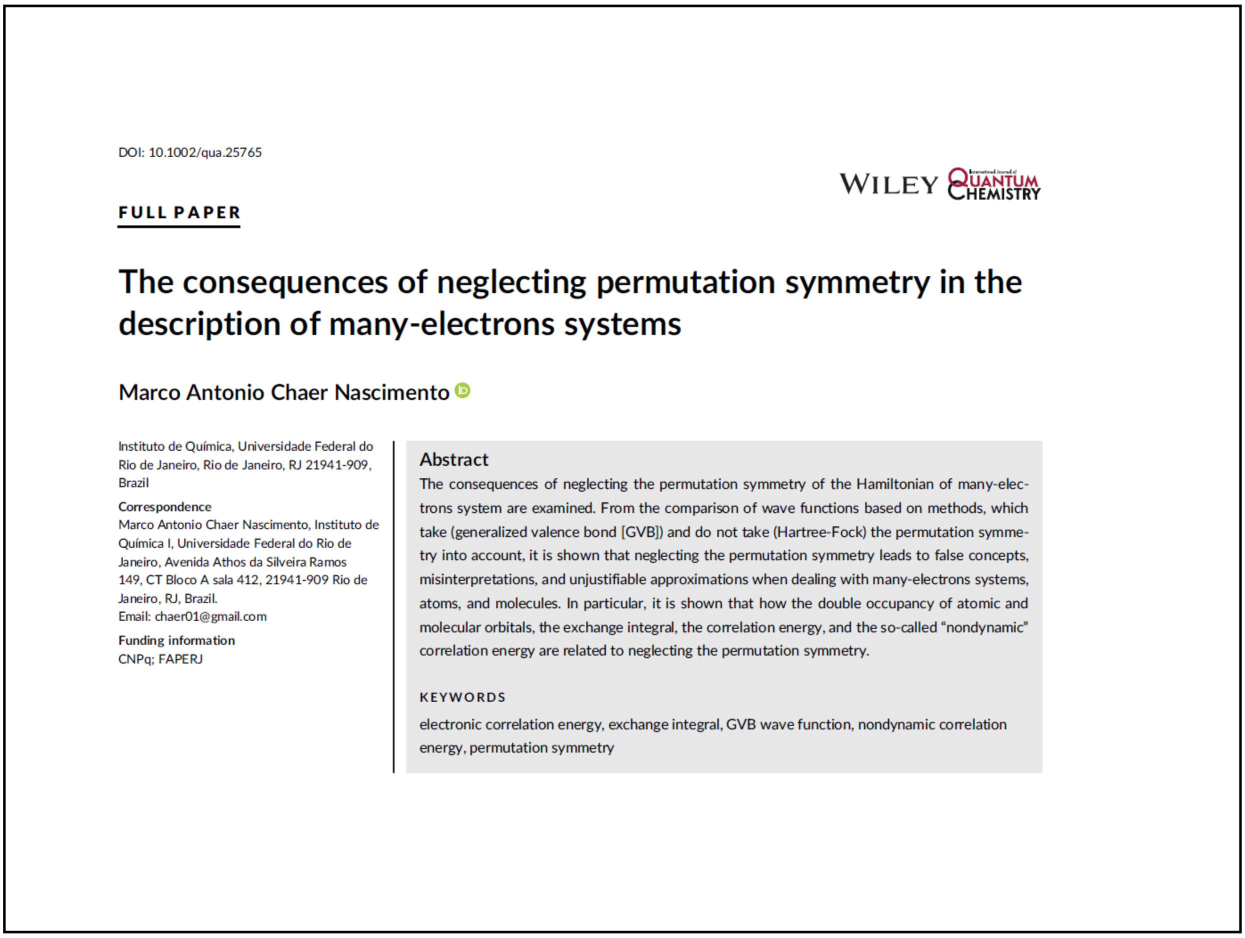
and references therein.



DOI: 10.1002/qua.25765

WILEY International Journal of QUANTUM CHEMISTRY

FULL PAPER

The consequences of neglecting permutation symmetry in the description of many-electrons systems

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Abstract

The consequences of neglecting the permutation symmetry of the Hamiltonian of many-electrons system are examined. From the comparison of wave functions based on methods, which take (generalized valence bond [GVB]) and do not take (Hartree-Fock) the permutation symmetry into account, it is shown that neglecting the permutation symmetry leads to false concepts, misinterpretations, and unjustifiable approximations when dealing with many-electrons systems, atoms, and molecules. In particular, it is shown that how the double occupancy of atomic and molecular orbitals, the exchange integral, the correlation energy, and the so-called "nondynamic" correlation energy are related to neglecting the permutation symmetry.

KEYWORDS

electronic correlation energy, exchange integral, GVB wave function, nondynamic correlation energy, permutation symmetry

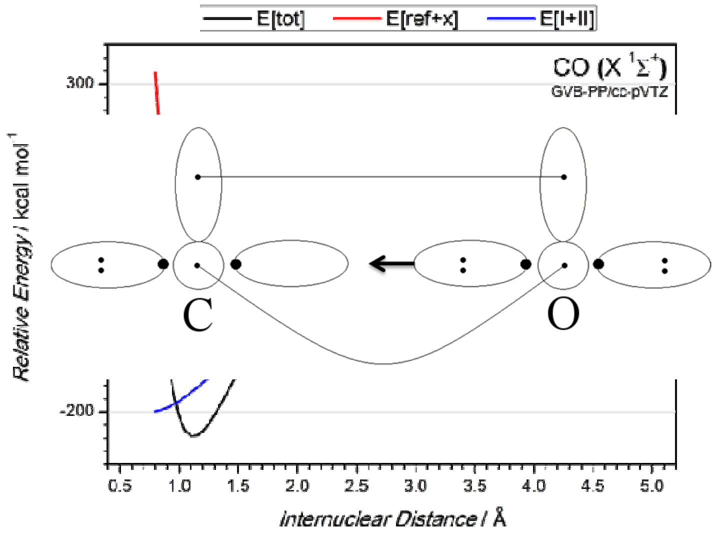
THE CO MOLECULE

μ_{CO} =0.120 D $C^{-}O^{+}$

μ_{CO} (GVB)= 0.112 D $C^{-}O^{+}$

- The (CO) molecule

μ_{CO} (HF_{num})= 0.265 D $C^{+}O^{-}$



GVB - *JCTC* (2014) *10* , 2322 HF_{num} *Comp. Phys. Reports* (1986) *4*, 313

HEXATRIENE - RYDBERG STATES

For GVB Calculations, see:

Chem. Phys. (1980) *53*, 265

THE GENERALIZED MULTISTRUCTURAL (GMS) WAVE FUNCTION AND APPLICATIONS TO SYMMETRY-BREAKING PROBLEMS.

Basic reference:

A Generalized Multistructural (GMS) Wavefunction.
E. Hollauer, M.A. Chaer Nascimento, *J. Chem.Phys.* (1993), *99*, 1207

DEFINITION:

$$\Psi_{GMS} = \sum_{i}^{N} c_i \, \psi_i$$

ψ_i represents "***structure i***" at:

- HF
- VB
- MCSCF
- CI
- ANY PLAUSIBLE COMBINATION

LEVEL

- EACH ψ_i IS INDEPENDENTLY OPTIMIZED OR SIMULTANEOUSLY WITH ALL THE OTHERS;
- $\{c_i\}$ ARE VARIATIONALLY DETERMINED.

EQUIVALENCE TO OTHER WAVE FUNCTIONS:

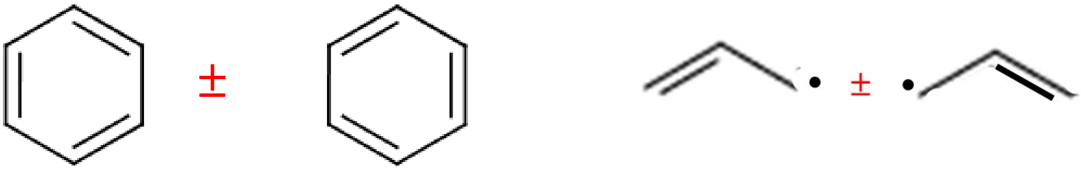
a) If $\psi_i = \psi_{VB}$ for $\forall i \Rightarrow \Psi_{GMS} \equiv \Psi_{VB}$

b) If $N=2$, $\psi_1 = \psi_{GVB/PP}$

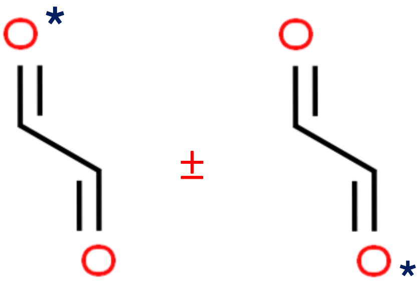
and $\psi_2 = \hat{R}\psi_1 \Rightarrow \Psi_{GMS} \equiv \Psi_{R-GVB}$ or $\equiv \Psi_{G-RVB}$

WHEN IS A GMS WAVE FUNCTION NEEDED?

a) MOLECULES WHICH CANNOT BE REPRESENTED BY A SINGLE CHEMICAL STRUCTURE.



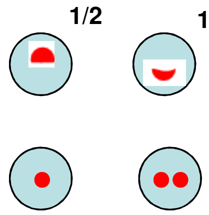
b) MOLECULES PRESENTING COUPLED LOCALIZED EXCITATIONS.



$n \rightarrow \pi^*$

c) CORE IONIZED OR EXCITED STATES OF MOLECULES

Ex: O_2



ionize $1\sigma_g$ →

MO description $D_{\infty h}$

broken symmetry $C_{\infty v}$

$\Psi_{GMS} =$

correct symmetry $D_{\infty h}$

d) NEAR DEGENERATED ATOMIC CONFIGURATIONS

Ni	**s^2d^8 - s^1d^9**	**~ 0.03 eV**
V	**s^2d^3 - s^1d^4**	**~ 0.10 eV**
Fe	**s^2d^6 - s^1d^7**	**~ 0.85 eV**

From which configuration should one start a calculation?

HF →

MCSCF → VH and NiH $4s^2 3d^n$ and $4s^1 3d^{n+1}$

STRONGLY MIXED

FeH

$^6\Delta$ $6\sigma^2\, 7\sigma^1\, 9\sigma^1\, \delta^1_{x^2-y^2}\, \delta^3_{xy}\, 3\pi^2_x\, 3\pi^1_y$ dominant

$^4\Delta$ strong mixture of the quartet coupling of the above configuration and

$6\sigma^2\, 9\sigma^2\, \delta^1_{x^2-y^2}\, \delta^2_{xy}\, 3\pi^1_x\, 3\pi^1_y$ ($4s^1 3d^7$)

$$\Psi_{\text{FeH}} = c_1\, \psi\, [\,\text{Fe}\, (4s^1 3d^7) - \text{H}\,] + c_2\, \psi\, [\,\text{Fe}\, (4s^2 3d^6) - \text{H}\,]$$

e) ELECTRONIC EXCITED STATES OF MIXED CHARACTER

^1B_u in linear polyenes

$\Psi_{GMS} = c_v$ ()* + c_R ()*

f) TO TAKE INTO ACCOUNT ELECTRONIC CORRELATION EFFECTS

ADVANTAGES OF THE GMS WAVE FUCNTION

- COMPACT
- EASY TO INTERPRET (IF POSSIBLE RETAINING THE SINGLE PARTICLE PICTURE) IN TERMS OF CHEMICAL STRUCTURES AND BONDS
- INCLUDES MOST OF THE IMPORTANT CORRELATION EFFECTS WITH LESS COMPUTATIONAL EFFORT.

SOME EXAMPLES

Volume 184, number 5,6 CHEMICAL PHYSICS LETTERS 4 October 1991

A generalized multi-structural wavefunction. The He_2^+ molecule as an example

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Received 2 June 1991; in final form 18 July 1991

Table 3
Results of CI calculations

Calculation	Energy (hartree)	D_e (eV)	R_e (bohr)
GMS-CI	−4.98377	2.340	2.0598
CASSCF/CI [a]	−4.91834	2.36	2.358
PNO/CI [b]	−4.98415	2.24	2.0626
VB/CI [c]	−4.98594	2.30	2.06
full-CI [d]	−4.99389	2.469	2.044
experimental		2.34 [e] 2.55 [f]	2.0424 [g]

[a] Ref. [29]. [b] Ref. [28]. [c] Ref. [15]. [d] Ref. [17].
[e] Ref. [26]. [f] Ref. [27]. [g] Ref. [30].

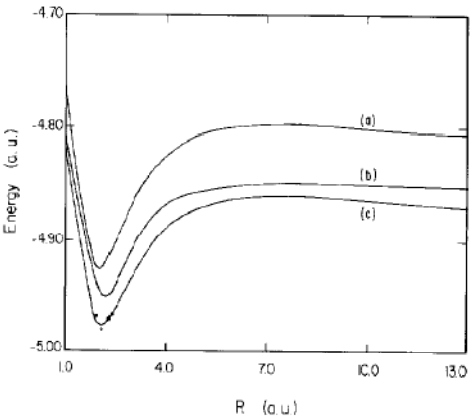


Fig. 4. Potential energy curves obtained with different wavefunctions, at the CI level: (a) VB; (b) orthogonal CI (see text); (c) GMS (CI) wavefunction; (○) ref. [17]; (●) ref. [28].

1) MOLECULES PRESENTING COUPLED LOCALIZED EXCITATIONS

$(n \rightarrow \pi^*)^{1,3}$

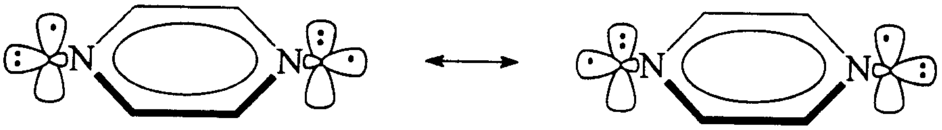


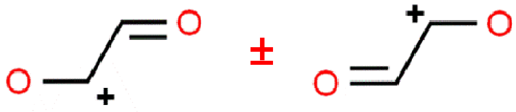
Table 4

Transition energies (eV) for the $(n \rightarrow \pi^*)^{1,3}$ excited states of the pyrazine molecule

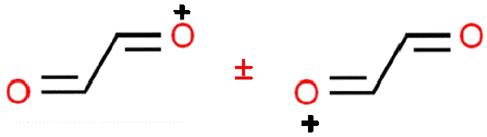
State	HF	CI-SD	GMS	Exp.
$^3B_{3u}$	4.52	3.51	3.27	3.33 [56,57]
$^1B_{3u}$	5.27	4.20	3.89	3.85 [56,58]
$^3B_{2g}$	6.23	5.21	4.77	4.59 [56]

A.G.H. Barbosa, M.A. Chaer Nascimento, *Theo. Comp. Chem. 10*, 117 (2002)

2) IONIC STATES OF TRANS-GLYOXAL MOLECULE



π^{-1} states



n^{-1} states

ground state: GVB(4/PP)   2 π bonds + 2 O lone pairs

ion states: GVB(3/PP)

2 π bonds + O lone pair n^{-1} states

1 π bond + 2 O lone pairs π^{-1} states

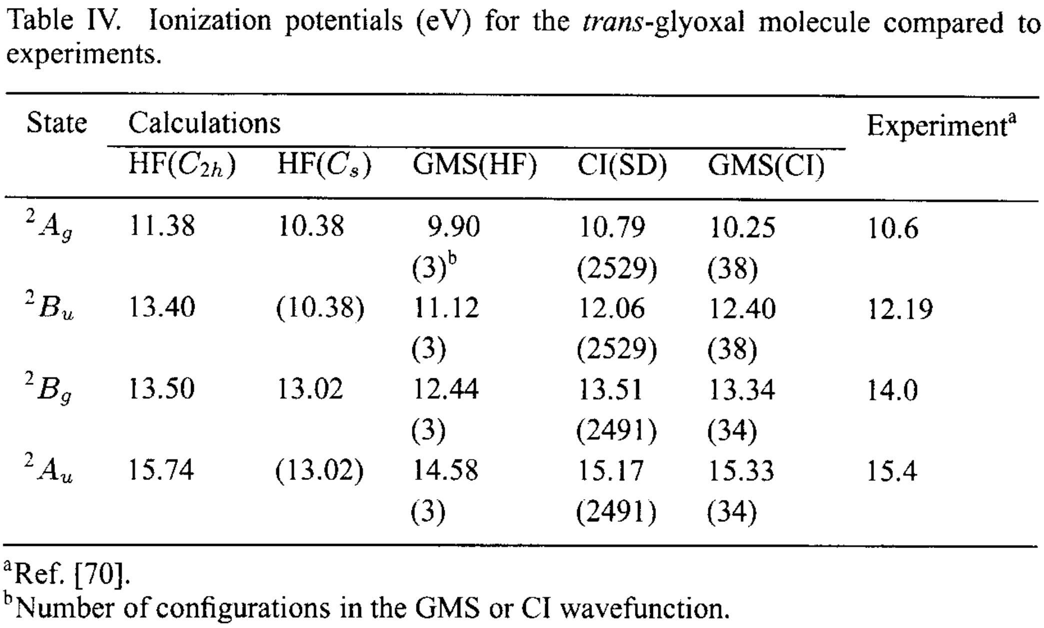


Table IV. Ionization potentials (eV) for the *trans*-glyoxal molecule compared to experiments.

State	Calculations					Experiment[a]
	HF(C_{2h})	HF(C_s)	GMS(HF)	CI(SD)	GMS(CI)	
^2A_g	11.38	10.38	9.90	10.79	10.25	10.6
			(3)[b]	(2529)	(38)	
^2B_u	13.40	(10.38)	11.12	12.06	12.40	12.19
			(3)	(2529)	(38)	
^2B_g	13.50	13.02	12.44	13.51	13.34	14.0
			(3)	(2491)	(34)	
^2A_u	15.74	(13.02)	14.58	15.17	15.33	15.4
			(3)	(2491)	(34)	

[a] Ref. [70].

[b] Number of configurations in the GMS or CI wavefunction.

E. Hollauer, M.A. Chaer Nascimento, *Chem. Phys.* (1993) *174*, 79

3) CORE IONIZED AND CORE EXCITED STATES OF MOLECULES

$$\psi_{\mathrm{GMS}} = c_1\varphi\,\underset{\mathrm{I}}{(\mathrm{N}\text{—}^{\circ}\text{—}\mathrm{N})} + c_2\{\varphi\,\underset{\mathrm{II}}{(\mathrm{N}\text{—}\mathrm{N}^{\circ})} \pm \varphi\,\underset{\mathrm{III}}{(\mathrm{N}^{\circ}\text{—}\mathrm{N})}\}$$

I : delocalized hole state

II and II : localized hole state

Coefficient c_2 can be used to define degree of localization

Same type of GMS wavefunction was used to study core excited states of C_2H_2 and CO_2 and core ionized states of O_2 molecules.

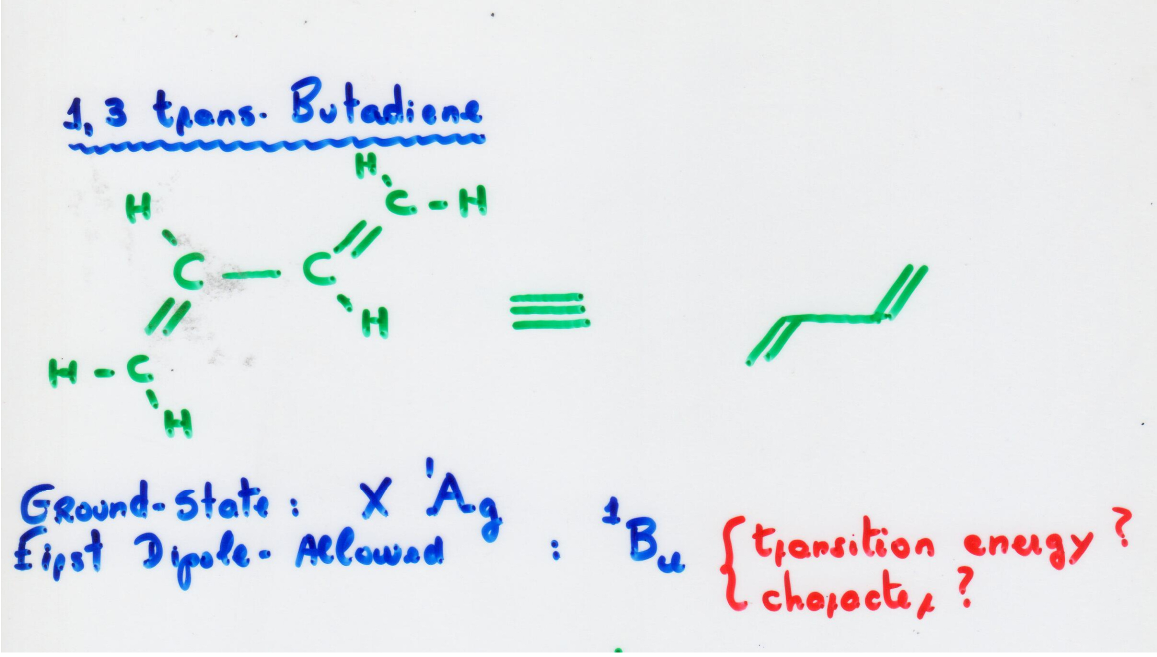
M.P. Miranda, C.E. Bielschosky, M.A. Chaer Nascimento, *J. Phys.* B28, L15 (1995)

Table V. Transition energies (ΔE), optical oscillator strengths ($f_{\rm on}$) and degrees of localization (d_l and τ_h^*/τ_h) for N_2, C_2H_2, CO_2 and O_2 molecules.

	ΔE (eV)		$f_{\rm on}$			
Transition	Theory	Experiment	Theory	Experiment	d_l	τ_h^*/τ_h
$N_2(12s7p1d)/[9s, 5p, 1d]$						
$1\sigma_g \rightarrow 1\pi_g$	402.62	401.1[a]			0.78	0.75[b]
$1\sigma_u \rightarrow 1\pi_g$	402.55		0.200	0.200,[c] 0.18[d]	0.78	
$C_2H_2(12s7p1d; 5s2p)/[10s5p1d; 3s1p]$						
$1\sigma_g \rightarrow 1\pi_g$	287.49	285.81[a]			0.67	0.60[e]
$1\sigma_u \rightarrow 1\pi_g$	287.47		0.175		0.67	
$CO_2(12s6p1d)/[10s, 4p, 1d]$						
$1\sigma_g \rightarrow 2\pi_u$	535.99	534.4,[f] 535.3[g]	0.093	0.12–0.13[h]	0.86	
$1\sigma_u \rightarrow 2\pi_g$	535.99				0.86	
$O_2(12s7p1d)/[9s, 5p, 1d]$						
$1\sigma_g \rightarrow {}^2\Sigma_g^-$	544.07	544.2[i]			0.82	
$1\sigma_g \rightarrow {}^4\Sigma_g^-$	543.31	543.1[i]			0.82	

[a]Ref. [76]; [b]Ref. [75]; [c]Ref. [77]; [d]Ref. [78]; [e]Ref. [79]; [f]Ref. [80]; [g]Ref. [81]; [h]Ref. [82]; [i]Ref. [83].

4) ELECTRONIC EXCITED STATES OF MIXED CHARACTER



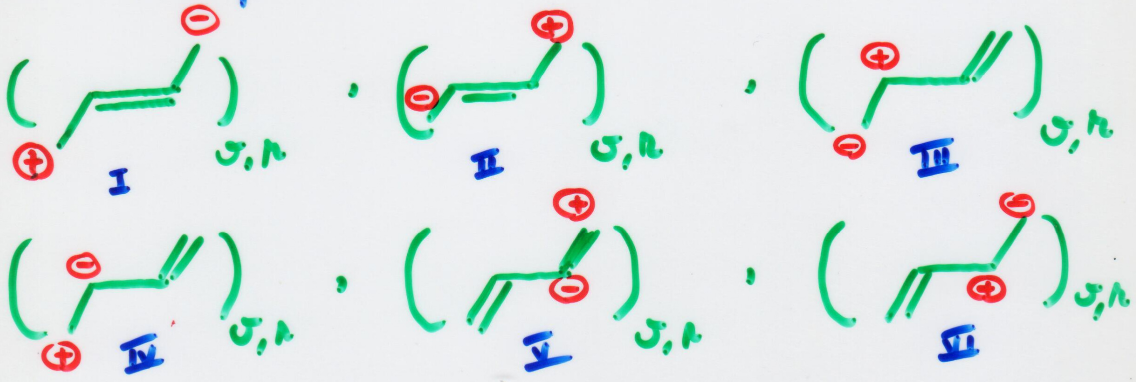
1,3 trans- Butadiene

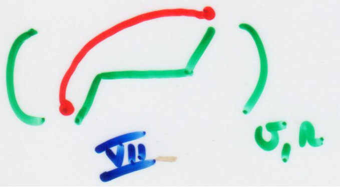
Ground-State : X ^1A_g

First Dipole- Allowed : ^1B_u $\left\{ \begin{array}{l} \text{transition energy ?} \\ \text{character ?} \end{array} \right.$

MO description :

GMS description:





$$\Psi_{GMS}\,({}^1B_u) = \qquad (c_V\,\psi_V + c_R\,\psi_R)$$

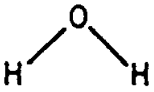
RESULTS:

ΔE $({}^1B_u - X\,{}^1A_g)$ = 6.14 eV **Exp. 5.95 eV**

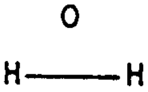
$$\Psi_{GMS}\,({}^1B_u) = 0.85\,\psi_R + 0.49\,\psi_V$$

W. B. Floriano (M.Sc. Thesis, Instituto de Química da UFRJ, 199).

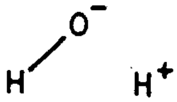
5) ELECTRONIC CORRELATION ENERGY



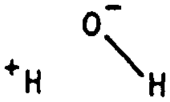
(IV)



(V)



(VI)



(VII)

$$\Psi_{\mathrm{GMS}}(^1A_1) = c_1\varphi_{\mathrm{IV}} + c_2\varphi_{\mathrm{V}} + c_3(\varphi_{\mathrm{VI}} + \varphi_{\mathrm{VII}}).$$

W.B. Floriano, S.R. Blaskowsky, M.A. Chaer Nascimento, *J.Mol.Struc. 335*, 51, 1995

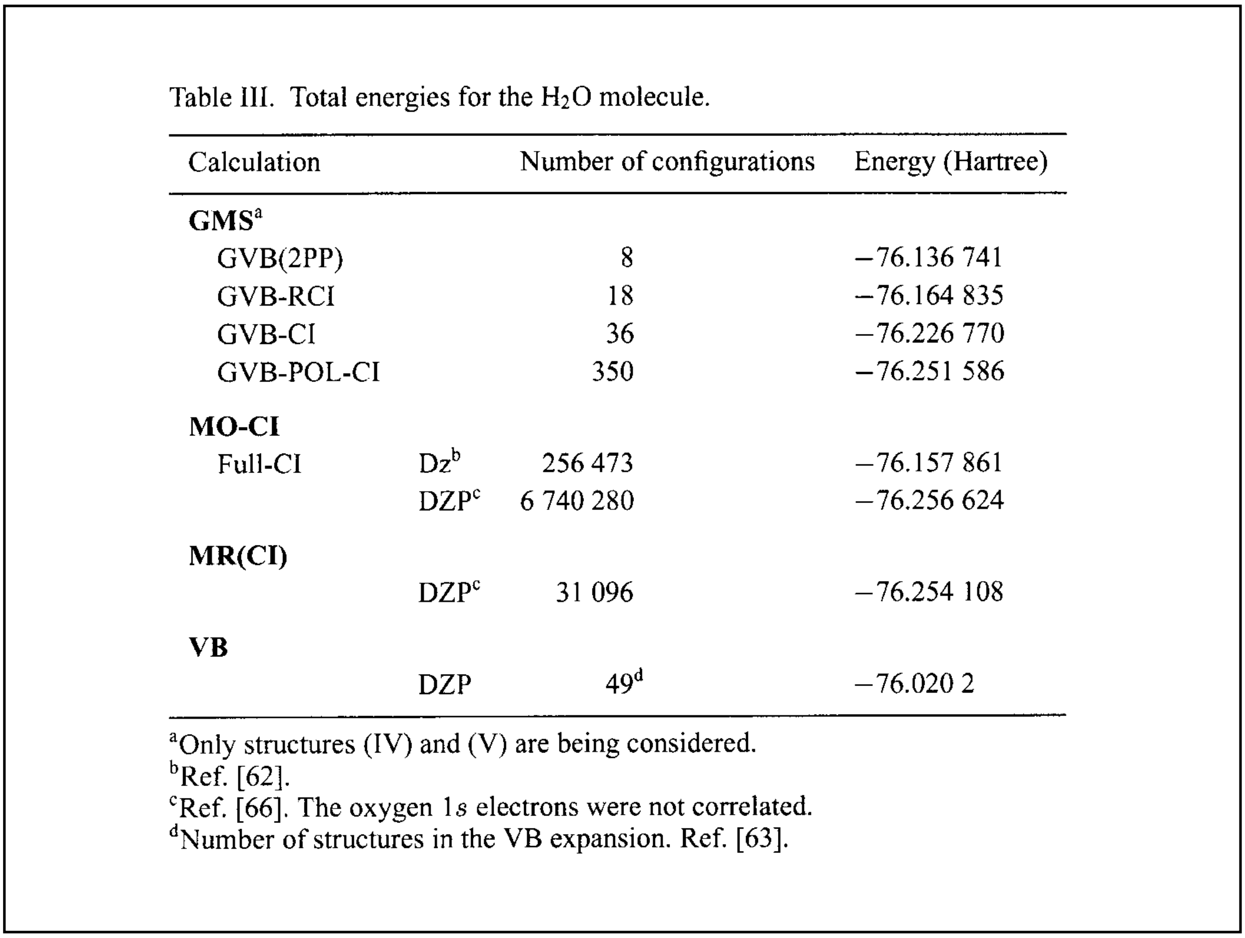


Table III. Total energies for the H_2O molecule.

Calculation		Number of configurations	Energy (Hartree)
GMS[a]			
GVB(2PP)		8	−76.136 741
GVB-RCI		18	−76.164 835
GVB-CI		36	−76.226 770
GVB-POL-CI		350	−76.251 586
MO-CI			
Full-CI	Dz[b]	256 473	−76.157 861
	DZP[c]	6 740 280	−76.256 624
MR(CI)			
	DZP[c]	31 096	−76.254 108
VB			
	DZP	49[d]	−76.020 2

[a] Only structures (IV) and (V) are being considered.

[b] Ref. [62].

[c] Ref. [66]. The oxygen 1*s* electrons were not correlated.

[d] Number of structures in the VB expansion. Ref. [63].

6) RELATIVE ACIDITY OF ALCOHOLS AND CARBOXYLIC ACIDS

DEFINITION:

$R\text{-}H \rightarrow R^- + H^+$ ΔG^o_T measures acidity

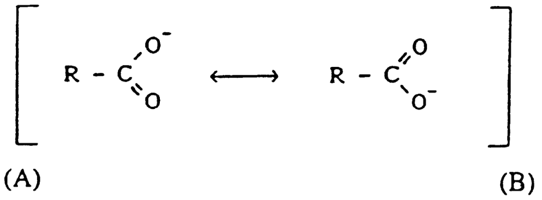
Usually ΔH^o_T , because entropic fator (mainly H^+) cancels out in a comparison of the relative acidities.

CALCULATE:

$$\Delta E^o_{eq} = (RH)_{min} - R^-_{min} \xrightarrow{ZPE} \Delta E^0_0 \rightarrow \Delta H^0_0 \xrightarrow{T} \Delta H^0_T$$

WHY ARE CARBOXYLIC ACIDS ARE MORE ACIDIC THAN ALCOHOLS ?

Generally accepted explanation:



Resonance stabilization
of the carboxylate.

Siggel and Thomas: **Indutive effects (acid) are responible for differences in acidity.**

JACS 108, 4360 (1986)

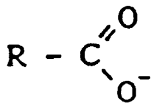
QUESTIONS:

a) By how much is the carboxylate stabilized by resonance?

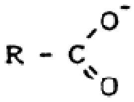
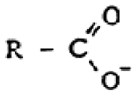
b) How to quantify it?

THE GMS APPROCH:

a) Solve for the localized structure at the GVB level:

$\Psi^{GVB} =$ 

b) Construct:

$\Psi^{GVB}_{GMS} =$  + 

c) Take $\Delta E = E\,[\,\Psi^{GVB}_{GMS}\,] - E\,[\Psi_{GVB}]$ as the resonance contribution.

Table VI. Gas-phase acidities at the GVB + CI and GMS + CI levels of calculation.

	CH_3OH	HCOOH	C_2H_5OH	CH_3COOH
$\Delta E^0_{\text{eq.}}$	0.6206	0.5922	0.6149	0.6005
Corrections (eV)				
ΔE^t_T	0.038	0.038	0.038	0.038
ΔE^r_T	0.0	0.0	0.0	0.0
ΔE^v_T	0.0	0.0	0.0	0.0
$\Delta(PV)$	0.025	0.025	0.025	0.025
$\Delta(ZPE)$	−0.423	−0.381	−0.419	−0.374
Resonance:	0.0	−0.779	0.0	−0.753
ΔH^0_{28} (This work)				
(kcal/mol)	381.11	346.26	377.62	352.13
(eV)	16.52	15.02	16.37	15.27
(Hartree)	0.6073	0.5520	0.6018	0.5612
Ref. [88]				
(kcal/mol)	383.26	343.14	380.03	343.60
(eV)	16.62	14.88	16.48	14.90
(Hartree)	0.6108	0.5468	0.6056	0.5476
Experiment [94] (kcal/mol)	379.14	345.19	376.13	348.46
(eV)	16.44	14.97	16.30	15.11
(Hartree)	0.6042	0.5501	0.5994	0.5553

CONCLUSION:

- **Resonance is the effect responsible for the larger acidity of carboxylic acids**

- **In the absence of resonance, methanol and ethanol would be more acidic than formic and acetic acid, respectively.**

J.D. Motta Neto, M.A. Chaer Nascimento, *J.Phys.Chem. 100,* 15105 (1996)

7) ELECTRON IMPACT INNER-SHELLS EXCITATION

Ex: N_2 $1\sigma_g \rightarrow 1\pi_g$ and $1\sigma_u \rightarrow 1\pi_g$ transition

$$\psi_{\mathrm{GMS}} = c_1 \underset{\mathrm{I}}{\varphi\,(\mathrm{N—^{\circ}—N})} + c_2\{\underset{\mathrm{II}}{\varphi\,(\mathrm{N—N^{\circ}})} \pm \underset{\mathrm{III}}{\varphi\,(\mathrm{N^{\circ}—N})}\}$$

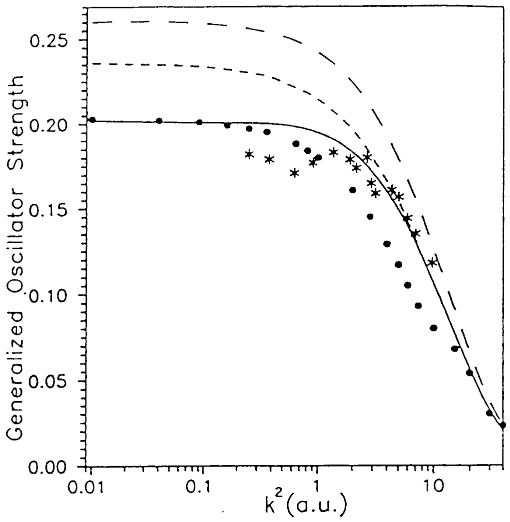


Figure 1. Total generalized oscillator strength for the preionization peak compared to experiments and other theoretical results: ——— GMS(CI); — — — (HFFC); - - - - Rescigno and Orel [85]; ● exp. of Camilloni *et al.* [77]; * exp. of Barbieri and Bonham [78].

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THE GVB SELF-CONSISTENT PROCEDURE

Exemplo: átomo de He.

a) Hartree-Fock:

$$\text{He (HF)} = \begin{vmatrix} 1s(1)\,\alpha(1) & 1s(1)\,\beta(1) \\ 1s(2)\,\alpha(2) & 1s(2)\,\beta(2) \end{vmatrix}$$

$$= \mid 1s(1)\,1s(2)\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)] \mid$$

$$= \mid 1s\,\overline{1s} \mid$$ (forma diagonal)

b) GVB ou SCVB:

$$\text{He (GVB)} = \mid \varphi_a\,\overline{\varphi_b} \mid - \mid \overline{\varphi_a}\,\varphi_b \mid$$

Pergunta: Como obter os orbitais φ_a e φ_b ?

Resposta: Os orbitais φ_a e φ_b “ótimos” são aqueles que minimizam o funcional:

$$E_{GVB} = \langle\psi_{GVB}|\, H \,|\, \psi_{GVB}\rangle \;/\; \langle\psi_{GVB}|\, \psi_{GVB}\rangle$$

Equações GVB

$$\psi_{GVB} = \varphi_a\, \varphi_b + \varphi_b\, \varphi_a \equiv ab + ba$$

$$E_{GVB} = \langle\psi_{GVB}|\, H\, |\, \psi_{GVB}\rangle / \langle\psi_{GVB}|\, \psi_{GVB}\rangle = N/D \quad (1),$$

onde ,

$$N = [\langle a|h|a\rangle + \langle b|h|b\rangle + J_{ab}] + [2\, \langle a|h|a\rangle\, S_{ab} + K_{ab}] \quad (2)$$

$D = 1 + S^2_{ab}$ e $S_{ab} = \langle a|b\rangle$.

Expandindo φ_a e φ_b na base $\{\chi_\mu\}$, obtemos:

$$\varphi_a = \Sigma_\mu \; c_{\mu a} \chi_\mu \qquad \text{e} \qquad \varphi_b = \Sigma_\mu \; c_{\mu b} \chi_\mu \qquad (3).$$

Aplicando as condições variacionais:

$$\frac{\partial E}{\partial c_{\mu a}} = 0 \qquad \text{e} \qquad \frac{\partial E}{\partial c_{\mu b}} = 0 \qquad (4),$$

obtemos, para φ_a :

$$< \chi_\mu \mid (H^a - \varepsilon_a \mid \varphi_a > \; = 0 \qquad (5),$$

onde:

$$\varepsilon_a = E - < b|h|b >$$

$$\text{e} \qquad H^a = (h + J_b + K_b) + P_b \, h + h \, P_b - E \, P_b \qquad (6)$$

$$P_b = |b> <b|$$

Introduzindo (3) em (5), obtemos a equação para φ_a :

$$\Sigma_\nu < \chi_\mu \mid (H^a - \varepsilon_a \mid \chi_\nu > \; c_{\nu a} \; = \; 0 \qquad (7)$$

ou $$\tilde{H}^a \tilde{C}_a \; = \; \varepsilon_a \tilde{S} \tilde{C}_a \qquad (8).$$

O elemento típico $H^a_{\mu\nu}$ é dado por:

$$H^a_{\mu\nu} = \; < \chi_\mu \mid H^a \mid \chi_\nu > \;\; = \;\; <\chi_\mu \mid (h + J_b + K_b) \chi_\nu> +$$
$$+ \; <\chi_\mu \mid b > < b \mid h \mid \chi_\nu> \; + \; <\chi_\mu \mid h \mid b > <b \mid \chi_\nu> \; -$$
$$- \; E \; <\chi_\mu \mid b > <b \mid \chi_\nu> \qquad (9).$$

Para fins de comparação:

$$H^{HF}_{\mu\nu} \; = \; <\chi_\mu \mid (h + J_b) \chi_\nu> \qquad (10).$$

Para o orbital φ_b , obteríamos uma equação similar:

$$\tilde{H}^b \tilde{C}_b = \varepsilon_b \tilde{S} \tilde{C}_b \qquad (11).$$

CONCLUSÃO:

Cada orbital GVB é obtido a partir da resolução de uma equação própria. Por isso eles são univocamente determinados.

HOW TO CONSTRUCT WAVE FUCNTIONS WHICH RESPECT PERMUTATION SYMMETRY

9) HOW TO CONSTRUCT WF WHICH SATISFY PAULI PRINCIPLE AND PRESENT THE CORRECT PERMUTATIONAL SYMMETRY ?

The symmetric S_N group : a very brief review:

a) Given N identical "objects" , the symmetric group S_N is the group formed by all possible permutations among them.

b) The number of irreducible representations of S_N is equal to the number of partitions of N :

$\lambda_1 + \lambda_2 + \lambda_3 + \ldots\ldots + \lambda_t = N$, with

$\lambda_1 \geq \lambda_2 \geq \lambda_3 \geq \ldots\ldots \geq \lambda_t$

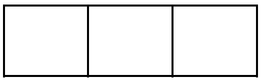
$[\lambda_1 , \lambda_2 , \lambda_3 , \ldots\ldots , \lambda_t]$ partition

Examples :

S_2 $n = 2$	[2] , [1,1] ≡ $[1^2]$	2 IR
S_3 $n = 3$	[3] , [2,1] , [1,1,1] ≡ $[1^3]$	3 IR
S_4 $n = 4$	[4] , [3,1] , [2,2] , [2,1,1] , [1,1,1,1]	5 IR

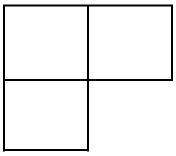
c) **Each partition is represented by a diagram, the Young diagram, formed by disposing identical "cells", one after the other, in rows, the number of cells in each row given by the value of λ.**

[3]



$\lambda_1 = 1$

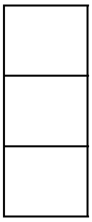
[2,1]



$\lambda_1 = 2$

$\lambda_2 = 1$

[1^3]



$\lambda_1 = 1$

$\lambda_2 = 1$

$\lambda_3 = 1$

Notice that, independent of the value of N, any symmetric group, S_N , will have the partitions [N] and [1^N]

d) **The dimension of a given IR is equal to the number of Young tableaux which can be constructed by filling the Young diagrams in such a way that the numbers increase from left to right, along the rows, and from top to bottom along the columns. (Ex. S_3)**

The tableaux constructed according to this rule are called the Standard Young tableaux.

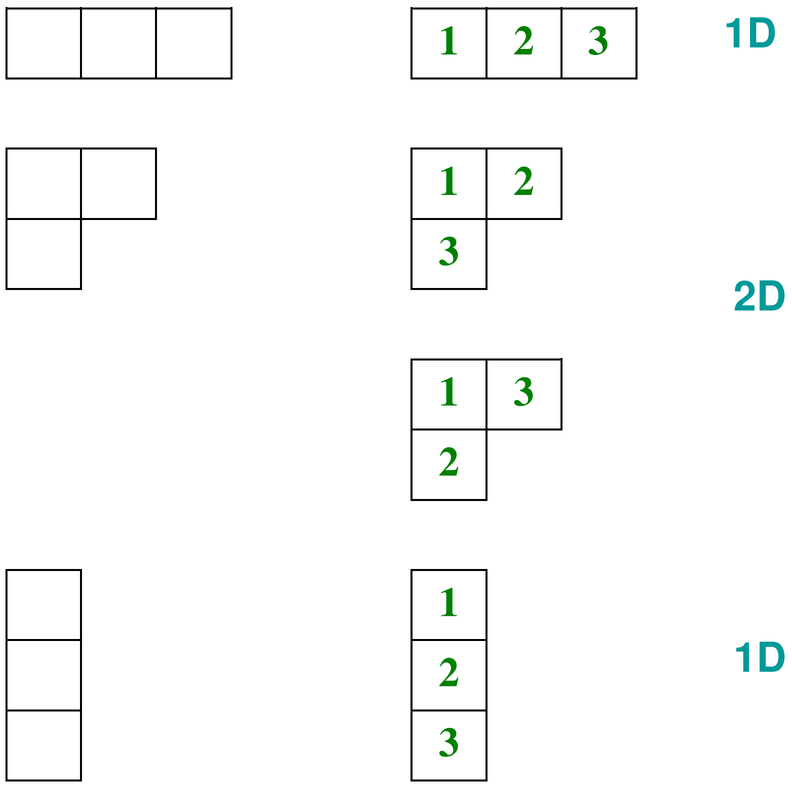


Diagram **Tableaux**

[3] 1D

[2,1] 2D

$[1^3]$ 1D

Notice that for any group S_N there is only one partition of the type [N] and one of the type [1^N], and that they give rise to the only two possible uni-dimensional IR of the group.

Once established the irreducible representations of the S_N and their respective dimensions, how to construct wave functions, which transform like the IRs of the group?

The Young Operator

Relative to a given standard Young tableau, let us define the operators :

P : exchanges two numbers in a row of the tableau. (horizontal permutation)

Q : exchanges two numbers in a column of the tableau. (vertical permutation)

With these two operators one can define :

$S = \Sigma_P P$ The symmetrizer operator relative the the rows of the Young tableau (summation over all horizontal permutations)

$A = \Sigma_Q (-1)^q Q$ The anti-symmetrizer operator relative to the columns of the Young tableau (summation over all vertical permutations), where q is the parity

The product Y = A.S defines the Young operator for a given tableau. In principle, in order to generate a basis for an IR associated to a given partition, one has to construct the Young operators for each one of the tableaux associated to that partition.

Once the Young operators, for each IR of S_N, have been built, spatial and spin wave functions transforming like a particular IR can be generated simply by applying the corresponding Young operators to functions of the spatial and spin variables respectively. Ex: $Y_{[2,1]}\ f\,(r_1,r_2,\ldots r_N)$

$Y_{[2,1]}\ g\,(s_1,s_2,\ldots s_N)$

We have already seen that, for any group S_N , there is one, and ONLY ONE, partition of the type [N] and [1^N], and that both these partitions give rise to UNI-dimensional IRs. How does the Young operator look like for these two IRs ?

$$Y_{[N]} \equiv S \quad \text{and} \quad Y_{[1,1\ldots]} \equiv A$$

$$Y_{[N]}\begin{cases} f\,(r_1,r_2,\ldots r_N) \\ g\,(s_1,s_2,\ldots s_N) \end{cases}$$

totally symmetric spatial
or
spin wave functions

$$Y_{[1,1,..]}\begin{cases} f\,(r_1,r_2,\ldots r_N) \\ g\,(s_1,s_2,\ldots s_N) \end{cases}$$

totally anti-symmetric spatial
or
spin wave functions

8) INDEPENDENT-PARTICLE MODELS

- Extremely useful for interpreting and rationalizing the results of quantum chemical calculations.

- Most of our understanding about the structure and properties of atoms and molecules derives from calculations based on IPM models.

Mandatory Features :

- The state of each individual particle of the system (one-electron states) must be uniquely defined. This feature allows:

a) to associate important properties, such as ionization potentials, electron affinities etc., to specific 1-e states of the many-electron system;
b) to interpret electronic spectra as resulting from changes in individual particle states;
c) to interpret the formation of chemical bonds in terms of individual 1-e states from the isolated atoms.

- The model should provide approximate solutions which retain all the symmetries of the exact solution of the system.

Which symmetries ?

- Permutation symmetry of the spatial and spin parts of the total wave function (**always present**)

- Point group symmetry (if exhibited by the hamiltonian of the system)

- Pauli symmetry : total wave function **MUST** be antisymmetric

$$\Psi(r,s;\xi) = \Sigma_{i,k}\, c_{ik}\, \psi_i\,(r;\xi)\, \chi_k\,(s)$$

10) IPM WAVE FUNCTIONS WITH THE CORRECT SYMMETRIES

According to the antisymmetry principle, the total wave function for a many-electron system MUST be totally antisymmetric with respect to the permutation of any two electrons. Within the IP approximation, functions $f(r_1,r_2,\ldots r_N)$ and $g(s_1,s_2\ldots s_N)$ are products of spatial $\{\varphi_1\varphi_2\varphi_3\ \varphi_4 \ldots\varphi_N\}$ and spin $\{\alpha\beta\alpha\beta\alpha\beta..\}$ parts.

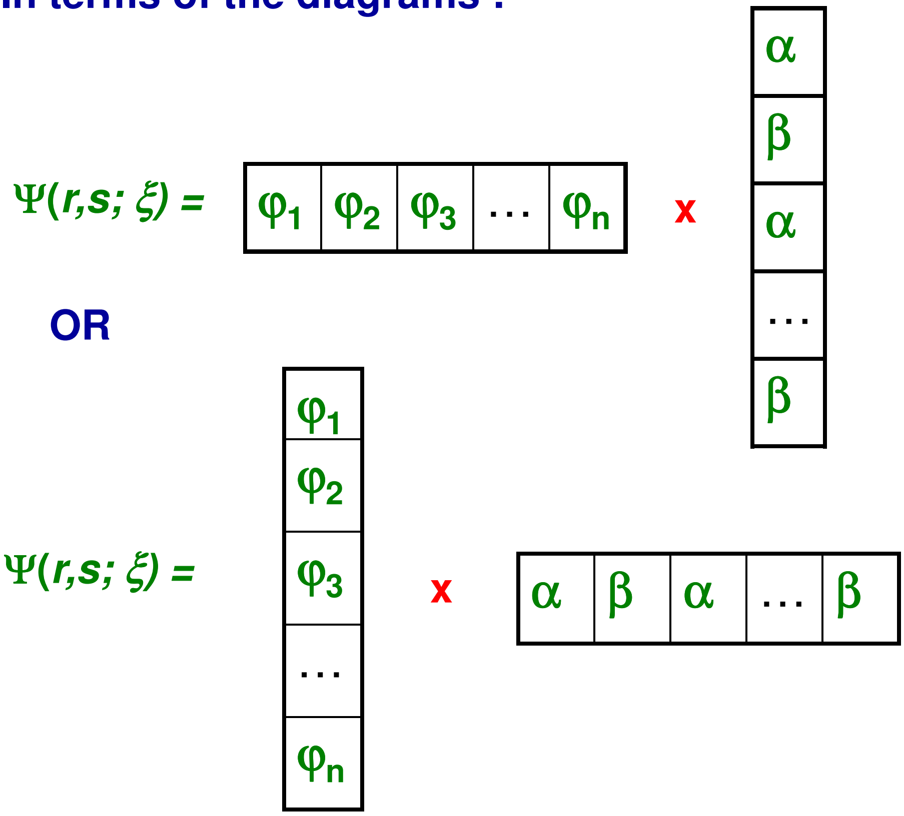
Two possibilities:

$$\Psi(r,s;\xi) = Y_{[N]}\{f(r_1,r_2,\ldots r_N)\} \quad \mathrm{x} \quad Y_{[1,1..]}\{g(s_1,s_2\ldots s_N)\}$$

or

$$\Psi(r,s;\xi) = Y_{[1,1..]}\{f(r_1,r_2,\ldots r_N)\} \quad \mathrm{x} \quad Y_{[N]}\{g(s_1,s_2\ldots s_N)\}$$

In terms of the diagrams :



$$\Psi(r,s;\xi) = \begin{array}{|c|c|c|c|c|}\hline \varphi_1 & \varphi_2 & \varphi_3 & \cdots & \varphi_n \\ \hline \end{array} \times \begin{array}{|c|}\hline \alpha \\ \hline \beta \\ \hline \alpha \\ \hline \cdots \\ \hline \beta \\ \hline \end{array}$$

OR

$$\Psi(r,s;\xi) = \begin{array}{|c|}\hline \varphi_1 \\ \hline \varphi_2 \\ \hline \varphi_3 \\ \hline \cdots \\ \hline \varphi_n \\ \hline \end{array} \times \begin{array}{|c|c|c|c|c|}\hline \alpha & \beta & \alpha & \cdots & \beta \\ \hline \end{array}$$

Beautiful, isn' it? YES, but we have a serious problem.

Because only two spin states are allowed for ANY electron in earth, it is IMPOSSIBLE to construct one spin function, totally anti-symmetric, for more than TWO electrons!! This is exactly equivalent to say that diagrams with more than 2 rows are not allowed for generating spin wave functions.

It is very easy to show that $$Y_{[1^N]} \begin{array}{|c|}\hline \alpha \\ \hline \beta \\ \hline \cdots\cdot \\ \hline \cdots \\ \hline \end{array} = 0 \text{ , for } N > 2 \text{ .}$$

In fact we have another serious problem regarding the spin wave function. Again, because only two spin states are allowed, one can only construct totally symmetric spin functions for a system where ALL the electrons are in the SAME SPIN STATE. That is, only for the highest spin state of the system.

That is, the only two possibilities for generating totally symmetric spin functions would be :

$$Y_{[N]} \quad \begin{array}{|c|c|c|c|c|}\hline \alpha & \alpha & \alpha & \ldots & \alpha \\ \hline \end{array}$$

$$Y_{[N]} \quad \begin{array}{|c|c|c|c|c|}\hline \beta & \beta & \beta & \ldots & \beta \\ \hline \end{array}$$

IN SUMMARY: starting from the **totally symmetric** and the **totally antisymmetric** representations of S_N, there are only **two possibilities** for constructing total wave functions satisfying the Pauli principle:

For N=2 : $\Psi(r,s;\xi) = Y_{[2]}\begin{array}{|c|c|}\hline \varphi_1 & \varphi_2 \\ \hline \end{array} \times Y_{[1,1]}\begin{array}{|c|}\hline \alpha \\ \hline \beta \\ \hline \end{array}$ **singlet**

For any vale of N :

$$\Psi(r,s;\xi) = Y_{[1^N]}\begin{array}{|c|}\hline \varphi_1 \\ \hline \varphi_2 \\ \hline \ldots \\ \hline \varphi_n \\ \hline \end{array} \times Y_{[N]}\begin{array}{|c|c|c|c|}\hline \alpha & \alpha & \ldots & \alpha \\ \hline \end{array}$$

Highest Spin state

Therefore, except for these two cases, total wave functions satisfying Pauli principle must be constructed as linear combination of products, of spatial and spin parts, which transform like some other IR of the S_N group :

$$\Psi = \Sigma_{i,k} \; c_{ik} \; \psi_i(\mu)\chi_k(\delta)$$

$\psi_i(\mu)$: spatial part transforms like the μ IR of S_N
$\chi_k(\delta)$: spin part transforms like the δ IR of S_N

How can we be sure that such a combination will be totally antisymmetric with respect to the permutation of any two electrons of the system ?

Wigner : the representations (μ) and (δ) must be *dual*, i.e., of the *same dimension*, and they must be the *transpose of each other*.

$$\Psi = \Sigma_i \, \psi_i(\mu) \, \tilde{\chi}_i(\mu)$$

General Procedure:

a) Given the multiplicity of the system (2S+1, where S is the total spin), construct all the tableaux corresponding to the given spin value, and obtain their “dual representations”, the transposed tableaux corresponding to the spatial part.

b) Construct the Young operators, Y = A.S , corresponding to all the tableaux, and operate with them on the products of spatial $\{\varphi_1\varphi_2\varphi_3\ \varphi_4 \ldots\varphi_N\}$ and spin $\{\alpha\beta\alpha\beta\alpha\beta..\}$ parts, in order to generate spatial and spin wave functions, ψ_i and χ_i , which transform like the "μ" repreentation of S_N

c) Set up the total wave function as :

$$\Psi = \Sigma_i\ \psi_i(\mu)\ \chi_i(\tilde{\mu})$$

Ex: 2-e Singlet

Spin part :

$$\begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline \end{array} \qquad Y = A\,(\alpha\beta) = \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

Spatial part :

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline \end{array} \qquad Y = S\,(\varphi_1\,\varphi_2) = \varphi_1(1)\,\varphi_2(2) + \varphi_1(2)\,\varphi_2(1)$$

$$\underset{A}{\Psi} = \underset{S}{\{\varphi_1(1)\varphi_2(2) + \varphi_1(2)\varphi_2(1)\}}\ \underset{A}{\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}}$$

Ex: 3-e Doublet

$$\begin{array}{lccccc}
\text{SPIN:} & Y_{T1} & \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & \multicolumn{1}{|c}{} \\ \cline{1-1}\end{array} & & Y_{T2} & \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 & \multicolumn{1}{|c}{} \\ \cline{1-1}\end{array} \\
 & & \times & + & & \times \\
\text{SPATIAL:} & Y_{T2} & \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 & \multicolumn{1}{|c}{} \\ \cline{1-1}\end{array} & & Y_{T1} & \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & \multicolumn{1}{|c}{} \\ \cline{1-1}\end{array}
\end{array}$$

$$Y_{T1} = [\,E - (13)]\,[\,E + (12)] \;=\; E + (12) - (13) - (13)\,(12)$$

$$Y_{T2} = [\,E - (12)]\,[\,E + (13)] \;=\; E - (12) + (13) - (12)\,(13)$$

Apart from a normalization factor, the total wave function is :

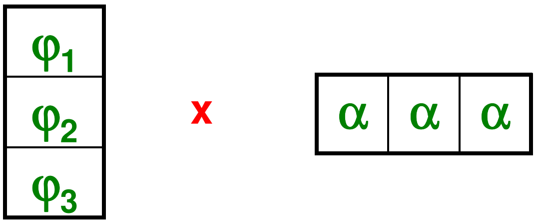
$$\Psi(r,s;\,\xi) = \{\, [\varphi_1\varphi_2\varphi_3 + \varphi_2\varphi_1\varphi_3 - \varphi_3\varphi_2\varphi_1 - \varphi_3\varphi_1\varphi_2]\,[\,\alpha\beta\alpha - \beta\alpha\alpha\,] +$$

$$+[\varphi_1\varphi_2\varphi_3 - \varphi_2\varphi_1\varphi_3 + \varphi_3\varphi_2\varphi_1 - \varphi_2\varphi_3\varphi_1]\,[\,\beta\alpha\alpha - \alpha\alpha\beta\,]\,\}$$

where: $\varphi_i\varphi_j\varphi_k \equiv \varphi_i(1)\,\varphi_j(2)\,\varphi_k(3)$

ATTENTION! This is not the expansion of a 3x3 determinant

Ex: 3-e Quartet



$$\begin{array}{|c|}\hline \varphi_1 \\ \hline \varphi_2 \\ \hline \varphi_3 \\ \hline \end{array} \quad \times \quad \begin{array}{|c|c|c|}\hline \alpha & \alpha & \alpha \\ \hline \end{array}$$

$\Psi(r,s;\xi) = [\varphi_1\varphi_2\varphi_3 + \varphi_3\varphi_1\varphi_2 + \varphi_2\varphi_3\varphi_1 - \varphi_3\varphi_2\varphi_1 - \varphi_1\varphi_3\varphi_2 - \varphi_2\varphi_1\varphi_3] \times [\alpha\alpha\alpha]$

This is the expansion of a 3x 3 determinant !

As the dimension of the representation "μ" increases, this procedure is not practical. However, the appropriate linear combination of products of the type $\psi_i(\mu)\ \chi_i(\tilde{\mu})$ is not hard to find. Since for any S_N there is ONE and only one totally anti-symmetric function, we can start with any function in the space $\psi_i(\mu)\ \chi_i(\tilde{\mu})$, and apply to it the projector operator of the totally anti-symmetric representation of S_N :

$$\varepsilon^{(1^N)} = (1/N!)\ \Sigma_P\ \delta_P\ P$$

to obtain: $\Psi = (1/N!)\ \Sigma_P\ \delta_P\ P\ [\ \psi_i^{(\mu)}(r_1,r_2\ldots r_N)\ \chi_i^{(\tilde{\mu})}(s_1,s_2\ldots s_N)\ ]$

where P operates on both the spatial and spin states.