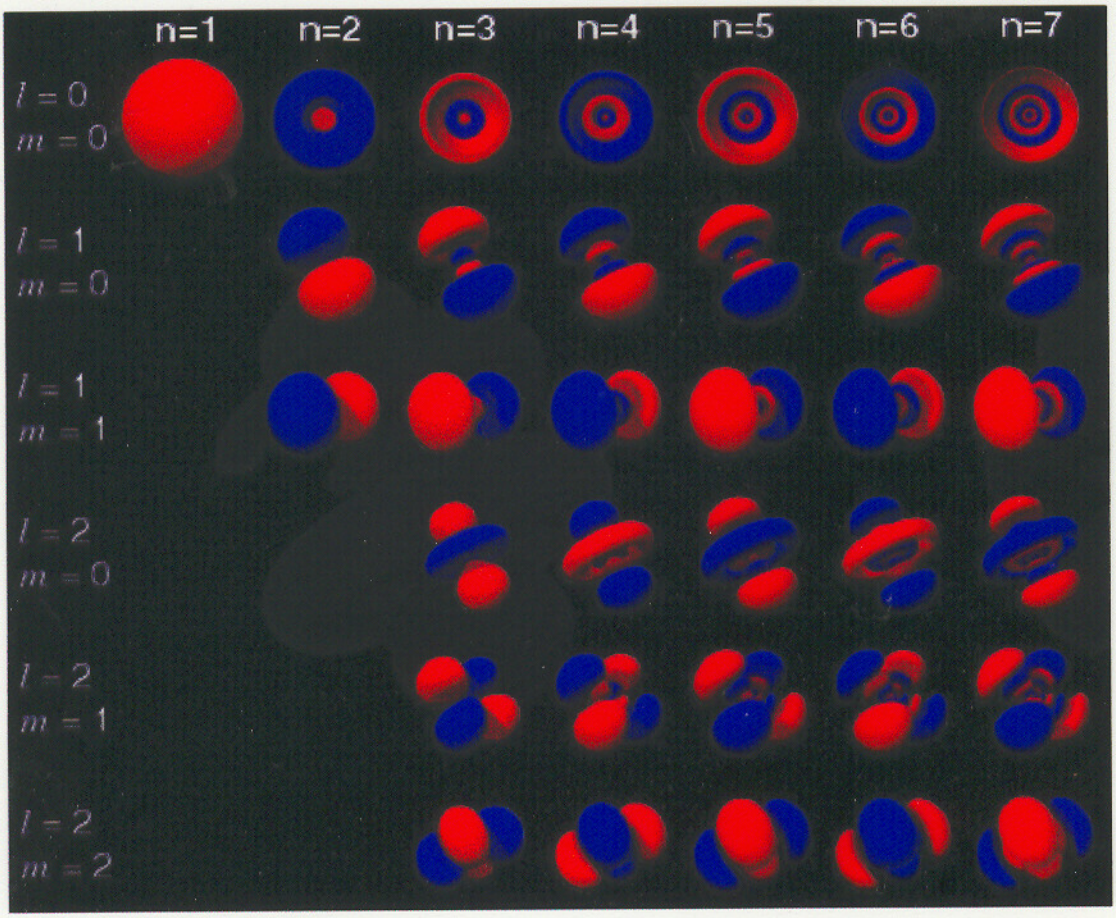
B3.1



The electron orbitals presented here represent a volume of space within which an electron would have a certain probability. For example, in a simple lowest-energy state hydrogen atom, the electrons are most likely to be found within a sphere around the nucleus of an atom. In a higher energy state, the shapes become lobes and rings. With the exception of the $n = 1$ orbital, all orbitals in the top row are cutaway to show the concentric spheres. For more details and a larger collection, see http://www.albany.net/~cprimus/self/orbtable.htm

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Some hydrogen orbitals | What's in a Star? | ChemConnections

1. FOR HIGHER n AND l : MORE LOBES AND RINGS, MORE CONCENTRIC SPHERES...

2. „THE INTERNAL NODES" OF ORBITALS DO NOT HAVE PHYSICAL OR CHEMICAL IMPORTANCE...

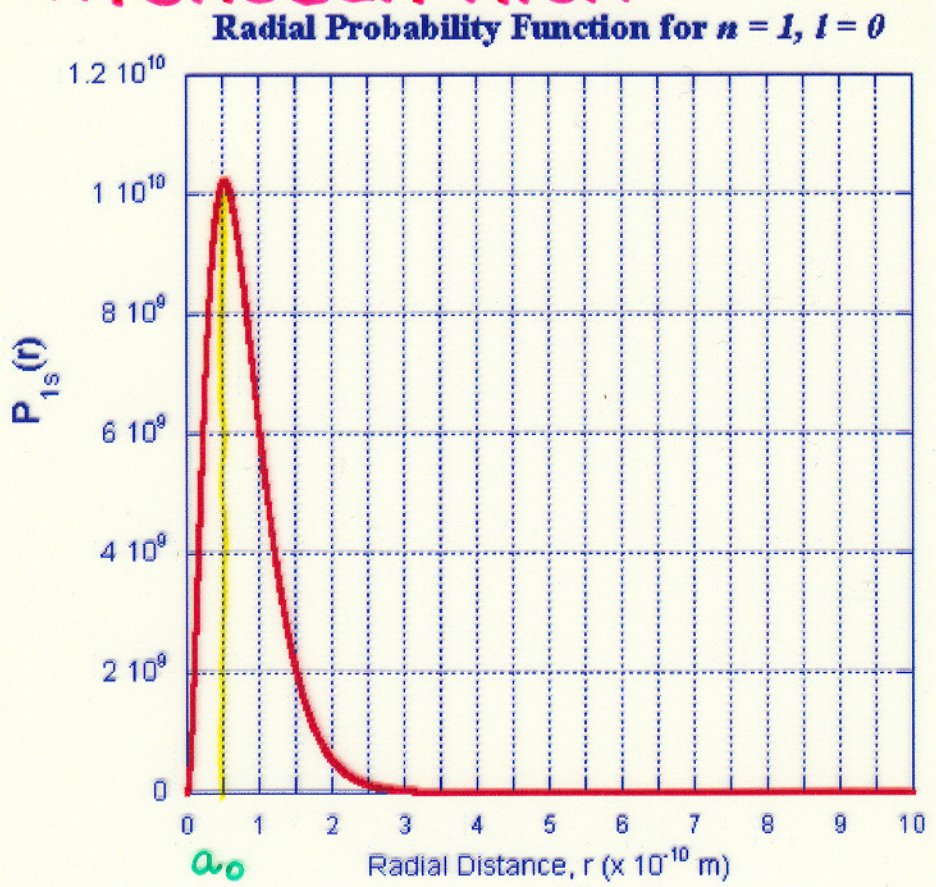
BUT

WHY THE RADIAL FUNCTIONS OF SUCH ORBITALS THAT HAVE THE SAME ANGULAR PARTS MUST HAVE NODES?

WHAT IS VALID IN THE CASE OF MANY ELECTRON ATOM?

B3.2

HYDROGEN ATOM



PROBLEM: FIND THE MOST PROBABLE DISTANCE OF ELECTRON FROM NUCLEUS IF THIS ELECTRON IS IN THE STATE OF 1S SYMMETRY FOR ATOMS WITH

$$Z = 1, 2, 3, 4, 59, 100$$

H He Li Be Pr U

RADIAL PROBABILITY

$$P \Rightarrow \varrho\, d\tau = |\psi(xyz)|^2 dx\,dy\,dz =$$

DENSITY

$$|\psi(r\vartheta\varphi)|^2 r^2 dr\, d\varphi \sin\vartheta\, d\vartheta$$

$$P(r) = r^2 \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\vartheta\, d\vartheta\, |\psi(r\vartheta\varphi)|^2$$

$$\psi_{1s} = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}$$ (SEE EXAMPLE ON B2.12)

$$P(r) = 4\pi r^2 |\psi_{1s}|^2 = 4\pi r^2 \frac{Z^3}{\pi a_0^3} e^{-2Zr/a_0} = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$$

$$\frac{dP(r)}{dr} = \frac{4Z^3}{a_0^3}\left(2r e^{-2Zr/a_0} - \frac{2Z}{a_0} r^2 e^{-2Zr/a_0}\right) = 0$$

$$\frac{4Z^3}{a_0^3} 2r\left(1 - \frac{Z}{a_0} r\right) e^{-2Zr/a_0} = 0 \Rightarrow$$

$\left(1 - \frac{Z}{a_0} r\right) = 0$

$$r \equiv r_{max} = \frac{a_0}{Z}$$ (CHECK $\frac{d^2P}{dr^2}$)

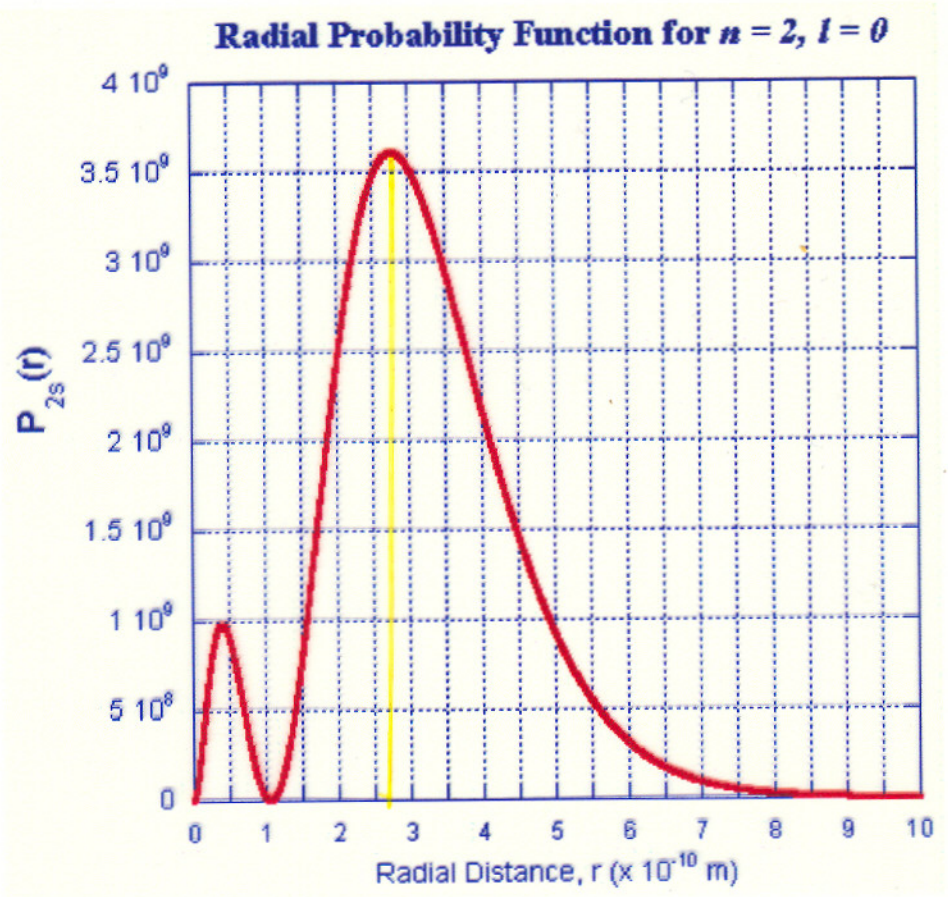
$$P(r_{max}) = \frac{4Z^3}{a_0^3} r_{max}^2 e^{-2Zr_{max}/a_0} = 4\frac{Z}{a_0} e^{-2}$$

$Z =$	1	2	3	4	59	100
	H	He	Li	Be	Pr	U
$r_{max} = a_0/Z$ [Å]	a_0	$\frac{1}{2}a_0$	$\frac{1}{3}a_0$	$\frac{1}{4}a_0$	$\frac{1}{59}a_0$	$\frac{1}{100}a_0$
	0.529	0.265	0.176	0.132	0.008967	0.00529

100 TIMES SMALLER!

CONCLUSIONS:

- HYDROGEN ORBITALS HAVE TO BE MODIFIED TO BE USED FOR THE DESCRIPTION OF MANY ELECTRON SYSTEM
- IS r_{max} A SIZE OF AN ATOM ???
- WHAT IS $\langle r \rangle$?



HOMEWORK: SOLVE THE PREVIOUS PROBLEM FOR

ψ_{2S}

PROBLEM: EVALUATE $\langle r \rangle_{1S}$ FOR $Z = 1, 2, 3, 4, 59, 100$

$$\langle r \rangle = \int \psi_{1S}\, r\, \psi_{1S}\, d\tau = \frac{Z^3}{\pi a_0^3} \int_0^\infty e^{-2Zr/a_0}\, r^3\, dr \cdot 4\pi = \frac{3}{2}\frac{a_0}{Z}$$

Z =	1	2	3	4	59	100
$\langle r \rangle$ =	$\frac{3}{2}a_0$	$\frac{3}{4}a_0$	$\frac{1}{2}a_0$	$\frac{3}{8}a_0$	$\frac{3}{118}a_0$	$\frac{3}{200}a_0$
[Å]	0.794	0.397	0.265	0.198	0.025	0.008

The Quantum Numbers		
name	**symbol**	**values**
Principal Quantum Number	**n**	**any integer from 1 to infinity**
Azimuthal Quantum Number	**L**	**any integer from 0 to n-1**
Magnetic Quantum Number	**m_L**	**any integer from -L to +L**
Spin Quantum Number	**m_s**	**+/- 1/2**

for the Worksheet

Generating a Table of Atomic Orbitals

Begin with the lowest value of n (n=1). Calculate all allowable values of L (in this case L =0, only). Name the orbital with the number of "n" and the letter which corresponds with "L," according to the table below:

L-value	orbital type
0	s
1	p
2	d
3	f

The orbital referred to above is the 1s orbital.

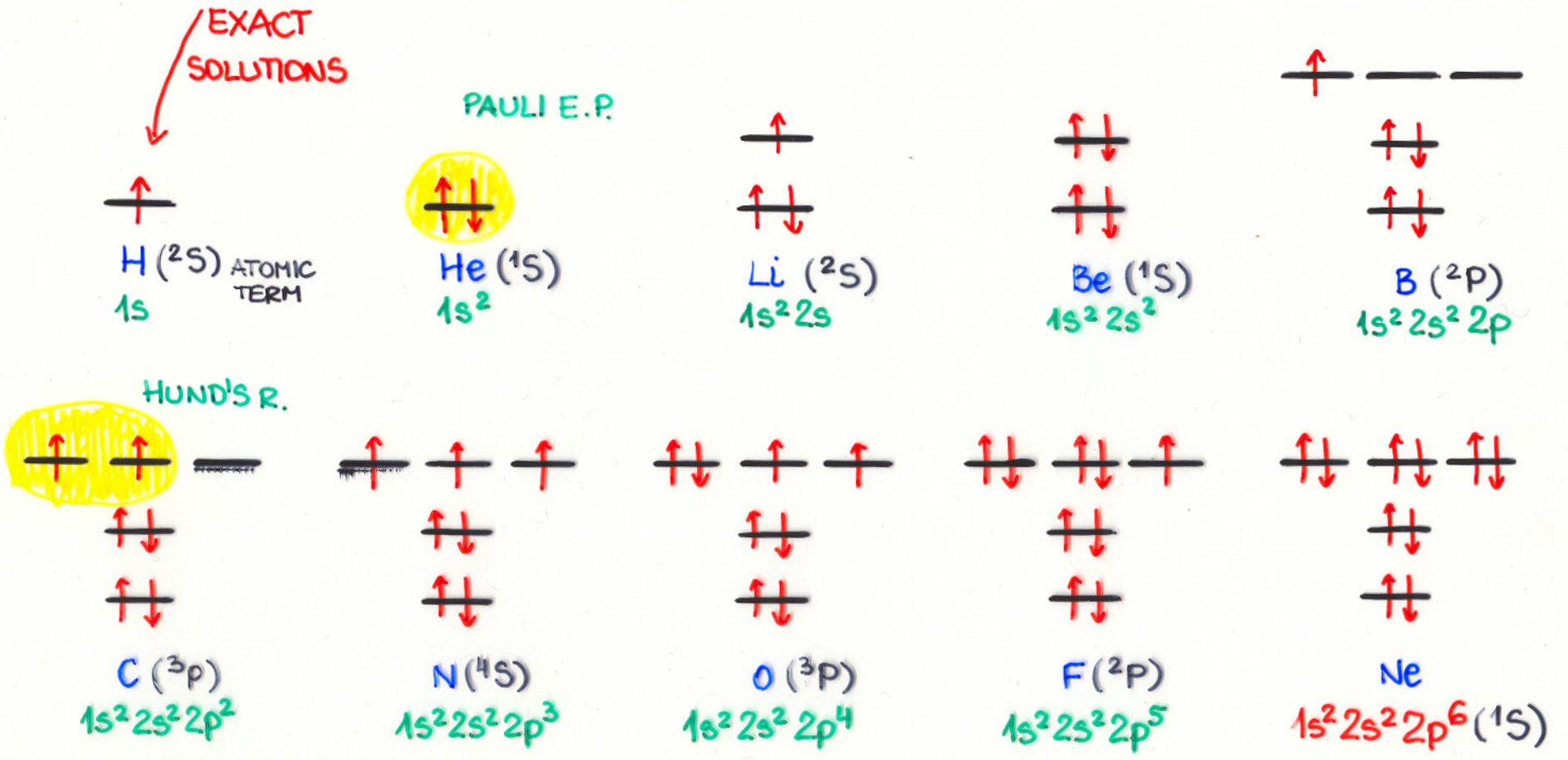
Orbitals are filled, lowest energy level first. The energy level of the orbital is approximated by adding the n and L values together and ordering the orbitals according to their n+L values. If n+L values are equal, orbitals with lower "n" values are filled first. According to the Pauli Exclusion Principle, no two electrons may have all four quantum numbers the same.

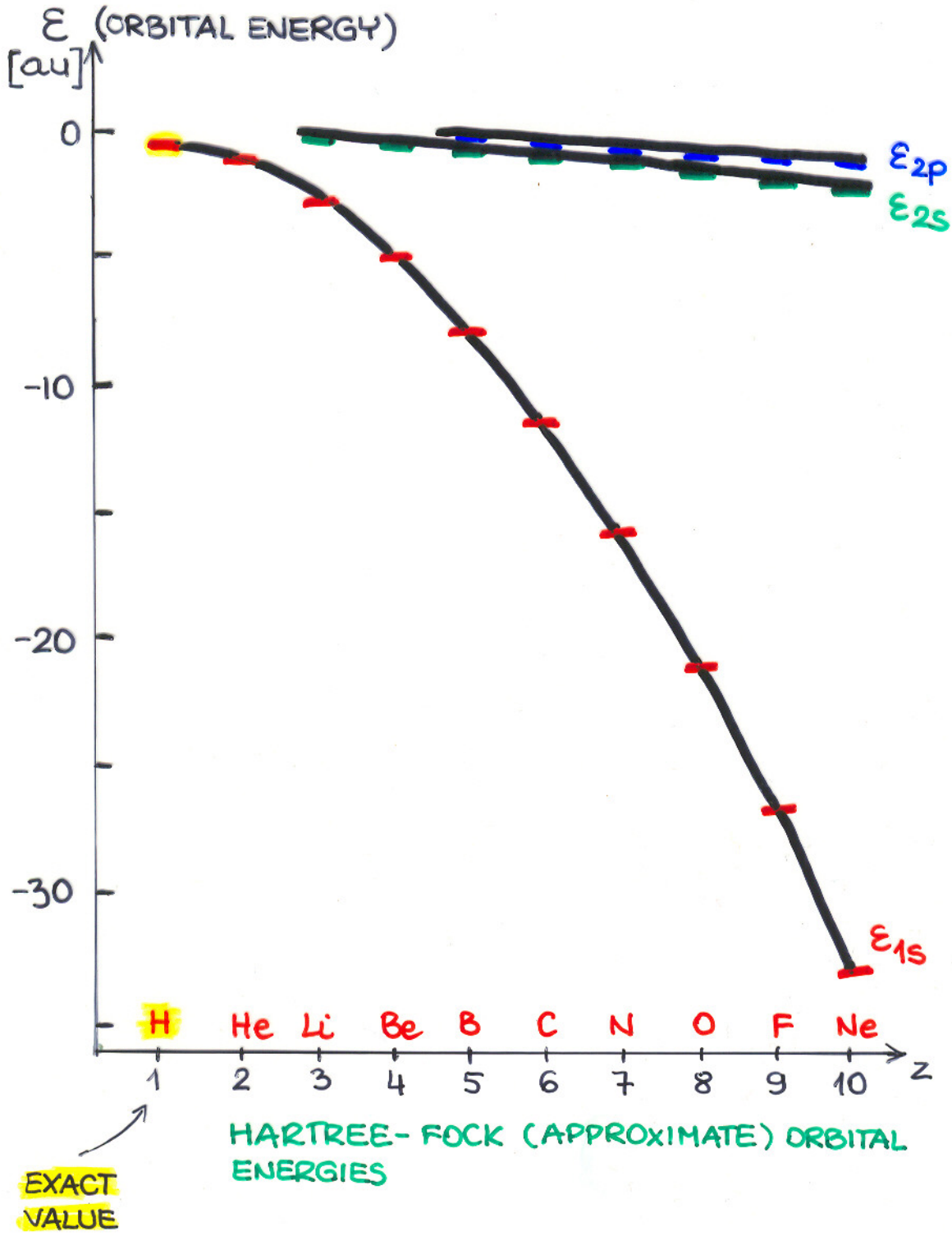
n	L	m_L	m_s	n+L	orbital name	order filled
1	0	0	+1/2, -1/2	1	1s	1
2	0	0	+1/2, -1/2	2	2s	2
2	1	-1	+1/2, -1/2	3	$2p_x$	3

n	l	m_l	m_s	n+l		ORDER
2	1	-1	+1/2, -1/2	3	$2p_x$	3
2	1	0	+1/2, -1/2	3	$2p_y$	3
2	1	+1	+1/2, -1/2	3	$2p_z$	3
3	0	0	+1/2, -1/2	3	3s	4
3	1	-1	+1/2, -1/2	4	$3p_x$	5
3	1	0	+1/2, -1/2	4	$3p_y$	5
3	1	+1	+1/2, -1/2	4	$3p_z$	5
3	2	-2	+1/2, -1/2	5	3d	7
3	2	-1	+1/2, -1/2	5	3d	7
3	2	0	+1/2, -1/2	5	3d	7
3	2	+1	+1/2, -1/2	5	3d	7
3	2	+2	+1/2, -1/2	5	3d	7
4	0	0	+1/2, -1/2	4	4s	6
4	1	-1	+1/2, -1/2	5	$4p_x$	8
4	1	0	+1/2, -1/2	5	$4p_y$	8
4	1	+1	+1/2, -1/2	5	$4p_z$	8
4	2	-2	+1/2, -1/2	6	4d	10
4	2	-1	+1/2, -1/2	6	4d	10
4	2	0	+1/2, -1/2	6	4d	10
4	2	+1	+1/2, -1/2	6	4d	10
4	2	+2	+1/2, -1/2	6	4d	10
4	3	-3	+1/2, -1/2	7	4f	
4	3	-2	+1/2, -1/2	7	4f	
4	3	-1	+1/2, -1/2	7	4f	
4	3	0	+1/2, -1/2	7	4f	
4	3	+1	+1/2, -1/2	7	4f	
4	3	+2	+1/2, -1/2	7	4f	
4	3	+3	+1/2, -1/2	7	4f	
5	0	0	+1/2, -1/2	5	5s	9
5	1	-1	+1/2, -1/2	6	$5p_x$	11
5	1	0	+1/2, -1/2	6	$5p_y$	11
5	1	+1	+1/2, -1/2	6	$5p_z$	11

atom	atomic number	electron configuration
H	1	$1s^1$ (meaning one electron in the 1s orbital)
He	2	$1s^2$
Li	3	$1s^2\ 2s^1$ or He $2s^1$
Be	4	$1s^2\ 2s^2$ or He $2s^2$
B	5	$1s^2\ 2s^2\ 2p_x^1$ or He $2s^2\ 2p_x^1$
C	6	$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$ or He $2s^2\ 2p_x^1\ 2p_y^1$ (* see Hund's Rule Below)
N	7	$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ or He $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$
O	8	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ or He $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$
F	9	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$ or He $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$
Ne	10	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$ or He $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$
Na	11	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^1$ or Ne $3s^1$
Mg	12	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2$ or Ne $3s^2$
Al	13	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^1$ or Ne $3s^2\ 3p_x^1$
Si	14	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^1 3p_y^1$ or Ne $3s^2\ 3p_x^1\ 3p_y^1$
P	15	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^1 3p_y^1 3p_z^1$ or Ne $3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
S	16	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^2 3p_y^1 3p_z^1$ or Ne $3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$
Cl	17	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^2 3p_y^2 3p_z^1$ or Ne $3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$
Ar	18	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^2 3p_y^2 3p_z^2$ or Ne $3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$
K	19	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^2 3p_y^2 3p_z^2\ 4s^1$ or Ar $4s^1$

ELECTRON CONFIGURATIONS




ε (ORBITAL ENERGY)
[au]
0
-10
-20
-30
ε_{2p}
ε_{2s}
ε_{1s}
H He Li Be B C N O F Ne
1 2 3 4 5 6 7 8 9 10
Z
HARTREE-FOCK (APPROXIMATE) ORBITAL ENERGIES
EXACT VALUE

COUPLING OF ANGULAR MOMENTA

N=2

$1e^-$: $\bar{l}_1, \bar{s}_1$; $2e^-$: $\bar{l}_2, \bar{s}_2$ $\Rightarrow$ $(n_1 l_1)^1 (n_2 l_2)^1$

a). $\vec{l}_1 + \vec{l}_2 = \vec{L}$, $\bar{s}_1 + \bar{s}_2 = \bar{S}$, $\bar{L} + \bar{S} = \vec{J}$ COUPLING **LS** $[H, L^2] = 0$ $[H, S^2] = 0$

b). $\bar{l}_1 + \bar{l}_2 = \bar{L}$, $\bar{L} + \vec{s}_1 = \vec{K}$, $\vec{K} + \vec{s}_2 = \vec{J}$ LK

c). $\bar{l}_1 + \bar{s}_1 = \bar{j}_1$, $\vec{j}_1 + \bar{l}_2 = \vec{K}$, $\vec{K} + \bar{s}_2 = \bar{J}$ jK

d). $\vec{l}_1 + \bar{s}_1 = \vec{j}_1$, $\bar{l}_2 + \bar{s}_2 = \bar{j}_2$, $\vec{j}_1 + \vec{j}_2 = \vec{J}$ COUPLING **jj** $[H, \vec{J}^2] = 0$

$$\underset{(m_{s_1})}{(2s_1+1)} \underset{(m_{l_1})}{(2l_1+1)} \underset{(m_{s_2})}{(2s_2+1)} \underset{(m_{l_2})}{(2l_2+1)} = 4(2l_1+1)(2l_2+1)$$

$$\equiv 4[l_1, l_2] \text{ (ATOMIC SPECTROSCOPY)}$$

NUMBER OF STATES FOR THE CONFIGURATION $(n_1 l_1)^1 (n_2 l_2)^1$

LS COUPLING RUSSELL-SAUNDERS

$^{2S+1}L_J$

2S+1 FOR L≥S
2L+1 FOR L<S
MULTIPLICITY

OBSERVED ATOMIC TERMS

L = 0 1 2 3 4 5 6 7 8
S P D F G H I K L

SPECTROSCOPIC TERMS (SPECTRAL TERMS)

2J+1 STATES ($M_J = -J, \ldots J$): MULTIPLET

EACH TERM ^{2S+1}L : (2S+1)(2L+1)-FOLD DEGENERATE

EXAMPLE: np n'f : $l_1 = 1$ $l_2 = 3$

$|l_1 - l_2| \leq L \leq l_1 + l_2$

$2 \leq L \leq 4$

$L = 2, 3, 4$

$|s_1 - s_2| \leq S \leq s_1 + s_2$

$0 \leq S \leq 1$

$S = 0, 1$

TERMS: ^1D ^3D ^1F ^3F ^1G ^3G

	^1D	^3D	^1F	^3F	^1G	^3G
	S=0 L=2	S=1 L=2	S=0 L=3	S=1 L=3	S=0 L=4	S=1 L=4
	J=2	J=1,2,3	J=3	J=2,3,4	J=4	J=3,4,5
LEVELS:	$^1D_2$	$^3D_1$ $^3D_3$ $^3D_2$	$^1F_3$	$^3F_2$ $^3F_4$ $^3F_3$	$^1G_4$	$^3G_3$ $^3G_5$ $^3G_4$

ARE ALL THESE VALUES OF TOTAL S AND L DEFINE ATOMIC TERMS? REMEMBER: SLATER DETERMINANT!

FUNCTION OF GOOD SYMMETRY: $|\gamma S M_S L M_L\rangle \Rightarrow |s m_s l m_l\rangle$

6. PERMUTATIONS – IF ALL PARTICLES IN A SYSTEM ARE THE SAME (IDENTICAL), THE HAMILTONIAN IS INVARIANT UNDER INTERCHANGE OF POSITION OF ANY TWO PARTICLES

$\hat{P}_{kl}$: OPERATOR OF PERMUTATION OF PARTICLES k AND l

$$\hat{P}_{kl} H = H \hat{P}_{kl}$$ INTEGRAL OF MOTION

SYMMETRY CONDITIONS

EXAMPLE: TWO PARTICLES

$$\hat{P}_{12} \Psi(1,2) = \lambda \Psi(1,2)$$

λ: REAL EIGENVALUE

$\hat{P}_{12}$: $P^2 = \mathbb{1}$, $P^+ = P^{-1}$; $P = P^{-1}$, $P = P^+$

$$\hat{P}_{12}^2 \Psi(1,2) = \lambda^2 \Psi(1,2)$$

$$\Psi(1,2) = \lambda^2 \Psi(1,2) \Rightarrow \lambda = \pm 1$$

$\hat{P}_{12} \Psi_S(1,2) = \Psi_S(1,2)$ SYMMETRIC FUNCTION

$\hat{P}_{12} \Psi_a(1,2) = -\Psi_a(1,2)$ ANTISYMMETRIC FUNCTION

FOR ARBITRARY NUMBER OF IDENTICAL PARTICLES: THE WAVEFUNCTION HAS TO BE OF THE SAME SYMMETRY WITH RESPECT TO THE INTERCHANGE OF ANY PAIR OF PARTICLES; THE SYMMETRY OF THE WAVEFUNCTION CANNOT BE CHANGED BY AN EXTERNAL PERTURBATION

NORMALIZED

SYMMETRIC FUNCTION

$$\frac{1}{\sqrt{N!}} \sum_P \hat{P} |\Psi\rangle = |\Psi_S\rangle$$

$N!$: NUMBER OF PERMUT.

BOSONS

(INTEGRAL SPIN)

$0, \hbar, 2\hbar, \ldots$

ANTISYMMETRIC FUNCTION

$$\frac{1}{\sqrt{N!}} \sum_P (-1)^{\varepsilon(P)} \hat{P} |\Psi\rangle = |\Psi_A\rangle$$

FERMIONS

(HALF-ODD-INTEGRAL SPIN)

$1/2\hbar, 3/2\hbar, 5/2\hbar \ldots$

ELECTRONS, PROTONS, NEUTRONS

CONCLUSION:

BASIC POSTULATE:

INDISTINGUISHABILITY OF IDENTICAL PARTICLES

ANTISYMMETRIC FUNCTION (IDENTICAL FERMIONS)

$$\Psi_A(1\dots N)=\frac{1}{\sqrt{N!}}\sum_{\hat{P}}(-1)^{\varepsilon(\hat{P})}\hat{P}\,\Psi(1\dots N)$$

SINGLE-PARTICLE APPROXIMATION (SINGLE-ELECTRON APP.)

$$\Psi(1,\dots N)=\varphi_1(1)\varphi_2(2)\dots\varphi_N(N)$$
$$?\pm\varphi_1(3)\varphi_2(2)\dots\varphi_N(N)$$
$$?\pm\varphi_1(5)\varphi_2(1)\dots\varphi_N(N)$$
$$\vdots$$

$\varphi_i(i)$ – SINGLE PARTICLE STATES

N! POSSIBILITIES

$N=2$

$$\Psi_A(1,2)=\frac{1}{\sqrt{2}}\left(\varphi_1(1)\varphi_2(2)-\varphi_1(2)\varphi_2(1)\right)=\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_1(1) & \varphi_1(2)\\ \varphi_2(1) & \varphi_2(2)\end{vmatrix}$$

$\varepsilon(P)=1$

SLATER DETERMINANT

IN GENERAL

$$\Psi_A(1\dots N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(N)\\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(N)\\ \vdots & \vdots & & \vdots\\ \varphi_N(1) & \varphi_N(2) & \dots & \varphi_N(N)\end{vmatrix}$$

ALL POSSIBILITIES (N!) TAKEN INTO ACCOUNT

PAULI PRINCIPLE INCLUDED!

EXAMPLE: $2\bar{e}$: f_1, f_2

$(x_1 x_2) = -(x_2, x_1)$

$X = (\bar{\tau}, \sigma)$

$s_1 = s_2 = 1/2$: $m_s = \frac{1}{2}$ $\quad \alpha(\sigma)$ $\quad (\overset{+}{f}_1, \overset{+}{f}_2, \uparrow)$

$= -\frac{1}{2}$ $\quad \beta(\sigma)$ $\quad (\bar{f}_1, \bar{f}_2, \downarrow)$

NOTA BENE: IF $f_1 \equiv 1s$, $f_2 \equiv 2s \Rightarrow$ EXCITED STATE OF He ATOM

S $\quad \chi_1 = N_1 \alpha(1)\alpha(2)$ $\quad \uparrow\uparrow$

S $\quad \chi_2 = N_2 \beta(1)\beta(2)$ $\quad \downarrow\downarrow$

S $\quad \chi_3 = N_3 \{\alpha(1)\beta(2) + \alpha(2)\beta(1)\}$ $\quad \uparrow\downarrow + \downarrow\uparrow$

A $\quad \chi_4 = N_4 \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$ $\quad \uparrow\downarrow - \downarrow\uparrow$

$$\Phi_S = \frac{1}{\sqrt{2}}\{f_1(1)f_2(2) + f_1(2)f_2(1)\}$$

$$\Phi_A = \frac{1}{\sqrt{2}}\{f_1(1)f_2(2) - f_1(2)f_2(1)\}$$

SEPARATION VALID ONLY FOR $2\bar{e}$!!!

$$\Psi(\bar{\tau}\sigma) \equiv \Psi_A(\bar{\tau}\sigma)$$

ORBITAL PART	SPIN FUNCTION	$\Psi_A(\bar{\tau}\sigma)$
S	A	$\Psi_1 = \Phi_S \chi_4$
A	S	$\underbrace{\Phi_A \chi_1}_{\Psi_2}$ $\underbrace{\Phi_A \chi_2}_{\Psi_3}$ $\underbrace{\Phi_A \chi_3}_{\Psi_4}$

$$\Psi_1(\bar{\tau}\sigma) = \frac{1}{\sqrt{2}}\{f_1(1)f_2(2) + f_1(2)f_2(1)\}_S \, N_4 \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}_A =$$

$$= a\{\overset{+}{f}_1(1)\bar{f}_2(2) - \bar{f}_1(1)\overset{+}{f}_2(2) + \bar{f}_1(2)\overset{+}{f}_2(1) - \overset{+}{f}_1(2)\bar{f}_2(1)\} =$$

$$= a\{\overset{+}{f}_1(1)\bar{f}_2(2) - \overset{+}{f}_1(2)\bar{f}_2(1) + \bar{f}_1(2)\overset{+}{f}_2(1) - \bar{f}_1(1)\overset{+}{f}_2(2)\} =$$

$$= a\left\{\begin{vmatrix} \overset{+}{f}_1(1) & \overset{+}{f}_1(2) \\ \bar{f}_2(1) & \bar{f}_2(2) \end{vmatrix} - \begin{vmatrix} \bar{f}_1(1) & \bar{f}_1(2) \\ \overset{+}{f}_2(1) & \overset{+}{f}_2(2) \end{vmatrix}\right\} = a\{|\overset{+}{f}_1(1)\bar{f}_2(2)| - |\bar{f}_1(1)\overset{+}{f}_2(2)|\}$$

LINEAR COMBINATION OF SLATER DETERMINANTS

Ψ_2? Ψ_3? Ψ_4?

ARE THESE FUNCTIONS OF GOOD SYMMETRY?

THEY ARE ANTISYMMETRIC BUT $[H, \hat{J}] = 0$ **!**

MATRIX ELEMENTS

$$\hat{F} = \sum_i^N \hat{f}(i)$$ ONE-PARTICLE OPERATORS

$$\hat{G} = \sum_{i<j}^N \hat{g}(ij)$$ TWO-PARTICLE OPERATORS

$$\Phi = |\psi_1(1)\psi_2(2)\ldots\psi_i(i)\ldots\psi_N(N)| \equiv$$

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \ldots & \psi_i(1) & \ldots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & & \psi_i(2) & & \psi_N(2) \\ \vdots & \vdots & & \vdots & & \vdots \\ \psi_1(i) & \psi_2(i) & & \psi_i(i) & & \psi_N(i) \\ \vdots & \vdots & & \vdots & & \vdots \\ \psi_1(N) & \psi_2(N) & & \psi_i(N) & & \psi_N(N) \end{vmatrix} \begin{matrix} \leftarrow \hat{f}(1) \\ \leftarrow \hat{f}(2) \\ \\ \leftarrow \hat{f}(i) \\ \\ \leftarrow \hat{f}(N) \end{matrix}$$

$\sum_i$ $\sum_{i<j}$: $\hat{g}(12)$, $\hat{g}(23)$, ⋮

$N \times N$

EXPANSION BY MINORS ("LAPLACIAN EXPANSION")

BRA: $\frac{1}{\sqrt{N}} \frac{1}{\sqrt{(N-1)!}} \sum_k^N (-1)^{1+k} \psi_k(1)\, \mathbb{D}^1_k(N-1)$

KET: $\frac{1}{\sqrt{N}} \frac{1}{\sqrt{(N-1)!}} \sum_l^N (-1)^{1+l} \psi_l(1)\, \mathbb{D}^1_l(N-1)$

$\langle \psi_i | \psi_k \rangle = \delta_{ik}$

$$\langle \Phi | \hat{F} | \Phi \rangle_{1,2,\ldots N} = \sum_{i=1}^N \frac{1}{N} \frac{1}{(N-1)!} \sum_{kl} (-1)^{2+k+l} \langle \psi_k(1) | f(i) | \psi_l(1) \rangle_1 \times$$

$$\langle \mathbb{D}^1_k(N-1) | \mathbb{D}^1_l(N-1) \rangle_{2,3,\ldots N} = \delta(kl)$$

$$= N \cdot \frac{1}{N} \sum_k^N \langle \psi_k(1) | f(1) | \psi_k(1) \rangle \Rightarrow$$

$$\langle \Phi | \hat{F} | \Phi \rangle = \sum_k \langle \psi_k(1) | f(1) | \psi_k(1) \rangle$$

$$\Phi(1\ldots N) = \frac{1}{\sqrt{N!}} \sum_{k,l} (1)^{1+2+k+l} \begin{vmatrix} \psi_k(1) & \psi_l(1) \\ \psi_k(2) & \psi_l(2) \end{vmatrix} \mathbb{D}^{12}_{kl}(N-2)$$

$$\frac{1}{\sqrt{N!}} = \frac{1}{\sqrt{N(N-1)(N-2)!}} = \frac{1}{\sqrt{(N-2)!}} \cdot \frac{1}{\sqrt{2}} \cdot \sqrt{\frac{2}{N(N-1)}}$$

NUMBER OF PAIRS $\frac{N(N-1)}{2} = \binom{N}{2}$

$$\langle\Phi|G|\Phi\rangle = \sum_{i<j} \langle\Phi|\hat{g}(ij)|\Phi\rangle = \frac{N(N-1)}{2}\langle\Phi|\hat{g}(12)|\Phi\rangle =$$

$$= \frac{N(N-1)}{2}\,\frac{2}{N(N-1)}\,\underbrace{\frac{1}{(N-2)!}}_{\frac{1}{N!}}\cdot\frac{1}{2}\sum_{kl}\sum_{rs}(-1)^{1+2+k+l+1+2+r+s}$$

$$\left\langle \begin{vmatrix}\psi_k(1)\psi_l(1)\\ \psi_k(2)\psi_l(2)\end{vmatrix} |\hat{g}(12)| \begin{vmatrix}\psi_r(1)\psi_s(1)\\ \psi_r(2)\psi_s(2)\end{vmatrix}\right\rangle \left\langle \mathbb{D}^{12}_{kl}(N-2)\,|\,\mathbb{D}^{12}_{rs}(N-2)\right\rangle_{3,..N}$$

$$\delta(kr)\,\delta(ls)$$

$$= \frac{1}{2}\sum_{kl}^{N}\left\langle \begin{vmatrix}\psi_k(1)\psi_l(1)\\ \psi_k(2)\psi_l(2)\end{vmatrix} |\hat{g}(12)| \begin{vmatrix}\psi_k(1)\psi_l(1)\\ \psi_k(2)\psi_l(2)\end{vmatrix}\right\rangle =$$

$$= \frac{1}{2}\sum_{kl}^{N}\langle \psi_k(1)\psi_l(2) - \psi_l(1)\psi_k(2)\,|\,g(12)\,|\,\psi_k(1)\psi_l(2) - \psi_l(1)\psi_k(2)\rangle =$$

$$= \frac{1}{2}\sum_{kl}\Big\{ \underbrace{\langle \psi_k(1)\psi_l(2)|g(12)|\psi_k(1)\psi_l(2)\rangle + \langle \psi_l(1)\psi_k(2)|g(12)|\psi_l(1)\psi_k(2)\rangle}_{\langle kl|g|kl\rangle \text{ „DIRECT"}} - \underbrace{\langle \psi_k(1)\psi_l(2)|g(12)|\psi_l(1)\psi_k(2)\rangle - \langle \psi_l(1)\psi_k(2)|g(12)|\psi_k(1)\psi_l(2)\rangle}_{-\langle kl|g|lk\rangle \text{ „EXCHANGE"}}$$

CAUSED BY ANTISYMMETRY!
(PURELY QUANTUM EFFECT)

$$\langle\Phi|G|\Phi\rangle = \sum_{kl}\{\langle kl|g|kl\rangle - \langle kl|g|lk\rangle\}$$

IF G = COULOMB INTERACTION:

$$\langle \overset{12}{k}\overset{12}{l}\|\overset{12}{k}\overset{12}{l}\rangle - \langle \overset{12}{k}\overset{12}{l}\|\overset{12}{l}\overset{12}{k}\rangle \equiv \langle \overset{12}{k}\overset{12}{l}\|\overset{12}{k}\overset{12}{l}\rangle_A$$

$$\langle \underset{11}{k}\underset{22}{k}\|\underset{11}{l}\underset{22}{l}\rangle - \langle \underset{11}{k}\underset{22}{l}\|\underset{11}{l}\underset{22}{k}\rangle \equiv \langle \underset{11}{k}\underset{22}{k}\|\underset{11}{l}\underset{22}{l}\rangle_A$$