Many electron atoms

Autumn 2008

Version: 01.12.2008 - FINAL (afternoon with corrections; Conf. mixing

$$\tag{1}$$

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1 Filling up the shells with electrons

In order to know and to, more or less, understand in which state an electron is bound we can use some basic rules. The generel idea is that the lowest energy-state is the most stable one. The exited states can in most cases fall in the lower state or ground state by emission of light.

The principles one need to know how to fill up the shells are the Pauli-principle and the Hund's rule.

2 Pauli-principle

The filling of the shells observed was explained by Pauli by formulating the **Pauli exclusion principle**:

Two electrons can not be in the same state, a state defined by all four possible quantum numbers n, l, m and m_s

Here n is principal the quantum number of the shell,

l, the angular momentum quantum number of the subshell,

m the magnetic quantum number

m_s denotes spin "up" and spin "down", $m_s = 1/2$ or $m_s = -1/2$

The Pauli principle was formulated mathematically by requiring that the multiparticle wavefunction is antisymmetric with respect to exchange of two particles.

If two particles coordinates are exchanged, the function must change sign. If two particles are in the same state, this requirement leads to **zero wavefunction**, thus impossible.

Figure 1: Atomic levels (shells)
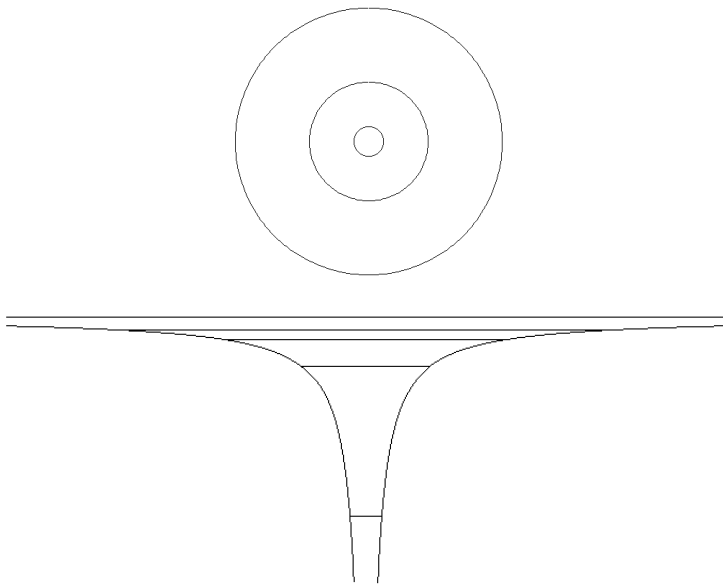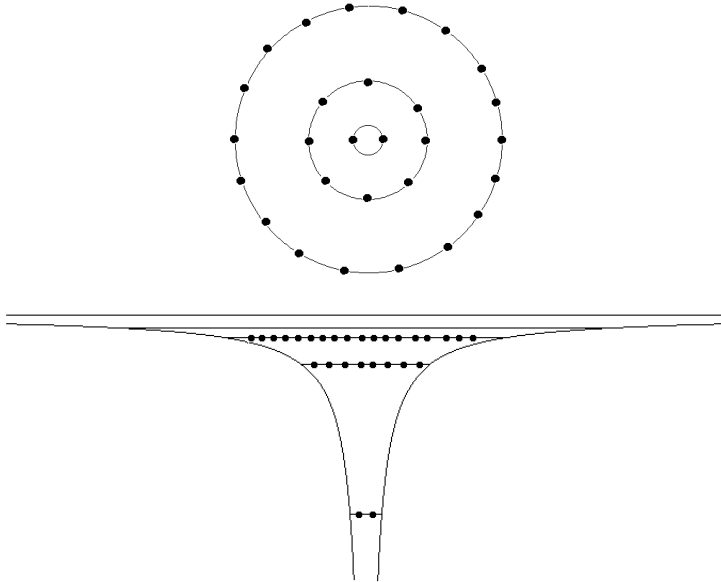
Figure 2: Atomic levels (shells) filled up to the element ....List of topics

3   Antisymmetric product function for n-particles

$$\Psi(x_1, x_2, ...x_n) \;=\; \sum_{perm(\alpha,\beta,...\nu)} (-1)^{P(perm(\alpha,\beta,...\nu))} perm\,(\phi_\alpha\phi_\beta....\phi_\nu)\,(x_1)(x_2)....(x_n)$$

where each term in the sum looks as $\phi_\beta(x_1)...\phi_\nu(x_2)...\phi_\alpha...$, summing over all permutations, and $P(perm(\alpha, \beta, ...\nu))$ is the number of swaps of the given permutation $perm(\alpha, \beta, ...\nu)$

This is very close to the definition of the determinant

$$\det(A) \;=\; \sum_{\sigma \in S_n} \left(\; \mathrm{sgn}(\sigma) \; \prod_{i=1}^{n} A_{i,\sigma(i)} \right)$$

The above in this notation

$$\Psi(x_1, x_2, ...x_n) \;=\; \sum_{\sigma \in S_n} \mathrm{sgn}(\sigma) \; \prod_{i=1}^{n} \phi_{\alpha_{\sigma(i)}}(x_i)$$

Slater determinant

The antisymmetric combination for n-particles can be written as a determinant in this way:

$$
\begin{vmatrix}
\phi_\alpha(x_1) & \phi_\alpha(x_2) & ... & \phi_\alpha(x_n) \\
\phi_\beta(x_1) & \phi_\beta(x_2) & ... & \phi_\beta(x_n) \\
... & ... & ... & ... \\
\phi_\nu(x_1) & \phi_\nu(x_2) & ... & \phi_\nu(x_n)
\end{vmatrix}
$$

For 3 particles:

3 particle Slater determinant

$$
\begin{vmatrix}
\phi_\alpha(x_1) & \phi_\alpha(x_2) & \phi_\alpha(x_3) \\
\phi_\beta(x_1) & \phi_\beta(x_2) & \phi_\beta(x_3) \\
\phi_\gamma(x_1) & \phi_\gamma(x_2) & \phi_\gamma(x_3)
\end{vmatrix}
$$

List of topics

3×3 determinant

$$\begin{vmatrix} \phi_\alpha(1) & \phi_\alpha(2) & \phi_\alpha(3) \\ \phi_\beta(1) & \phi_\beta(2) & \phi_\beta(3) \\ \phi_\gamma(1) & \phi_\gamma(2) & \phi_\gamma(3) \end{vmatrix} \longrightarrow$$

$$
\begin{array}{ccc}
\phi_\alpha(1) & \phi_\alpha(2) & \phi_\alpha(3) \\
\phi_\beta(1) & \phi_\beta(2) & \phi_\beta(3) \\
\phi_\gamma(1) & \phi_\gamma(2) & \phi_\gamma(3) \\
\phi_\alpha(1) & \phi_\alpha(2) & \phi_\alpha(3) \\
\phi_\beta(1) & \phi_\beta(2) & \phi_\beta(3)
\end{array}
$$

$$\phi_\alpha(1)\,\phi_\beta(2)\,\phi_\gamma(3) \quad + \quad \phi_\beta(1)\,\phi_\gamma(2)\,\phi_\alpha(3) \quad + \quad \phi_\gamma(1)\,\phi_\alpha(2)\,\phi_\beta(3)$$

$$- \phi_\gamma(1)\,\phi_\beta(2)\,\phi_\alpha(3) \quad - \phi_\alpha(1)\,\phi_\gamma(2)\,\phi_\beta(3) \quad - \phi_\beta(1)\,\phi_\alpha(2)\,\phi_\gamma(3)$$

List of topics

4 Hund's rule

Hund's rule is the manifestation of the same effect as we have seen in the parahelium - orthohelium effect (the "second" rule)

Hund's first rule

Full shells and subshells do have a total circular momentum of zero.

This can be calculated and is allways valid.

Hund's second rule

The total spin S should allways have the highest possible value. So as many of the single electron spins as possible should be parallel.

The second rule appears more empirical and applies to a different magnetic quantum number of the electrons with parallel spins. If is of course not allowed to break the Pauli-principle.
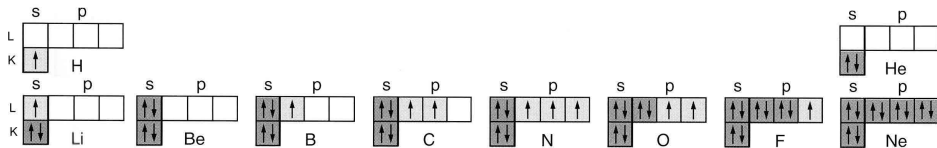
5 Example for the Hund's rule

Figure 3: Electron spins of the first elements.

The elements carbon C, nitrogen N and oxygen O are those where the Hund's rule have the biggest influence. We see electrons with parallel spins in the states $m = -1, 0, +1$, depending on the element. The magnetic quantum number m gives more or less the "direction" of the circular moment l. The s-states are the states where $l = 0$ and the p-states those where $l = 1$. The names for $l = (2, 3, 4, ...)$ are $(d, e, f, ...)$.

The shell-name of the shell $n = (1, 2, 3, 4, ...)$ is $(K, L, M, N, ...)$.

In cases with more electrons do we get some exceptions. For example is the 4s subshell earlier filled than the 3d. This is caused by the smaller distance of the 4s to the core and thus by the lower energy, which is more stable. The mentioned rules work well for general considerations and for atoms with not to many electrons.

6   Number of states

Usefull to know is the largest possible number of states for a given n which means until a special shell is filled.

$$N_{max} = 2 \cdot \sum_{l=0}^{n-1}(2l + 1) = 2n^2. \tag{2}$$

We get this formula by adding all the possible quantum number configurations:
We get for each n every l in the range $(0, 1, ..., n - 1)$,
for each l every m in the range $(-l, ..., -1, 0, 1, ..., l)$
and for each of these states 2 spin possibilities.

7 Ionization energies

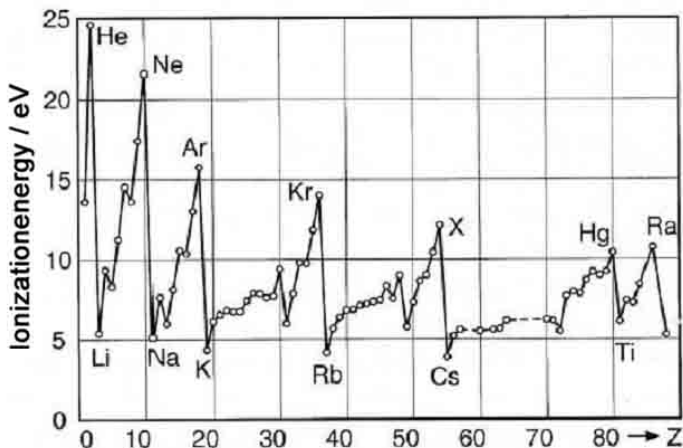

Figure 4: Ionization energies. The shell properties would explain the structure in general - Periodic table and the Selfconsistent field   List of topics

Especially at the first elements, we see the minimums at the elements with just one electron in the last shell and a maximum at the noble gas elements. The small minimums are caused by filled subshells or by the maximum of parallel standing spins. After argon, it is more difficult to observe general tendences.

The shell properties would explain the structure in general

But there should be no closed shell at argon

Details - Periodic table and the Selfconsistent field

8 Hartree - Selfconsistent field

Interaction energy of two charges depends on their distance $|\vec{r}_1 - \vec{r}_2|$:

$$W(|\vec{r}_1 - \vec{r}_2|) = \frac{q_1 q_2}{|\vec{r}_1 - \vec{r}_2|}$$

The two charges are an electron and a little volume dV at $\vec{r}_2$ containing charge cloud of density ρ

$$q_1 \to (-e) \qquad q_2 \to \rho(\vec{r}_2)dV \qquad \to \quad \rho(\vec{r}_2)d^3r_2$$
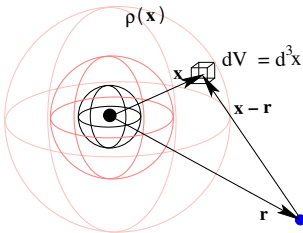
The interaction energy of these two charges is

$$dW(|\vec{r}_1 - \vec{r}_2|) = \frac{(-e)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}d^3r_2$$

Interaction with a cloud; summing over all the small volume elements - it means integrating over the whole volume of the cloud gives the potential energy

$$W(\vec{r}) = \int \frac{(-e)\rho(\vec{x})}{|\vec{r} - \vec{x}|} \, d^3x$$

If the charge cloud represents one electron in state $\psi_i(\vec{x})$

$$\rho(\vec{x}) = (-e)|\psi_i(\vec{x})|^2$$

If we have N electrons, each in its state, the total density becomes

$$\rho(\vec{x}) = (-e)\sum_{i=1}^{N} |\psi_i(\vec{x})|^2$$

and again integrating gives the potential energy due to the interaction with a (probability based density) cloud of electrons

$$W(\vec{r}) = \int \frac{(-e)^2 \sum\limits_{i=1}^{N} |\psi_i(\vec{x})|^2}{|\vec{r} - \vec{x}|} \, d^3x$$

Now solving the Schrödinger equation with $W(\vec{r})$,

$$(T + V + W)\,\psi_i(\vec{x}) = E_i\psi_i(\vec{x})$$

We first need to know the $W(\vec{r})$, but that depends on all the other N solutions

$$W(\vec{r}) = \int \frac{(-e)^2 \sum\limits_{i=1}^{N} |\psi_i(\vec{x})|^2}{|\vec{r} - \vec{x}|}\, d^3x$$

Approximation chain: First we choose some simple approximation, e.g. the hydrogen-like states, or we might know the states foranother atom. We call it

$$\psi_i^{(0)}(\vec{x})$$

From the set of all N $\psi_i^{(0)}$ we construct

$$W^{(1)}(\vec{r}) = \int \frac{e^2 \sum\limits_{i=1}^{N} |\psi_i^{(0)}(\vec{x})|^2}{|\vec{r} - \vec{x}|}\, d^3x$$

In atomic units the whole Schrödinger equation is

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + W^{(1)}(\vec{r})\right)\psi_i^{(1)}(\vec{x}) = E_i^{(1)}\psi_i^{(1)}(\vec{x})$$

1. step - choose arbitrary set of $\psi_i^{(0)}$

$$\psi_i^{(0)}(\vec{x}) \qquad \rightarrow \qquad W^{(1)}(\vec{r}) = \int \frac{\sum\limits_{i=1}^{N} |\psi_i^{(0)}(\vec{x})|^2}{|\vec{r} - \vec{x}|} \; d^3x \qquad (3)$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + W^{(1)}(\vec{r}) \right) \psi_i^{(1)}(\vec{x}) = E_i^{(1)}\psi_i^{(1)}(\vec{x})$$

2. step: take the set of $\psi_i^{(1)}$ from the 1. step

$$\psi_i^{(1)}(\vec{x}) \qquad \rightarrow \qquad W^{(2)}(\vec{r}) = \int \frac{\sum\limits_{i=1}^{N} |\psi_i^{(1)}(\vec{x})|^2}{|\vec{r} - \vec{x}|} \; d^3x$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + W^{(2)}(\vec{r}) \right) \psi_i^{(2)}(\vec{x}) = E_i^{(2)}\psi_i^{(2)}(\vec{x})$$

3. step: take the set of $\psi_i^{(2)}$ from the 2. step

$$\psi_i^{(2)}(\vec{x}) \qquad \rightarrow \qquad W^{(3)}(\vec{r}) = \int \frac{\sum\limits_{i=1}^{N} |\psi_i^{(2)}(\vec{x})|^2}{|\vec{r} - \vec{x}|} \, d^3x$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + W^{(3)}(\vec{r}) \right) \psi_i^{(3)}(\vec{x}) = E_i^{(3)}\psi_i^{(3)}(\vec{x})$$

This chain can continue, until the set of $\psi_i^{(n)}$ produces a potential $W^{(n+1)}$ which is the same as $W^{(n)}$, which was the one to determine $\psi_i^{(n)}$. The potentials and functions become consistent, hence the name *Selfconsistent field*.

Criterium for self-consistency: the (n+1)-th solution does not differ from th n-th solution

$$\int \sum_{i=1}^{N} \left| \, |\psi_i^{(n+1)}(\vec{x})|^2 \; - \; |\psi_i^{(n)}(\vec{x})|^2 \, \right| d^3x \quad < \epsilon \tag{4}$$

where $\epsilon \propto 10^{-8}$ as a typical value.

9   Ionization potentials of atoms

Z	Sym	Name	I[eV]	core	Configuration
1	H	Hydrogen	13,60		(1s)
2	He	Helium	24,59		$(1s)^2$
3	Li	Lithium	5,39	[He]	(2s)
4	Be	Beryllium	9,32	[He]	$(2s)^2$
5	B	Boron	8,30	[He]	$(2s)^2$ (2p)
6	C	Carbon	11,26	[He]	$(2s)^2$ $(2p)^2$
7	N	Nitrogen	14,53	[He]	$(2s)^2$ $(2p)^3$
8	O	Oxygen	13,62	[He]	$(2s)^2$ $(2p)^4$
9	F	Fluorine	17,42	[He]	$(2s)^2$ $(2p)^5$
10	Ne	Neon	21,56	[He]	$(2s)^2$ $(2p)^6$
11	Na	Sodium	5,14	[Ne]	(3s)
12	Mg	Magnesium	7,65	[Ne]	$(3s)^2$
13	Al	Aluminum	5,99	[Ne]	$(3s)^2$ (3p)
14	Si	Silicon	8,15	[Ne]	$(3s)^2$ $(3p)^2$
15	P	Phosphorus	10,49	[Ne]	$(3s)^2$ $(3p)^3$
16	S	Sulfur	10,36	[Ne]	$(3s)^2$ $(3p)^4$
17	Cl	Chlorine	12,97	[Ne]	$(3s)^2$ $(3p)^5$
18	Ar	Argon	15,76	[Ne]	$(3s)^2$ $(3p)^6$

18	Ar	Argon	15,76	[Ne]	$(3s)^2$ $(3p)^6$
19	K	Potassium	4,34	[Ar]	$(4s)$
20	Ca	Calcium	6,11	[Ar]	$(4s)^2$
21	Sc	Scandium	6,54	[Ar]	$(3d)$ $(4s)^2$
22	Ti	Titanium	6,82	[Ar]	$(3d)^2$ $(4s)^2$
23	V	Vanadium	6,74	[Ar]	$(3d)^3$ $(4s)^2$
24	Cr	Chromium	6,77	[Ar]	$(3d)^5$ $(4s)$
25	Mn	Manganese	7,44	[Ar]	$(3d)^5$ $(4s)^2$
26	Fe	Iron	7,87	[Ar]	$(3d)^6$ $(4s)^2$
27	Co	Cobalt	7,86	[Ar]	$(3d)^7$ $(4s)^2$
28	Ni	Nickel	7,64	[Ar]	$(3d)^8$ $(4s)^2$
29	Cu	Copper	7,73	[Ar]	$(3d)^{10}(4s)$
30	Zn	Zinc	9,39	[Ar]	$(3d)^{10}(4s)^2$
31	Ga	Gallium	6,00	[Ar]	$(3d)^{10}(4s)^2$ $(4p)$
32	Ge	Germanium	7,90	[Ar]	$(3d)^{10}(4s)^2$ $(4p)^2$
33	As	Arsenic	9,81	[Ar]	$(3d)^{10}(4s)^2$ $(4p)^3$
34	Se	Selenium	9,75	[Ar]	$(3d)^{10}(4s)^2$ $(4p)^4$
35	Br	Bromine	11,81	[Ar]	$(3d)^{10}(4s)^2$ $(4p)^5$
36	Kr	Krypton	14,00	[Ar]	$(3d)^{10}(4s)^2$ $(4p)^6$

List of topics

| 36 | Kr | Krypton | 14,00 | [Ar] | $(3d)^{10}(4s)^2$ $(4p)^6$ |
37	Rb	Rubidium	4,18	[Kr]	$(5s)$
38	Sr	Strontium	5,70	[Kr]	$(5s)^2$
39	Y	Yttrium	6,38	[Kr]	$(4d)$ $(5s)^2$
40	Zr	Zirconium	6,84	[Kr]	$(4d)^2$ $(5s)^2$
41	Nb	Niobium	6,88	[Kr]	$(4d)^4$ $(5s)$
42	Mo	Molybdenum	7,10	[Kr]	$(4d)^5$ $(5s)$
43	Tc	Technetium	7,28	[Kr]	$(4d)^5$ $(5s)^2$
44	Ru	Ruthenium	7,37	[Kr]	$(4d)^7$ $(5s)$
45	Rh	Rhodium	7,46	[Kr]	$(4d)^8$ $(5s)$
46	Pd	Palladium	8,34	[Kr]	$(4d)^{10}$
47	Ag	Silver	7,58	[Kr]	$(4d)^{10}(5s)$
48	Cd	Cadmium	8,99	[Kr]	$(4d)^{10}(5s)^2$
49	In	Indium	5,79	[Kr]	$(4d)^{10}(5s)^2$ $(5p)$
50	Sn	Tin	7,34	[Kr]	$(4d)^{10}(5s)^2$ $(5p)^2$
51	Sb	Antimony	8,64	[Kr]	$(4d)^{10}(5s)^2$ $(5p)^3$
52	Te	Tellurium	9,01	[Kr]	$(4d)^{10}(5s)^2$ $(5p)^4$
53	I	Iodine	10,45	[Kr]	$(4d)^{10}(5s)^2$ $(5p)^5$
54	Xe	Xenon	12,13	[Kr]	$(4d)^{10}(5s)^2$ $(5p)^6$
55	Cs	Cesium	3,89	[Xe]	$(6s)$

Screened potential and Centrifugal barrier
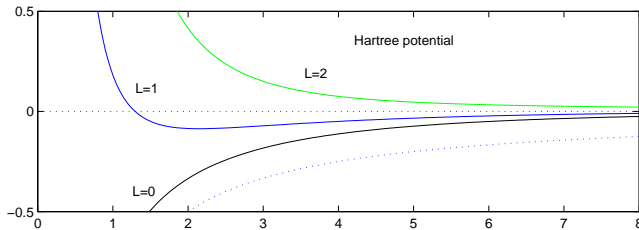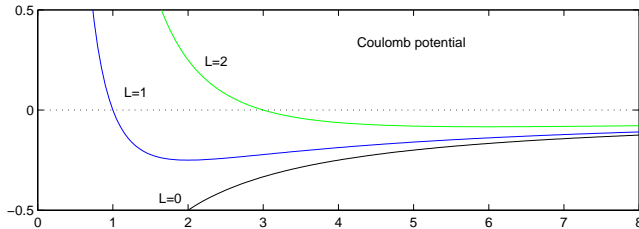
$$\left(-\frac{Z}{r}\right) + \frac{L(L+1)}{r^2} \qquad vs. \qquad \left(-\frac{Z-1}{r}e^{-\alpha r} - \frac{1}{r}\right) + \frac{L(L+1)}{r^2} \qquad (5)$$
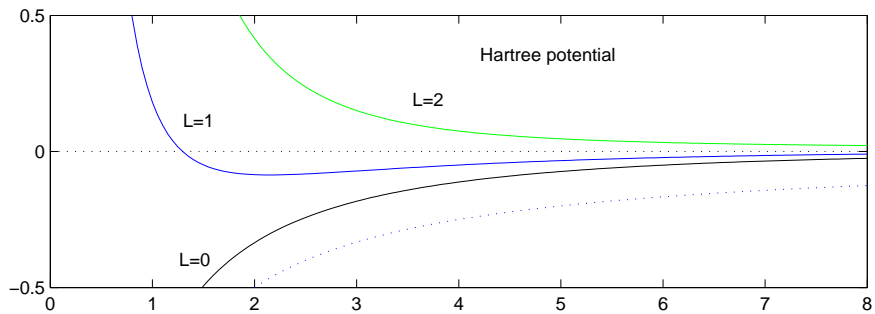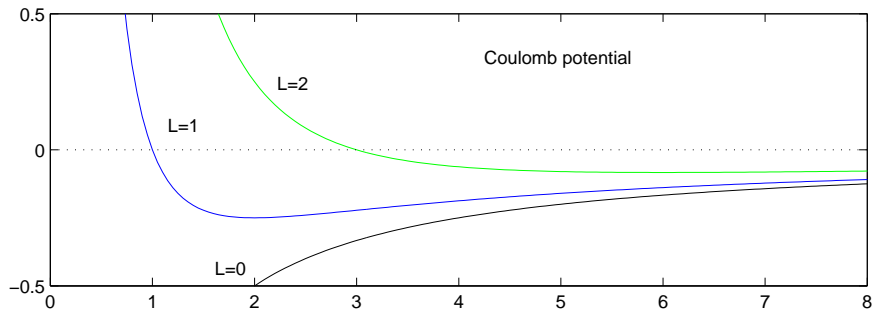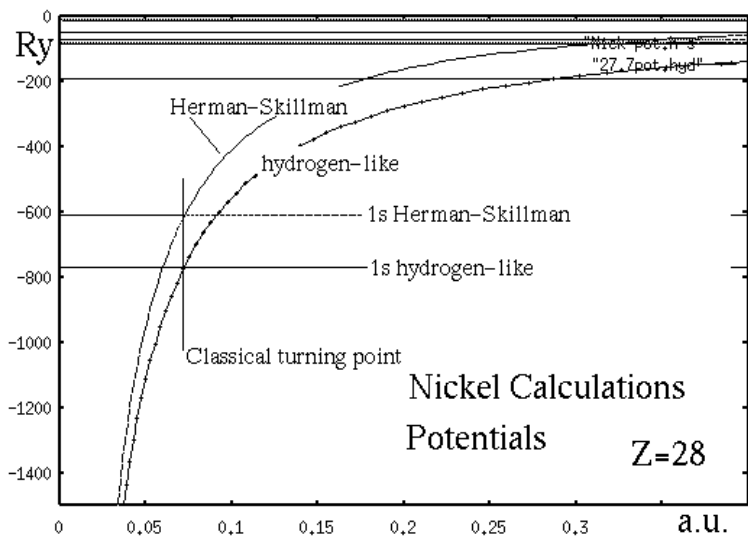
Figure 5: Selfconsistent field calculations compared to coulomb - real results

Here we note the position of the turning point - same for both Coulomb and SCF case. This is true only for the 1s states. List of topics
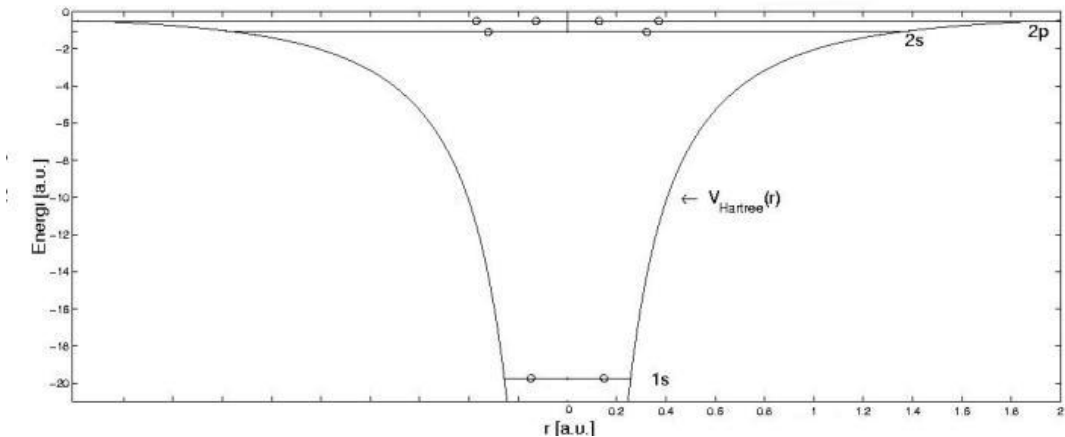
Figure 6: Hartree Atomic potential

This figure shows results for oxygen with the potential and energies obtained from a calculation with SCF program
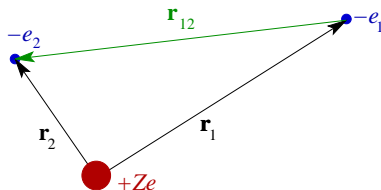
10 Energy for N-particles

The Slater determinant

$$\Phi_{a,b,...N}^{HF}(r_1, r_2, ...r_N) \rightarrow \begin{vmatrix} \psi_a(r_1)\psi_b(r_1)......\psi_N(r_1) \\ \psi_a(r_2)\psi_b(r_2)......\psi_N(r_2) \\ .... \\ \psi_a(r_N)\psi_b(r_N)......\psi_N(r_N) \end{vmatrix}$$

Evaluates to

$$\begin{aligned} \langle \Phi^{HF} | H | \Phi^{HF} \rangle &= \sum_{j=1}^{N} \langle \psi_j | T - \frac{Ze^2}{r} | \psi_j \rangle \\ &+ \sum_{(i,j)pairs} \langle \psi_j \psi_i | \frac{e^2}{|\vec{r} - \vec{r'}|} | \psi_j \ \psi_i \rangle \\ &- \sum_{(i,j)pairs} \langle \psi_j \psi_i | \frac{e^2}{|\vec{r} - \vec{r'}|} | \psi_i \ \psi_j \rangle \end{aligned} \qquad (6)$$

The last term - exchange energy

For Helium

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 \; - \; \frac{Z\,e^2}{r_1} \; - \; \frac{\hbar^2}{2m_e}\nabla_{r_2}^2 \; - \; \frac{Z\,e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right]\Psi\left(\mathbf{r}_1, \mathbf{r}_2\right) \; = \; E\,\Psi\left(\mathbf{r}_1, \mathbf{r}_2\right)$$

$$\Phi_{a,b}^{HF}\left(r_1, r_2\right) = \frac{1}{\sqrt{2}}\left|\begin{array}{cc}\psi_a(r_1) & \psi_b(r_1) \\ \psi_a(r_2) & \psi_b(r_2)\end{array}\right| = \frac{1}{\sqrt{2}}\left[\psi_a(r_1)\psi_b(r_2) - \psi_b(r_1)\psi_a(r_2)\right]$$

and the energy becomes

$$\begin{aligned}\left\langle\Phi^{HF}\right| H \left|\Phi^{HF}\right\rangle \; &= \; \langle\psi_a|\,T - \frac{Ze^2}{r}\,|\psi_a\rangle + \langle\psi_b|\,T - \frac{Ze^2}{r}\,|\psi_b\rangle \\ &+ \; \langle\psi_a\psi_b|\,\frac{e^2}{|\vec{r} - \vec{r}'|}\,|\psi_a\,\psi_b\,\rangle - \langle\psi_a\psi_b|\,\frac{e^2}{|\vec{r} - \vec{r}'|}\,|\psi_b\,\psi_a\,\rangle \; (7)\end{aligned}$$

The last term - exchange energy - and there is only one pair.

List of topics   Lithium example

For N-particles - the repulsion - we sum over pairs of coordinates

$$\left[\sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_{r_i}^2 - \frac{Ze^2}{r_i} \right) + \sum_{(i,j)pairs} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right] \Phi\left(r_1, r_2, ... r_N\right) = E\Phi\left(r_1, r_2, ... r_N\right)$$

With independent particles - Product function

$$\Phi\left(r_1, r_2, ... r_N\right) \approx \psi_1(r_1)\psi_2(r_2)......\psi_N(r_N)$$

$$E = \langle\Phi| H |\Phi\rangle \quad \rightarrow \quad \sum_{j=1}^{N} \langle\psi_j| T - \frac{Ze^2}{r} |\psi_j\rangle + \sum_{(i,j)pairs} \langle\psi_j\psi_i| \frac{e^2}{|\vec{r} - \vec{r}\,'|} |\psi_j \ \psi_i \rangle$$

The sum over coordinate pairs becomes sum over pairs of orbitals
This remains true for Slater determinants - but it must be shown.
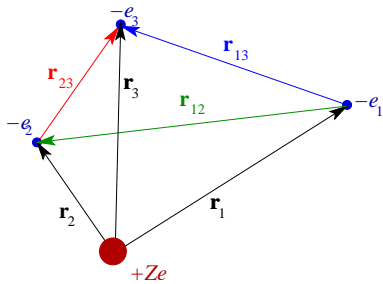There are $N!$ terms in the Slater determinant, the left and right give $(N!)^2$
terms, and there are $N(N+1)$ coordinate pairs. Thus $N(N+1)(N!)^2$ terms.
Due to the normalization, this becomes only $2N(N+1)$ terms, $N(N+1)$
direct terms and $N(N+1)$ exchange term
Next slide: Lithium example -with coordinates
Following after: Counting the number of nonzero terms (Lithium)

Lithium $6 \times 6 \times 3$-pair terms

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 \; - \; \frac{Z\,e^2}{r_1} \; - \; \frac{\hbar^2}{2m_e}\nabla_{r_2}^2 \; - \; \frac{Z\,e^2}{r_2} \; - \; \frac{\hbar^2}{2m_e}\nabla_{r_3}^2 \; - \; \frac{Z\,e^2}{r_3} \right.$$

$$\left. + \; \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \; + \; \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_3|} \; + \; \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_3|} \right] \Psi\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3\right) \; = \; E \; \Psi\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3\right)$$

$$(8)$$

$$\frac{1}{\sqrt{3!}}\left\{ \; \psi_\alpha(1)\,\psi_\beta(2)\,\psi_\gamma(3) \; + \; \psi_\beta(1)\,\psi_\gamma(2)\,\psi_\alpha(3) \; + \; \psi_\gamma(1)\,\psi_\alpha(2)\,\psi_\beta(3) \right.$$

$$\left. - \; \psi_\gamma(1)\,\psi_\beta(2)\,\psi_\alpha(3) \; - \; \psi_\alpha(1)\,\psi_\gamma(2)\,\psi_\beta(3) \; - \; \psi_\beta(1)\,\psi_\alpha(2)\,\psi_\gamma(3) \right\}$$

$$\frac{1}{\sqrt{3!}}\left\{|a\ b\ c\rangle+|c\ a\ b\rangle+|b\ c\ a\rangle-|b\ a\ c\rangle-|c\ b\ a\rangle-|a\ c\ b\rangle\right\}$$

$$\langle a\ b\ c|\ \frac{e^2}{r_{23}}\ |a\ b\ c\rangle \qquad\qquad \langle a\,|\,a\rangle\langle b\ c\,|\,\frac{e^2}{r_{23}}\,|\,b\ c\rangle$$

$$+\langle a\ b\ c|\ \frac{e^2}{r_{23}}\ |c\ a\ b\rangle \qquad \langle a\,|\,c\rangle\langle b\ c\,|\,\frac{e^2}{r_{23}}\,|\,a\ b\rangle$$

$$+\langle a\ b\ c|\ \frac{e^2}{r_{23}}\ |b\ c\ a\rangle \qquad \langle a\,|\,b\rangle\langle b\ c\,|\,\frac{e^2}{r_{23}}\,|\,c\ a\rangle$$

$$-\langle a\ b\ c|\ \frac{e^2}{r_{23}}\ |b\ a\ c\rangle \qquad \langle a\,|\,b\rangle\langle b\ c\,|\,\frac{e^2}{r_{23}}\,|\,a\ c\rangle$$

$$-\langle a\ b\ c|\ \frac{e^2}{r_{23}}\ |c\ b\ a\rangle- \qquad \langle a\,|\,c\rangle\langle b\ c\,|\,\frac{e^2}{r_{23}}\,|\,b\ a\rangle$$

$$-\langle a\ b\ c|\ \frac{e^2}{r_{23}}\ |a\ c\ b\rangle \qquad \langle a\,|\,a\rangle\langle b\ c\,|\,\frac{e^2}{r_{23}}\,|\,c\ b\rangle$$

Evaluation of the first six terms of the total 36 terms. For each further group of 6 a very similar procedure would follow. From each six, two remain, totaling 12 nonzero terms

11 N particles in Slater determinant - Total Energy Summary

$$
\begin{aligned}
\langle\Phi|\, H\, |\Phi\rangle \;\; = \;\; & \sum_{j=1}^{N} \langle\psi_j|\, T - \frac{Ze^2}{r}\, |\psi_j\rangle + \sum_{(i,j)pairs} \langle\psi_j\psi_i|\, \frac{e^2}{|\vec{r}-\vec{r'}|}\, |\psi_j\, \psi_i\,\rangle \\
& - \sum_{(i,j)pairs} \langle\psi_j\psi_i|\, \frac{e^2}{|\vec{r}-\vec{r'}|}\, |\psi_i\, \psi_j\,\rangle \qquad\qquad (9)
\end{aligned}
$$

We will use also a more compact notation, instead of orbitals ψ_i we use orbitals $|\alpha\rangle$, i.e. the index becomes the name of the function

$$
\langle\Phi|\, H\, |\Phi\rangle \;\; = \;\; \sum_{\alpha}\langle\alpha|(T+V)|\alpha\rangle + \sum_{pairs\ \alpha\beta} \left[\langle\alpha\beta|V_{ee}|\alpha\beta\rangle - \langle\alpha\beta|V_{ee}|\beta\alpha\rangle\right] \quad (10)
$$

Schrödinger equation from variational principle: minimize

$$\frac{\langle\Phi|\,H\,|\Phi\rangle}{\langle\Phi\mid\Phi\rangle}$$

which can be written as *minimalization with constraint* $\langle\Phi\mid\Phi\rangle = 1$; minimize

$$\langle\Phi|\,H\,|\Phi\rangle - \lambda\,\langle\Phi\mid\Phi\rangle \qquad \langle\Phi\mid\Phi\rangle - 1 = 0 \qquad \lambda \quad \text{Lagrange multiplier}$$

Derivative - differential

$$f(x) \rightarrow \frac{df(x)}{dx} \quad \rightarrow \quad df = \frac{df(x)}{dx}dx$$

Functional derivative - functional $\mathcal{F}(f)$; variation of the functions $f(x)$, δf

$$\mathcal{F}(f) \quad \rightarrow \frac{\delta\mathcal{F}(f)}{\delta f} \quad \rightarrow \quad \delta\mathcal{F} = \frac{\delta\mathcal{F}(f)}{\delta f}\delta f \qquad (11)$$

Variation of $\langle\Phi|\,H\,|\Phi\rangle$ is taken (considering the complex nature of $|\Phi\rangle$) as

$$\delta\left(\langle\Phi|\,H\,|\Phi\rangle\right) = \langle\delta\Phi|\,H\,|\Phi\rangle$$

With arbitrary variations $|\delta\Phi\rangle$

$$\langle\delta\Phi|\,H\,|\Phi\rangle - \lambda\,\langle\delta\Phi\mid\Phi\rangle \quad \longrightarrow \quad H\,|\Phi\rangle - \lambda\,|\Phi\rangle = 0 \quad \longrightarrow \quad H\,|\Phi\rangle = \lambda\,|\Phi\rangle$$

Thus the Lagrange multiplier plays the role of energy eigenvalue

Deriving Hartree-Fock: For N electrons this energy must be minimized

$$\langle\Phi|\ H\ |\Phi\rangle\ =\ \sum_\alpha \langle\alpha|(T+V)|\alpha\rangle + \sum_{pairs\ \alpha\beta} [\langle\alpha\beta|V_{ee}|\alpha\beta\rangle - \langle\alpha\beta|V_{ee}|\beta\alpha\rangle] \quad (12)$$

with respect to the N orbitals $|\alpha\rangle$, $|\beta\rangle$, *etc.* ,

with N conditions $\langle\alpha|\alpha\rangle = 1$, $\langle\beta|\beta\rangle = 1$, i.e.

with N Lagrange multipliers ε_α, ε_β ....

$$\langle\delta\Phi(\alpha\to\delta\alpha)|\ H\ |\Phi\rangle\ -\ \varepsilon_\alpha\ \langle\delta\alpha\ |\ \alpha\rangle\ =\ 0$$

Which results in N equations (one for each of the N orbitals)

$$\langle\delta\alpha|(T+V)|\alpha\rangle + \sum_\beta [\langle(\delta\alpha)\beta|V_{ee}|\alpha\beta\rangle - \langle(\delta\alpha)\beta|V_{ee}|\beta\alpha\rangle] - \varepsilon_\alpha\ \langle\delta\alpha\ |\ \alpha\rangle\ = 0 \quad (13)$$

Leaving for a while out the exchange-related term, we can as in prev. slide reduce this by removing $\langle\delta\alpha|$

$$(T+V)|\alpha\rangle + \sum_\beta [\langle\beta|V_{ee}|\beta\rangle]\,|\alpha\rangle - \varepsilon_\alpha\ |\ \alpha\rangle\ = 0$$

which is exactly the Hartree method. The exchange term leads to complications $\rightarrow$
List of topics

Reducing the full equation

$$\langle\delta\alpha|(T+V)|\alpha\rangle + \sum_\beta \left[\langle(\delta\alpha)\beta|V_{ee}|\alpha\beta\rangle - \langle(\delta\alpha)\beta|V_{ee}|\beta\alpha\rangle\right] - \varepsilon_\alpha \langle\delta\alpha \mid \alpha\rangle = 0 \quad (14)$$

we get the **Hartree Fock Equations (N orbitals)**

$$(T+V)|\alpha\rangle + \sum_\beta \left[\langle\beta|V_{ee}|\beta\rangle\right]|\alpha\rangle - \sum_\beta \left[\langle\beta|V_{ee}|\alpha\rangle\right]|\beta\rangle - \varepsilon_\alpha \mid \alpha\rangle = 0$$

The complexity of the exchange term becomes clear when we write it explicitly with coordinates and integrations.

Hartree Fock Equations: The direct term and the exchange term:

$$\mathcal{W}_{HF} = \mathcal{W}^d - \mathcal{W}^{ex}$$

$$\mathcal{W}_{HF}\psi_a(\mathbf{r}) = \left[\sum_b^{occ} \int \psi_b(\mathbf{x})\frac{e^2}{|\mathbf{r}-\mathbf{x}|}\psi_b(\mathbf{x})d^3x\right]\psi_a(\mathbf{r}) - \left[\sum_b^{occ} \psi_b(\mathbf{r})\int \psi_b(\mathbf{x})\frac{e^2}{|\mathbf{r}-\mathbf{x}|}\psi_a(\mathbf{x})d^3x\right]$$

where the exchange potential is *nonlocal*

$$\mathcal{W}^d\psi_a \rightarrow \mathcal{W}^d(\mathbf{r})\psi_a(\mathbf{r}) \qquad\qquad \mathcal{W}^{ex}\psi_a(\mathbf{r}) \rightarrow \int \mathcal{W}^{ex}(\mathbf{r},\mathbf{x})\psi_a(\mathbf{x})d^3x$$

Hartree-Fock total energy and sum of orbital energies

with a shorthand notation

$$\varphi_\alpha(\mathbf{r}) \quad \to \quad |\varphi_\alpha\rangle \quad \to \quad |\alpha\rangle$$

Slater determinant

$$\Phi_{\alpha,\beta,....,\nu} \quad \to \quad |\alpha, \beta, ..., \nu\rangle$$

We have started our work with the Hartree-Fock equations by evaluating

$$\langle \Phi_{\alpha,\beta,....,\nu}| \left[T + V + \sum_{pairs\ ij} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] |\Phi_{\alpha,\beta,....,\nu}\rangle \tag{15}$$

This we have evaluated as

$$\langle \Phi| \ H \ |\Phi\rangle \ = \ \sum_\alpha \langle \alpha|(T+V)|\alpha\rangle + \sum_{pairs\ \alpha\beta} \left[\langle \alpha\beta|V_{ee}|\alpha\beta\rangle - \langle \alpha\beta|V_{ee}|\beta\alpha\rangle \right] \tag{16}$$

From this expression we have obtained Hartree-Fock equations by the variational procedure.

The Hartree-Fock equation can be then written as

$$\left[T + V + \sum_\beta \langle\beta|\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\beta\rangle \right] \, |\alpha\rangle - \sum_\beta \left[\langle\beta|\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\alpha\rangle \right] \, |\beta\rangle \;\; = \;\; \varepsilon_\alpha \, |\alpha\rangle \quad (17)$$

We form the matrix element with the given $\langle\alpha|$

$$\langle\alpha| \left[T + V + \sum_\beta \langle\beta|\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\beta\rangle \right] \, |\alpha\rangle - \langle\alpha| \left[\sum_\beta \langle\beta|\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\alpha\rangle \right] |\beta\rangle \;\; = \;\; \varepsilon_\alpha \quad (18)$$

since $\langle\alpha|\alpha\rangle = 1$. This can be rewritten as

$$\varepsilon_\alpha \;\; = \;\; \langle\alpha|(T+V)|\alpha\rangle + \sum_{\beta\neq\alpha} \left[\langle\beta\alpha|V_{ee}|\beta\alpha\rangle - \langle\beta\alpha|V_{ee}|\alpha\beta\rangle \right] \quad (19)$$

And now we can explore what is the sum of all ε_α

$$\sum_\alpha \varepsilon_\alpha \;\; = \;\; \sum_\alpha \langle\alpha|(T+V)|\alpha\rangle + \sum_\alpha \sum_{\beta\neq\alpha} \left[\langle\beta\alpha|V_{ee}|\beta\alpha\rangle - \langle\beta\alpha|V_{ee}|\alpha\beta\rangle \right] \quad (20)$$

which we can compare with the above $\langle \Phi | \, H \, | \Phi \rangle$

$$\langle \Phi | \, H \, | \Phi \rangle \;\; = \;\; \sum_\alpha \langle \alpha | (T+V) | \alpha \rangle + \sum_{pairs \; \alpha\beta} [\langle \alpha\beta | V_{ee} | \alpha\beta \rangle - \langle \alpha\beta | V_{ee} | \beta\alpha \rangle] \quad (21)$$

The two expressions are very similar, but they differ in fact by all the interaction term, since it is counted twice in the sum:

$$\sum_\alpha \sum_{\beta \neq \alpha} F_{\alpha\beta} \;\; = \;\; 2 \sum_{pairs \; \alpha\beta} F_{\alpha\beta}$$

for any set of objects that are symmetric $F_{\alpha\beta} = F_{\beta\alpha}$

Our objects are symmetric, because they are in fact of the type $H_{\alpha\beta,\alpha\beta}$. The wavefunctions are antisymmetric, $|\alpha\beta\rangle = -|\beta\alpha\rangle$.

Thus, surprisingly perhaps

$$\langle \Phi | \, H \, | \Phi \rangle \;\; \neq \;\; \sum_\alpha \varepsilon_\alpha$$

but as we derived here List of topics

$$\langle \Phi | \, H \, | \Phi \rangle \;\; = \;\; \sum_\alpha \varepsilon_\alpha - \sum_{pairs \; \alpha\beta} [\langle \alpha\beta | V_{ee} | \alpha\beta \rangle - \langle \alpha\beta | V_{ee} | \beta\alpha \rangle] \quad (22)$$

Evaluation of the repulsion term using the multipole expansion

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{LM} \frac{4\pi}{2L+1} \; \frac{r_<^L}{r_>^{L+1}} \; Y_{LM}^\star (\hat{r}_1) \, Y_{LM} (\hat{r}_2) \tag{23}$$

where

$$r_< = r_1, \quad r_> = r_2 \quad \text{for} \quad |\mathbf{r}_1| \; < \; |\mathbf{r}_2|$$
$$r_< = r_2, \quad r_> = r_1 \quad \text{for} \quad |\mathbf{r}_1| \; > \; |\mathbf{r}_2|$$

Evaluation of the matrix element in general case

$$\int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \psi_{n_1 l_1 m_1}^\star (\mathbf{r}_1) \, \psi_{n_2 l_2 m_2}^\star (\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{n_1 l_1 m_1} (\mathbf{r}_1) \, \psi_{n_2 l_2 m_2} (\mathbf{r}_2) \tag{24}$$

is performed separately over the radial and angular parts

$$\int r_1^2 dr_1 \int d\hat{r}_1 \int r_2^2 dr_2 \int d\hat{r}_2 \qquad R_{n_1 l_1}^\star(r_1) Y_{l_1 m_1}^\star (\hat{r}_1) \, R_{n_2 l_2}^\star(r_2) Y_{l_2 m_2}^\star (\hat{r}_2)$$
$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \qquad R_{n_1 l_1}(r_1) Y_{l_1 m_1} (\hat{r}_1) \, R_{n_2 l_2}(r_2) Y_{l_2 m_2} (\hat{r}_2) \tag{25}$$

where $d\hat{r}_i$ means the integration over $d\Omega_i = \sin\theta_i d\theta_i d\varphi_i$. List of topics

The evaluation of general case - angular integrals of three Y_{lm}'s

$$C^L = \int Y^{\star}_{l_i m_i}(\theta, \varphi) Y_{LM}(\theta, \varphi) Y_{l_i m_i}(\theta, \varphi) d\Omega \qquad (26)$$

For the case of both s-states, $l_i = 0 \quad m_i = 0$ only $L = 0 \quad M = 0$ are non-zero; The sum reduces to one term. The angular factors give value one, since the $(Y_{L=0 M=0})^2 = (4\pi)^{-1}$ cancels the corresponding factor in the multipole expansion and due to the normalization.

List of topics

12 Configuration mixing

Consider the usual:

$$H_x(x)\varphi_\alpha(x) = E_\alpha \varphi_\alpha(x)$$
$$H_y(y)\chi_\beta(y) = E_\beta \chi_\beta(y)$$

For any $\Phi(x)$

$$\Phi(x) = \sum c_\alpha \varphi_\alpha(x)$$

For any $\Xi(x)$

$$\Xi(y) = \sum d_\beta \chi_\beta(y)$$

Take now a general $\Psi(x, y)$. First look at y as a parameter, $\Psi(x, y_0)$

$$\Psi(x, y_0) \to \Phi(x) = \sum c_\alpha(y_0)\varphi_\alpha(x)$$

for every y_0 ; Thus we get a new function of y;

$$c_\alpha(y) = \sum d_\beta(\alpha)\chi_\beta(y)$$

Inserting back:

$$\Psi(x,y) = \sum d_\beta(\alpha)\chi_\beta(y)\varphi_\alpha(x)$$

Or, with a simpler notation

$$\Psi(x,y) = \sum d_{\beta\alpha}\chi_\beta(y)\varphi_\alpha(x)$$

In the case of Helium, for example, the $H(x)$ and $H(y)$ are identical and so are the $\chi_\beta(y)$ and $\varphi_\alpha(x)$. This becomes configuration mixing.

$$\Psi(x,y) = \sum d_{\beta\alpha}\varphi_\beta(y)\varphi_\alpha(x)$$

The coefficients are found by diagonalization.

For three coordinate sets - e.g. for Lithium :

$$\Psi(x,y,z) = \sum D_{\gamma\beta\alpha}\varphi(z)\varphi_\beta(y)\varphi_\alpha(x)$$

END OF THE PRESENTATION