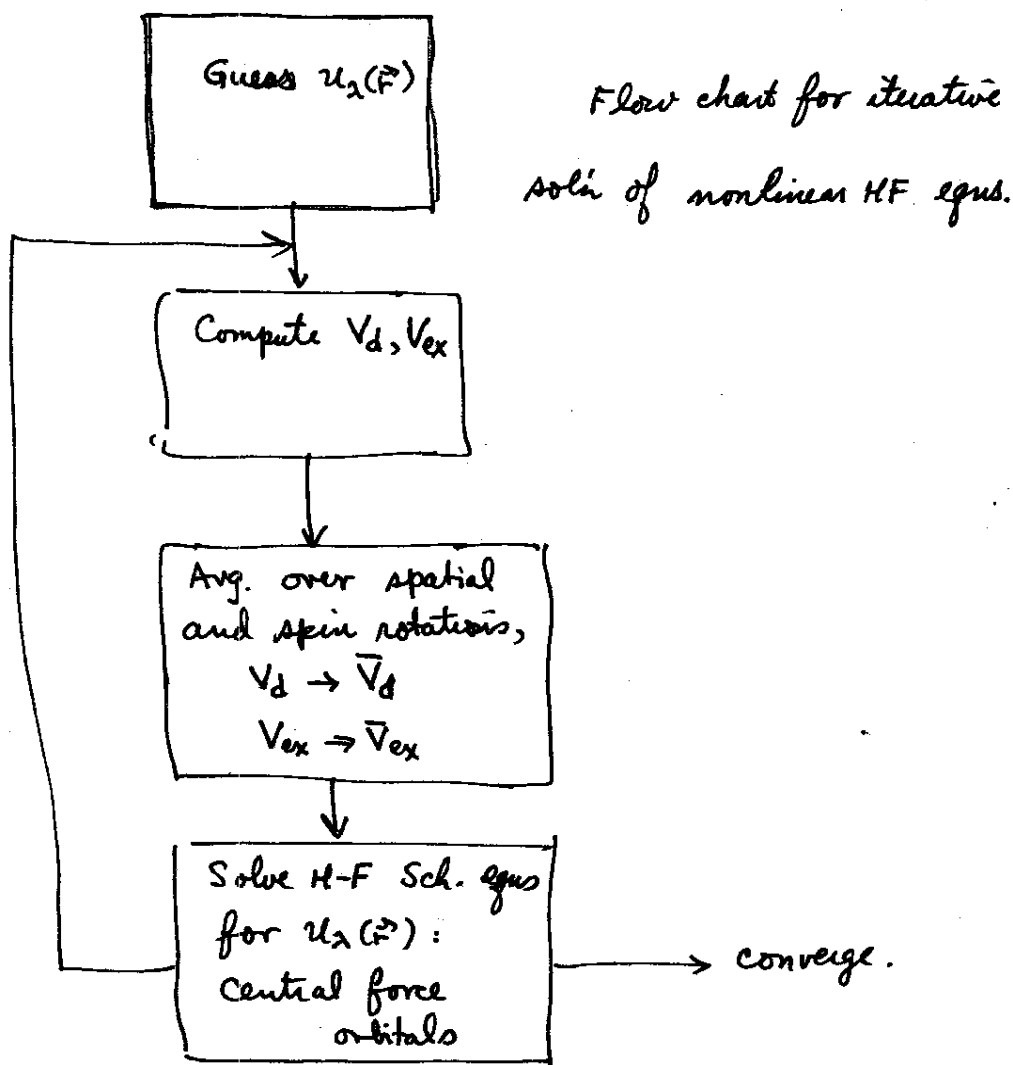


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HF eqns:

$$\left(\frac{p^2}{2} - \frac{Z}{r}\right) u_\lambda(\vec{r}) + \bar{V}_d(r) u_\lambda(\vec{r}) - (\bar{V}_{ex} u_\lambda)(\vec{r}) = \epsilon_\lambda u_\lambda(\vec{r}).$$

With averaging step inserted (actually not necessary in case of complete subshells), solns to HF eqn. are central force eigenfns, i.e.,

$$u_\lambda(\vec{r}) = R_{nl}(r) Y_{lm}(\Omega)$$

$$\lambda = (n \ l \ m_l \ m_s) \quad \text{central force quantum numbers}$$

$$\epsilon_\lambda = \epsilon_{nl} \quad (\text{indep. of } m_l, m_s).$$

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Then Slater det $|\Phi\rangle$ (the HF soln) is composed of central force orbitals in the self-consistent potentials. Once the self-consistent potentials are known, we have a rotationally invariant, single particle hamiltonian,

$$h = \frac{p^2}{2} - \frac{Z}{r} + \bar{V}_d - \bar{V}_{ex}$$

and the orbitals u_λ are eigenfns of h ,

$$h u_\lambda = E_\lambda u_\lambda.$$

More exactly, they are the lowest N eigenfns of h in energy. With fixed \bar{V}_d, \bar{V}_{ex} , h possesses a complete set of orthonormal eigenfns (single-particle eigenfns).

The main drawback of $|\Phi\rangle$ as a soln for the ground state of the atom is that it is not an eigenstate of all of the exactly conserved quantities of H . The list of operators that commute with H and their quantum numbers is

L^2	L_z	S^2	S_z	π	E_{ij}
L	M_L	S	M_S	π	-1

The state $|\Phi\rangle$ is an eigenstate of L_z, S_z, π and E_{ij} , but not L^2, S^2, E_{ij} because we are using a Slater det. L_z because

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$$L_z = \sum_{i=1}^N L_{iz},$$

and each orbital $u_\lambda = u_{n\ell m_\ell}$ is an eigenstate of one of the L_{iz} with eigenvalue $m_{\ell i} \hbar$. The electrons are permuted among all the orbitals in the Slater det., but since the sum

$$\sum_{i=1}^N m_{\ell i}$$

is invariant under permutations of the electron labels, the value of M_L is the same for all $N!$ terms in the Slater det. Thus

$$M_L = \sum_{i=1}^N m_{\ell i}$$

Similarly,

$$M_S = \sum_{i=1}^N m_{s i}$$

As for parity, each orbital $u_\lambda = u_{n\ell m_\ell}$ has parity $(-1)^\ell$, so

$$\pi = \prod_{i=1}^N (-1)^{\ell_i}$$

which is also invariant under permutations of particle labels.

But similar arguments don't apply to L^2, S^2 , which are not additive quantum numbers.

We fix this up with a perturbation approach, which can be carried out after the H-F eqns have been solved for a given electron configuration, e.g., $1s^2 2s^2 2p^2$ for carbon.

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We define

$$H_0 = \sum_{i=1}^N h_i = \sum_{i=1}^N \left(\frac{p_i^2}{2} - \frac{Z}{r_i} + \bar{V}_{d,i} - \bar{V}_{ex,i} \right)$$

$$H_1 = - \sum_{i=1}^N (\bar{V}_{d,i} - \bar{V}_{ex,i}) + \sum_{i < j} \frac{1}{r_{ij}}$$

$$H_2 = \sum_{i=1}^N \xi(r_i) \vec{L}_i \cdot \vec{S}_i$$

Here H_0 is the sum of single particle Hamiltonians determined self-consistently by a given electron configuration. H_1 subtracts off the average central fields $\bar{V}_d - \bar{V}_{ex}$ and adds back the inter-electron interactions. H_1 is said to contain residual Coulomb effects, since the rotationally invariant average has been removed. Notice that $H_0 + H_1$ is the exact basic N -elec. Hamiltonian. H_2 contains the spin-orbit terms. We omit the other fine structure corrections and treat H_2 somewhat schematically.

For low Z atoms, it turns out $H_1 \ll H_2$. Thus we treat just H_0 as an unpert. Ham and H_1 as a pertn; then $H_0 + H_1$ as an unpert. Ham. and H_2 as a pertn. For high Z atoms $H_2 \gg H_1$. Then we treat H_0 as an unpert. Ham. and H_2 as a pertn; then $H_0 + H_2$ as an unpert. Ham. and

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H_1 as a pertn.

The low Z scheme is called LS or Russell-Saunders coupling, while the high Z method is called jj-coupling.

We will concentrate on the low Z case (LS coupling).

To treat H_0 as an unperturbed Hamiltonian we must first understand its symmetries, eigenstates, ~~at~~ degeneracies, etc. The HF state $|\Phi\rangle$ is an eigenstate of H_0 ,

$$H_0|\Phi\rangle = E_0|\Phi\rangle$$

where

$$E_0 = \sum_{\lambda=1}^N E_{\lambda} = \sum_{nl} \nu_{nl} E_{nl},$$

i.e. it is the sum of the HF pseudo-eigenvalues E_{λ} , which is also a sum \mathcal{B} over subshells of the subshell energy E_{nl} times the number of electrons in the subshell ν_{nl} (the occupation number). The electron configuration, which is assumed fixed for the duration of this discussion, determines ν_{nl} . The maximum number of electrons in subshell nl is $2(2l+1)$. We speak of complete or incomplete subshells, depending on whether they are filled or not.

In general the HF state is not unique for a given electron

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configuration, because the energy is independent of the choice of magnetic quantum numbers (m_l, m_s). There is only one choice of magnetic quantum numbers in a complete subshell, but in incomplete subshells the electrons can be arranged in the various states in different ways. For example, in B (boron) with config. $1s^2 2s^2 2p$, the one $2p$ electron can go into any one of $6 = 2(2l+1)$ (for $l=1$) states, with magnetic qu. #'s

m_l	m_s
1	$1/2$
0	$-1/2$
-1	$1/2$
1	$-1/2$
0	$1/2$
-1	$-1/2$

For C (carbon) with config $1s^2 2s^2 2p^2$, the 2 electrons in the $2p$ subshell can go in

$$\binom{6}{2} = \frac{6!}{2! 4!} = 15$$

ways. For nitrogen, it is

$$\binom{6}{3} = 20$$

ways, etc. The binomial coefficient is the number of ways of selecting unordered subsets of a set of objects (here orbitals). The subsets are unordered because ~~of~~ the

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electrons are identical; for example in carbon, it makes no difference if we assign electrons 1 and 2 the quantum numbers

$$\begin{array}{c|cc} & m_l & m_s \\ \hline 1 & 1 & -1/2 \\ 2 & 0 & 1/2 \end{array} \quad \text{OR} \quad \begin{array}{c|cc} & m_l & m_s \\ \hline 1 & 0 & 1/2 \\ 2 & 1 & -1/2 \end{array}$$

because all electrons are permuted among all orbitals by the Slater determinant.

Thus the ground state of H_0 is highly degenerate, in general. (The exception is when all subshells are completely filled.) We must think about degenerate perturbation theory, and we will try to avoid diagonalizing matrices when analyzing H_1 . This means choosing a symmetry adapted basis, that is, linear combinations of the unperturbed eigenstates that are eigenstates of the exact symmetries of the Hamiltonian (meaning here $H_0 + H_1$), including L^2, S^2 (as well as L_z, S_z which are automatic).

The degenerate eigenstates of H_0 are all Slater determinants that are made up out of central field orbitals with a given electron configuration. They differ only in their assignments of magnetic qu. numbers (m_l, m_s) in incomplete subshells. Let us call

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such an assignment an m-set, and denote the corresponding Slater determinants by $|\Phi\rangle = |m\text{-set}\rangle$. Then we wish to form linear combinations that are eigenstates of $L^2 L_z S^2 S_z$,

$$|L M_L S M_S\rangle = \sum_{m\text{-sets}} (\text{coefs}) |m\text{-sets}\rangle$$

Sometimes there will be more than one way to do this, and we will need another quantum number, say $|\gamma L M_L S M_S\rangle$. These are automatically eigenstates of π . There is only one parity for a given configuration, so we suppress this qu. #. The lin. combos above will form the symmetry adapted basis within the degenerate eigenspace of H_0 .

The problem of finding the coefs in the expansion above is like the problem of computing the Clebsch-Gordan coeff's, but more complicated because there are 2 kinds of ang. mom. that must be added (\vec{L} and \vec{S}), there may be more than 2 electrons in the incomplete subshells, and because of the requirements of antisymmetrization. We will concentrate on a simpler problem, namely, just determining the L and S values that can occur.

The L and S values of complete subshells are always 0,0,

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so we can concentrate on incomplete subshells only. Some examples: In B (boron), $1s^2 2s^2 2p$, there is only one electron in the $2p$ subshell, so its l, s values are the same as L, S (for the whole atom), and we have only $L=1, S=1/2$. This is denoted 2P , pronounced "singlet-P", where the super-script 1 stands for $2S+1$.

In C (carbon), $1s^2 2s^2 2p^2$ we have 2 electrons with $l=1, s=1/2$, so possible values of L, S are given by combining $1 \otimes 1$ and $\frac{1}{2} \otimes \frac{1}{2}$:

$$1 \otimes 1 = \begin{matrix} s & a & s \\ 0 \oplus & 1 \oplus & 2 \end{matrix}$$

$$\frac{1}{2} \otimes \frac{1}{2} = \begin{matrix} a & s \\ 0 \oplus & 1 \end{matrix}$$

where s, a stand for symmetric, antisymmetric under exchange. To get overall antisymmetry, we must combine s with a or vice versa. Resulting table of allowed L, S values,

L	S	not'n	# states = $(2L+1)(2S+1)$
2	0	1D	$5 \times 1 = 5$
1	1	3P	$3 \times 3 = 9$
0	0	1S	$1 \times 1 = 1$
total			15

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The total is $15 = \binom{6}{2}$, agreeing with our earlier combinatorial calculation. The ground ~~state~~^{config.} of C is 15-fold degenerate; as we say, it consists of 3 multiplets, 1D , 3P , 1S . Each of these has different energy when H_1 is turned on; however, the energy is still indep. of M_L, M_S , so the 15-fold degen. of H_0 splits into 3 levels with degens 5, 9, 1.

This method for C is not easily extended to > 2 electrons in a given subshell. Here we present another (tabular) method for C that does generalize. First list all the allowed m -sets and their M_L, M_S values.

	m_{e1}	m_{e2}	m_{s1}	m_{s2}	M_L	M_S
1	1	1	$1/2$	$-1/2$	2	0
2	1	0	$1/2$	$1/2$	1	1
3	1	0	$1/2$	$-1/2$	1	0
4	1	0	$-1/2$	$1/2$	1	0
5	1	0	$-1/2$	$-1/2$	1	-1
6	1	-1	$1/2$	$1/2$	0	1
7	1	-1	$1/2$	$-1/2$	0	0
8	1	-1	$-1/2$	$1/2$	0	0
9	1	-1	$-1/2$	$-1/2$	0	-1
10	0	0	$1/2$	$-1/2$	0	0
11	0	-1	$1/2$	$1/2$	-1	1
12	0	-1	$1/2$	$-1/2$	-1	0
13	0	-1	$-1/2$	$1/2$	-1	0
14	0	-1	$-1/2$	$-1/2$	-1	-1
15	-1	-1	$1/2$	$-1/2$	-2	0

Note 1: In row 1, $m_{e1} = m_{e2}$, so m_{s1} cannot = m_{s2} , otherwise