

# **Final Exam**

Wednesday April 25, 2007 2-5pm  
SSC 3102

# Calculating The Total Energy of the Ground-State Atom

One important result of the Hartree-Fock calculation is the total energy of the ground-state atom. We obtain the energies and wave functions of individual electrons as best as we can using the variational (self-consistent) method.

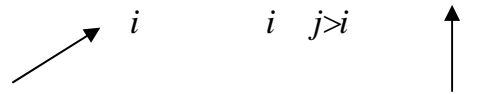
The total energy should be the sum of the energies of individual electrons?

However, this is not quite correct

In calculating the orbital energy,  $\epsilon_1$ , the self-consistent field method takes into account the repulsive interaction between  $e^-_1$  and  $e^-_2$ . The same is true for the calculation of  $\epsilon_2$ . Thus, the sum of the orbital energies will account the repulsive interaction of  $e^-_1$  and  $e^-_2$  twice, as well as those for all other pairs of electrons

This double counting of the repulsive energy must be corrected for

- For closed-subshell atoms

$$E_{total} = 2 \sum_i \epsilon_i - \sum_i \sum_{j>i} (2J_{ij} - K_{ij})$$


$J_{ij}$ : the Coulomb Integral  
 $K_{ij}$ : the Exchange Integral

2 e for each orbital From the repulsive interactions between electrons

## Hartree-Fock Calculation Results

Hartree-Fock calculations have been carried out for all elements in the periodic table. The important results for our purpose are the orbital energies and the effective nuclear charge.

The effective nuclear charge,  $\zeta$ :

	H(1)							He(2)
1s	1.00							1.69
	Li(3)	Be(4)	B(5)	C(6)	N(7)	O(8)	F(9)	Ne(10)
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2s	1.28	1.92	2.58	3.22	3.85	4.49	5.13	5.76
2p			2.42	3.14	3.83	4.45	5.10	5.76

- $\zeta$  takes into account that an electron farther from the nucleus experiences a smaller effective nuclear charge than that experienced by the inner electron
- The difference between the true nuclear charge and  $\zeta$  is the direct measure of the shielding
- $\zeta \cong$  nuclear charge for 1s orbital, but falls off rapidly for the outermost electron as  $n$  increases
- Electrons of smaller  $n$  values are more effective in shielding electrons with greater  $n$  values from the nuclear charge.
- However, electrons in the same shell are much less effective, so that  $Z - \zeta$  increases as we move across the periodic table, with some subtle effects

# Hartree-Fock Calculations on the Orbital Energies

Hartree-Fock calculations show that the orbital energies,  $\epsilon_l$  for many- $e^-$  atoms depend on both the principal quantum number,  $n$  and angular momentum quantum number,  $l$ .

Within a shell of a principal quantum number,  $n$ ,  $\epsilon_{ns} < \epsilon_{np} < \epsilon_{nd} < \dots$

Recall that for the H-atom,  $\epsilon_{ns} = \epsilon_{np} = \epsilon_{nd} = \dots$

## The origin of the energy - level splitting

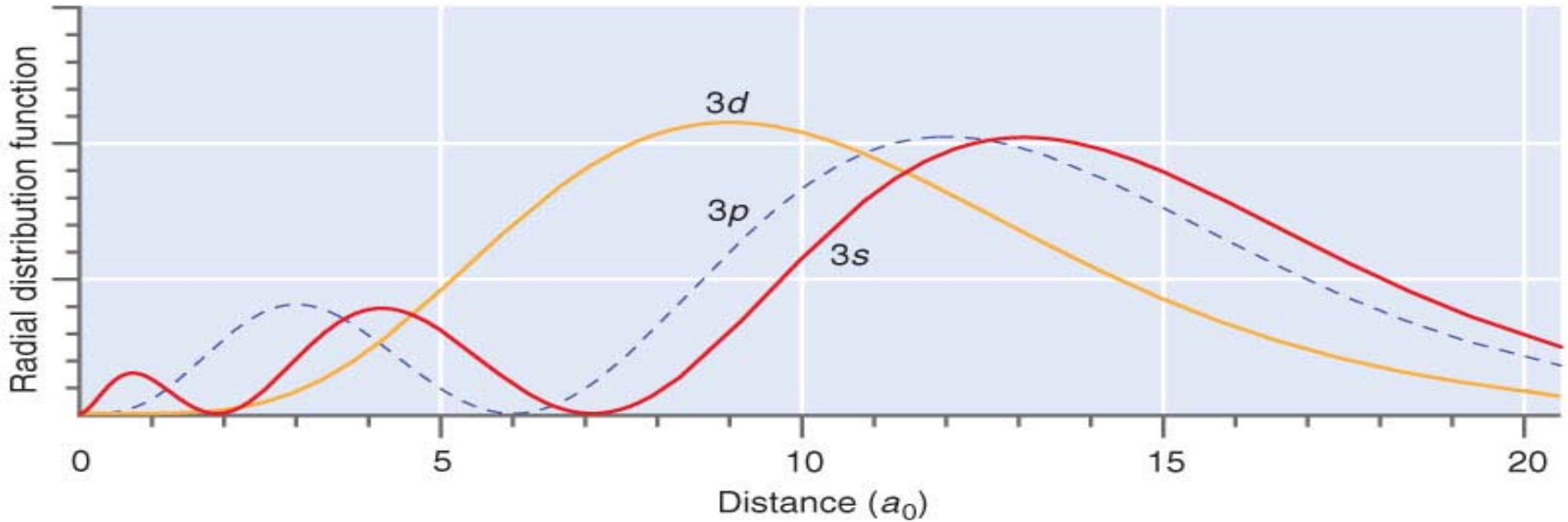
Consider the potential energy due to attraction between the nucleus and the electron

It falls off as:  $\frac{1}{r}$

Consider the radial distribution functions.

Probability of finding the electron close to the nucleus:  $3s > 3p > 3d$

$\Rightarrow$  Shielding from the nuclear charge:  $3s < 3p < 3d$



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The effective nuclear charge  $\zeta_{Z_e}$  experienced by an electron:  $3s > 3p > 3d$

In the HF calculations,  $\epsilon_i$  is determined by the average radial distribution of all electrons; that is,  $\epsilon_i$  is calculated, **assuming a certain configuration**

e.g., Sc

Sc can have configurations

	$[\text{Ar}]4s^23d^1$
	$[\text{Ar}]4s^13d^2$
	$[\text{Ar}]4s^03d^3$

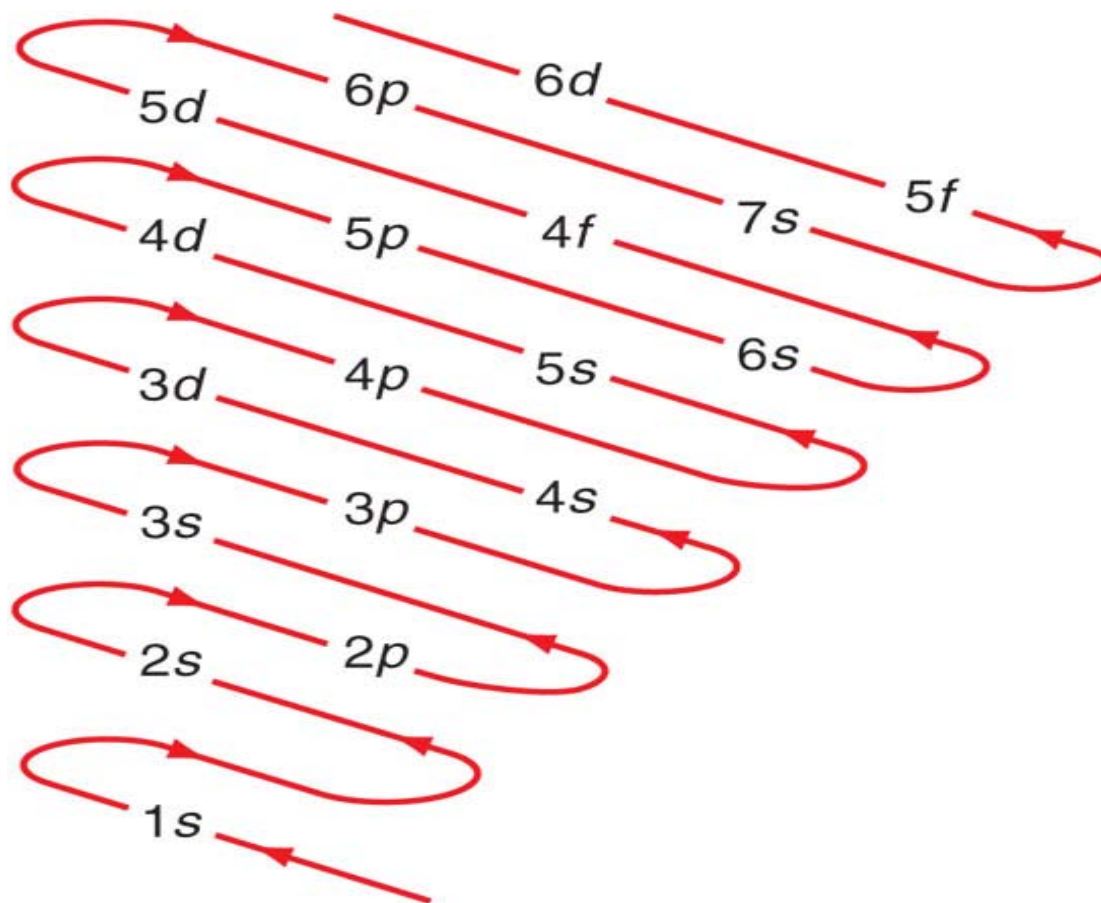
The electron density distribution is different for these configurations.

Thus,  $\epsilon_{4s}$  and  $\epsilon_{3d}$  will be different for each of these configuration.

**$\epsilon_{4s}$  calculated assuming  $[\text{Ar}]4s^23d^1 \neq \epsilon_{4s}$  calculated assuming  $[\text{Ar}]4s^13d^2$**

The known configurations of most atoms follows the **Aufbau Principle** (C020!!)  
= the general order in which the atomic orbitals is filled.

A number of atoms show departures from this order due for example to Hund's rule of maximum spin multiplicity. Ion configurations are particularly tricky to predict on this basis.



The general order in  $\epsilon_i$  does not fully explain the electronic configurations of atoms in the periodic table.

In fact, Hartree-Fock calculations predict:

$\epsilon_{4s} < \epsilon_{3d}$  for the ground states of K and Ca

$\epsilon_{4s} > \epsilon_{3d}$  for the ground states of other elements

However, the observed configurations for the transition metal elements Sc to Zn show that the 4s orbital is filled first.

**TABLE 10.2**

### Configurations for Fourth Row Atoms

Nuclear Charge	Element	Electron Configuration	Nuclear Charge	Element	Electron Configuration
19	K	[Ar]4s <sup>1</sup>	25	Mn	[Ar]4s <sup>2</sup> 3d <sup>5</sup>
20	Ca	[Ar]4s <sup>2</sup>	26	Fe	[Ar]4s <sup>2</sup> 3d <sup>6</sup>
21	Sc	[Ar]4s <sup>2</sup> 3d <sup>1</sup>	27	Co	[Ar]4s <sup>2</sup> 3d <sup>7</sup>
22	Ti	[Ar]4s <sup>2</sup> 3d <sup>2</sup>	28	Ni	[Ar]4s <sup>2</sup> 3d <sup>8</sup>
23	V	[Ar]4s <sup>2</sup> 3d <sup>3</sup>	29	Cu	[Ar]4s <sup>1</sup> 3d <sup>10</sup>
24	Cr	[Ar]4s <sup>1</sup> 3d <sup>5</sup>	30	Zn	[Ar]4s <sup>2</sup> 3d <sup>10</sup>



**The reason:** The stability of an electron configuration is determined by the total energy of the atom. But the total energy is not the mere sum of the orbital energies; that is, stability consideration cannot be based on orbital energies alone

One way to determine if it is favorable in neutral atoms to fill the s orbital before the d orbital is to consider the energetic cost of moving a 4s electron to 3d orbital.

$$\Delta E(4s \rightarrow 3d) \approx (\epsilon_{3d} - \epsilon_{4s}) + [E_{\text{repulsive}}(3d, 3d) - E_{\text{repulsive}}(3d, 4s)]$$

Difference in the orbital energy

Difference in the repulsive energy of the two configuration

Because the d-electrons are more localized than the s electrons, the repulsive energies follow the order

$$E_{\text{repulsive}}(3d,3d) > E_{\text{repulsive}}(3d,4s) > E_{\text{repulsive}}(4s,4s)$$

For the transition metal series, the magnitude of the difference in the repulsive term is greater than that of the orbital energies.

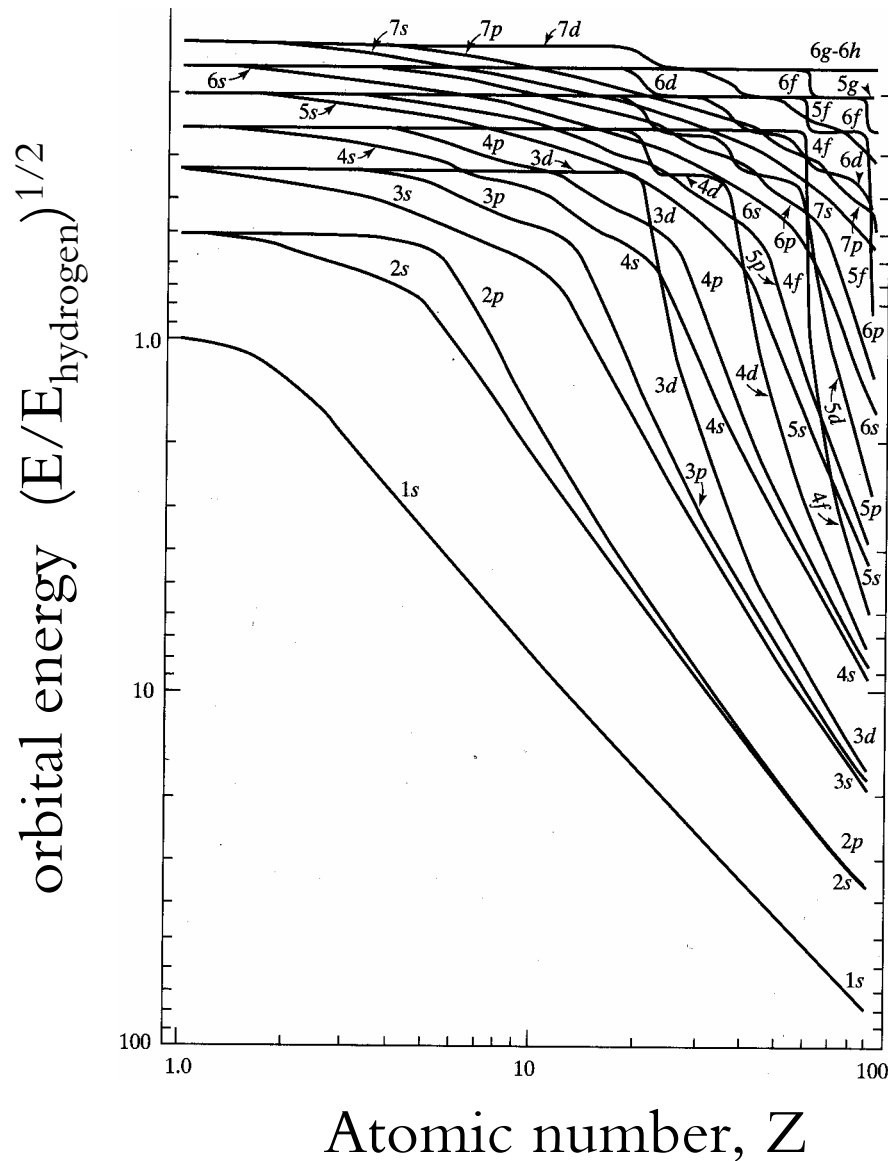
Therefore, the promotion of  $4s^23d^1$  to  $4s^13d^2$  or  $4s^03d^3$  does not occur.

Although  $\epsilon_{4s} > \epsilon_{3d}$  for these elements, the energy lowering from the orbital energy would be more than offset by the energy increase resulting from electron repulsion.

This also explains the seemingly anomalous configurations for the doubly charged ions in the Sc – Zn series:  $[\text{Ar}]4s^03d^n$ , where  $n = 1, \dots, 10$ .

The removal of two electrons significantly increases the effective charge felt by the remaining electrons. As a result, both  $\epsilon_{4s} > \epsilon_{3d}$  are lowered substantially, but  $\epsilon_{3d}$  is lowered more. As a result  $\epsilon_{3d} - \epsilon_{4s}$  becomes more negative, and its magnitude larger than that of the repulsive term.

# Still Hartree-Fock does a pretty good job



Agrees well with experimentally determined orbital energies.