

# Contradictions in the quantum mechanical explanation of the periodic table

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**Abstract.** Quantum theory is thought to explain the periodic law which underlies the periodic table (PT); however, the lengths of the periods remain unexplained. Also, this explanation depends on two empirical rules, namely Madelung's  $n+l$  rule and Hund's rule. Furthermore, even Madelung's rule fails to explain the ground state configuration for many elements. Toward achieving an explanation of the periodic table, the Hartree-Fock (HF) method has been applied in this paper to calculate energies of various possible configurations of transition metals in the fourth and fifth periods. These calculations for Cr, Cu and Ni do not agree with the spectroscopically observed ground state configurations. We further calculated the nonrelativistic and relativistic energies of the various possible configurations of second row transition metals such as niobium, palladium, molybdenum and silver for which Madelung's rule predicts the wrong ground state configuration. In contrast to Cr and Cu, the observed ground state configuration of these elements is found to be associated with the lowest energy by HF calculations.

## 1. Introduction:

The periodic table of the chemical elements graphically displays Mendeleev's periodic law from 1869, which states the following:

"If all the elements are arranged in the order of their atomic weight, a periodic repetition of properties is obtained. This is expressed by the law of periodicity; the properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence on, or (expressing ourselves algebraically) form a periodic function of the atomic weights of the elements." [1]

However this periodic function has the feature that the lengths of the periods increase as atomic weight or atomic number ( $Z$ ) increases. Since the earliest days of Bohr's model of the hydrogen atom, it has been the goal of physicists and chemists to explain this periodic function using quantum theory. But Eric Scerri [2] has argued that the lengths of the periods remain unexplained. The key to explaining the lengths of the periods revolves around explaining why the orbitals fill the way that they do as  $Z$  increases and why a particular orbital configuration is actually the ground state. As a first



approximation, one can employ the *aufbau* principle and the Madelung's  $n+l$  rule for rationalizing the ground state configuration of the chemical elements as the atomic number increases. Still, a number of transition metals such as Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag, Pt, and Au do not have the ground state configuration that one would expect based on this approximation. Furthermore, in spite of a number of attempts, Madelung's rule has not been derived from the principles of quantum theory [3].

Herein, we turn to the Hartree-Fock theory in an effort to explain the ground state configuration of the transition metals.

## 2. Hartree-Fock Theory

The Hartree-Fock theory is based on the following matrix equation which can be derived from the Schrodinger equation using a number of approximations. Let's consider the case of an electron in a closed shell:

$$\mathbf{FC}=\mathbf{SC}\boldsymbol{\varepsilon}$$

where the wave function,  $\psi_i$  for electron 1 is expanded into a set of  $b$  basis functions,  $\chi$ , with coefficients,  $c_{si}$ , and these coefficients form a column matrix,  $\mathbf{C}$ :

$$\psi_i(1) = \sum_{s=1}^b c_{si} \chi_s$$

where the matrix elements,  $F_{rs}$ , of  $\mathbf{F}$  are as follows:

$$\begin{aligned} F_{rs} &= H_{rs} + \sum_{t=1}^b \sum_{u=1}^b \sum_{j=1}^{n/2} c_{tj} c_{uj} [2(rs|tu) - (ru|ts)] \\ (rs|tu) &= \iint \frac{\chi_r(1)\chi_s(1)\chi_t(2)\chi_u(2)}{r_{12}} dv_1 dv_2 \\ (ru|ts) &= \iint \frac{\chi_r(1)\chi_u(1)\chi_t(2)\chi_s(2)}{r_{12}} dv_1 dv_2 \\ H_{rs} &= \int \chi_r(1) \left[ \frac{1}{2} \nabla_1^2 - \frac{1}{r_1} \right] \chi_s(1) dv_1 \end{aligned}$$

and where  $\mathbf{S}$  is the overlap matrix with elements:

$$S_{rs} = \iint \chi_r^* \chi_s dv$$

The total energy was calculated as follows:

$$\begin{aligned} E_{HF} &= \sum_{i=1}^{n/2} \varepsilon_i + \frac{1}{2} \sum_{r=1}^b \sum_{s=1}^b P_{rs} H_{rs} \\ P_{rs} &= \sum_{t=1}^b \sum_{u=1}^b \sum_{j=1}^{n/2} c_{rj} c_{sj} \end{aligned}$$

The HF method consists of starting with a trial basis function (which in the present study was a screened hydrogenic function), trial coefficients ( $\mathbf{C}$ ) and then calculating the matrix elements ( $F_{rs}$ ,  $S_{rs}$ ), orthogonalizing the basis set ( $b=20$  in the present study) and then diagonalizing the Fock matrix,  $\mathbf{F}$ , to obtain the orbital energies,  $\varepsilon_i$  which form  $\boldsymbol{\varepsilon}$ . This sequence is repeated until the coefficients,  $\mathbf{C}$ , of the basis functions converge on specific values.

Vanquickenborne et. al. [5] argued that one must calculate and compare the total energies of the various possible configurations. He performed HF calculations of some transition metal elements in the fourth period, but the various possible configuration of the transition metal elements in the fifth

period have never been examined systematically. There is a recent multiconfigurational Dirac-HF calculation of the various configurations of silver which agrees with experimental observations [6].

### 3. Determination of the ground states of transition metals using HF method

Using Fischer's Hartree-Fock-86 software [7], we first calculated the energies of the fourth period transition metals, and our results agreed with the results of calculations reported in the literature [2,5]. Thus, we did both relativistic and nonrelativistic calculations for three different configurations of Sc, Cr, Cu, Ni:  $3d^x4s^2$ ,  $3d^{x+1}4s^1$  and  $3d^{x+2}4s^0$ . Relativistic calculations were performed using the Breit-Pauli Hamiltonian [7]. For Cr, Cu and Ni, these calculations indicated a ground state configuration which is not in agreement with what is observed.

Then we turned our attention to the transition metals in the fifth period. We were interested to see if similar disagreement would be there for Mo and Ag, which are just below Cr and Cu in the periodic table. Our results are given in Table I. As noted above, Mo, Ag and other fifth period transition metals are observed to have ground state configurations which do not agree with Madelung's rule. In contrast with the results obtained for chromium and copper, our calculations for the elements in the fifth period indicate a ground state configuration which is in agreement with experiment. For example, in the case of Mo, we calculated a total energy of -4042.5323 hartrees for the configuration  $[\text{Kr}]4d^55s^1$  with the

**Table I. Calculation of total energy in hartrees of selected fifth period transition metals**

Element	Configuration	total energy relativistic	total energy nonrelativistic
Mo, Z=42	$[\text{Kr}]4d^45s^2, ^5D$	-4042.4446	-3975.4433
Mo, Z=42	$[\text{Kr}]4d^55s^1, ^7S$	-4042.5323	-3975.5495
Nb, Z=41	$[\text{Kr}]4d^45s^1, ^6D$	-3814.0362	-3753.5977
Nb, Z=41	$[\text{Kr}]4d^35s^2, ^4F$	-3814.0066	-3753.5520
Ru, Z=44	$[\text{Kr}]4d^75s^1, ^5F$	-4523.2092	-4441.5395
Ru, Z=44	$[\text{Kr}]4d^65s^2, ^5D$	-4523.1812	-4441.4873
Rh, Z=45	$[\text{Kr}]4d^85s^1, ^4F$	-4775.7498	-4685.8817
Rh, Z=45	$[\text{Kr}]4d^75s^2, ^4F$	-4775.6972	-4685.8012
Pd, Z=46	$[\text{Kr}]4d^85s^2, ^3F$	-5036.4903	-4937.7830
Pd, Z=46	$[\text{Kr}]4d^95s^1, ^3D$	-5036.5688	-4937.8935
Pd, Z=46	$[\text{Kr}]4d^{10}, ^1S$	-5036.5742	-4937.9210
Ag, Z=47	$[\text{Kr}]5s^14d^{10}, ^2S$	-5305.8197	-5197.6985
Ag, Z=47	$[\text{Kr}]5s^24d^9, ^2D$	-5305.6756	-5197.5179

term symbol,  $^7S$ . In comparison, we calculated that the energy of the configuration,  $[\text{Kr}]4d^45s^2 (^5D)$ , is -4042.4446 hartrees; thus the configuration,  $[\text{Kr}]4d^55s^1$ , is 0.0876 hartree (2.38 eV) lower in energy than  $[\text{Kr}]4d^45s^2$ . These calculations qualitatively agree with spectroscopic observations according to which the configuration  $[\text{Kr}]4d^55s^1$  is lower than  $[\text{Kr}]4d^45s^2$  by 1.53 eV [8].

### 4. Discussion and Conclusions:

It is well known that the HF theory calculates a total energy which is higher than the actual energy because it does not take into consideration instantaneous correlations in the motions of electrons. In this study of the fifth period transition metals, HF theory is able to correctly calculate the ground state

configuration but only in a qualitative way. In some cases the difference in energies of the various possible configurations is very small; hence an extremely accurate method is needed to correctly calculate the total energy and hence make a statement about what is the ground state configuration.

At a more general level, Eric Scerri [9] has expressed dissatisfaction with the level of explanation provided by HF theory or post-HF theories:

“Can the experimentally observed first configuration be predicted from first principles by quantum mechanics? No. In fact, all that quantum mechanical calculations do is compute which of these three configurations has the minimum energy. That is not the same as deriving the correct configuration from first principles.”

Even the picture of electrons occupying specific orbitals and having a particular configuration cannot be envisioned. An orbital is only a mathematical abstraction, and one cannot speak of an electron following any trajectory in spite of the fact that the theory formally has a variable,  $r$ , for the distance of the electron from the nucleus. Another point is that the wave function for the atom is actually a superposition of spin orbitals. For example, in the case of the lithium atom, the wave function is the following determinant (called a Slater determinant):

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(2) & 2s(3)\alpha(3) \end{vmatrix}$$

where  $1s(1)$  represents the product of a radial function and spherical harmonic function and where electron 1 can have the spin function,  $\alpha(1)$  or  $\beta(1)$ . In considering these determinantal wave functions, Slater [10] has remarked that “. . . it makes no sense to say that one particular electron occupies one particular spin-orbital.” It is well known that quantum theory presents a challenge to classical realism even at the macroscopic level, and macroscopic quantum mechanics has become an active area of contemporary research [11]. Gomatam [12] has outlined a novel way to move toward a macroscopic quantum mechanics that is compatible with a non-classical macrorealism.

## 5. References

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