Ionization Energies, Parallel Spins, and the Stability of Half-Filled Shells

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I. Trends in Ionization Energies

The variation in the ionization energies of the elements is often used as an example of the periodicity of atomic properties as a function of atomic number. When the first ionization energy is plotted against atomic number for the first 19 elements (Fig. 1) an obvious pattern appears. Ionization energy tends to decrease down a group and to increase across a period. It is generally agreed that these two trends arise from the following two effects:

1. Down a group, although the nuclear charge is increasing, the amount of shielding of the ionizing electron from the nuclear charge by inner shell electrons is also increasing, so keeping Z_{eff} (the effective nuclear charge) much more constant than one might expect. The distance between the ionizing electron and the nucleus is increasing, however, and so the overall attraction of the nucleus for the ionizing electron is lessened.
2. Across a period, the increasing nuclear charge is accompanied by only a small increase in shielding. The number of inner shells is constant, and electrons in the same (outermost) shell as the ionizing electron are not effective in their shielding, in that they do not interpose themselves between the electron in question and the nucleus. Thus the net attraction between the ionizing electron and the nucleus increases. (Superimposed on this are two second-order effects that work in opposite directions: (i) because the increasing nuclear charge pulls *inner* shells closer to the nucleus, penetration by outer shell electrons is less effective; the shielding potential of inner shells therefore increases slightly across the period, *decreasing* the ionization energy; however (ii) increasing nuclear charge also contracts the *outer* shell, bringing the ionizing electron closer to the nucleus, and *increasing* the attractive force.)

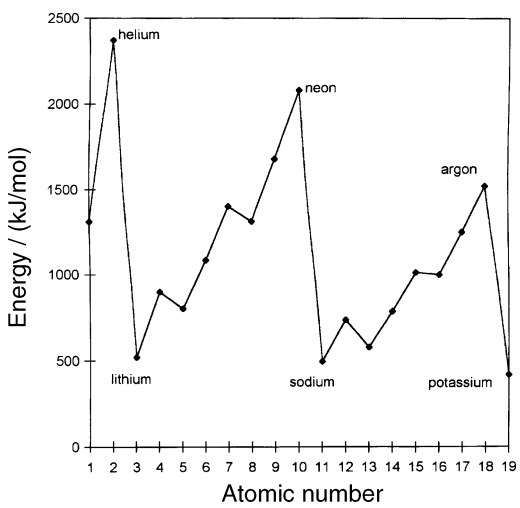

Figure 1. First ionization energies of the first 19 elements.

The increase in ionization energy across a period is not a regular trend. Discontinuities occur between groups II and III and between groups V and VI. The former is associated with the start of the occupancy of the *n*p orbitals. An electron in these orbitals is, on average, slightly farther from the nucleus than an electron in a *n*s orbital. More importantly, because the nodal plane of a p orbital passes through the nucleus (and hence there is zero probability of finding a p electron there), electrons in *n*p orbitals are more shielded from the nuclear charge than are electrons in *n*s orbitals, which have a significant positive electron density at the nucleus. Thus p electrons experience less nuclear–electron attraction.

II. Three Possible Explanations for the Group V/Group VI Discontinuity

The discontinuity between groups V and VI has been ascribed to various causes, some of which are more easily rationalized than others. Three major reasons can be found in textbooks:

A. In a shell having more than half its complement of electrons, one (or more) orbitals has to accommodate two electrons. These two electrons, sharing the same region of space, will experience an extra repulsion from each other over and above that experienced by electrons in separate orbitals (*1–3*).

B. Because of the Pauli exclusion principle, electrons with parallel (unpaired)[1] spins tend to avoid each other, thus decreasing the electrostatic repulsion between them. This will be the situation when filling the first half of the shell. When electrons are forced to doubly occupy orbitals in the second half, their spins are constrained to be paired (antiparallel).[2] Because they are no longer obliged to avoid each other, the electrostatic repulsion increases (*4*). This treatment is similar to the previous one but involves a spin factor as well as a distance factor.

C. Half-filled (and also completely filled) subshells of electrons have an intrinsic stability (*5, 6*).

The rest of this paper describes in detail and comments upon these three methods that have been used to explain the shape of the ionization energy–atomic number curve in this region.

If it were not such a commonly held view,[3] the third of these reasons could be dismissed without further comment, as it offers no *explanation* in terms of electrostatic or quantum mechanical interactions within the atom. Its justification seems to come from the desire to explain the observation that the ionization energy of a p^3 (or p^6) system is larger than that of the systems on either side (p^2 and p^4, or p^5 and s^1). The implication is that this ionization energy is higher than one might have expected, based on the assumption of a baseline drawn through the two adjacent values (see Fig. 2).

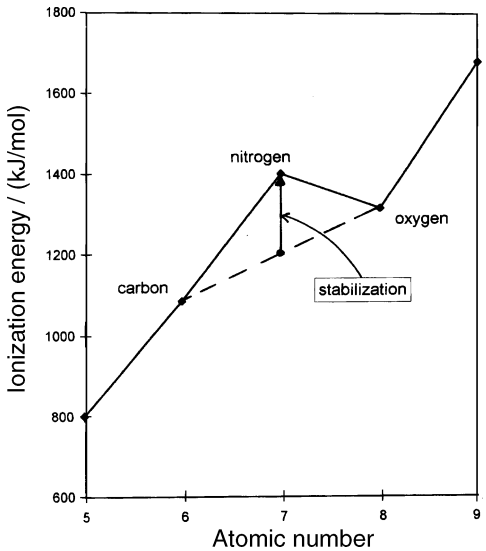

Figure 2. The "stabilization" of nitrogen.

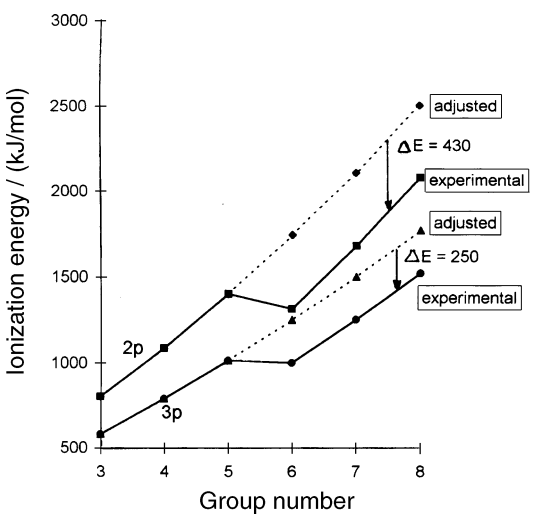

Figure 3. First ionization energies of the 2p and 3p blocks.

Table 1. Energy Calculations for Various p^n Configurations

No. of p Electrons	Sum of p_xp_y Repulsion Energies	Sum of p_xp_x Repulsion Energies	Total Inter-electron Repulsion Energy (E_{tot})	Loss of Inter-electron Repulsion on Ionization (δE)[a]
1	0	0	0	0
2	A	0	A	A
3	$3A$	0	$3A$	$2A$
4	$5A$	$A + B$	$6A + B$	$3A + B$
5	$8A$	$2A + 2B$	$10A + 2B$	$4A + B$
6	$12A$	$3A + 3B$	$15A + 3B$	$5A + B$

[a] $\delta E = E_{tot}(p^n) - E_{tot}(p^{n-1})$.

A more sophisticated treatment in terms of exchange energy (*5*), which also suggests that p^3 and p^6 systems have a special stability, is described later (method C).

As mentioned in section I, the initial expectation should be that the ionization energies increase regularly across a period owing to the increase in Z_{eff}. The increase from group III to group V is, in fact, fairly regular. So also is the increase from group VI to group VIII, but displaced downwards by 430 kJ mol^{-1} for the second period and 250 kJ mol^{-1} for the third period (see Fig. 3). Thus, rather than interpret Figure 1 in terms of the ionization energy of nitrogen being *larger* than expected, we should use Figure 3 to suggest than the ionization energy of oxygen, and also of fluorine and neon, is *less* than expected, by a constant amount for each. It is to the origin of this constant drop, ΔE, that we now turn.

III. Method A: Coulombic Repulsion between Electrons in the Same Orbital

Of the three reasons given in section II, the first, A, is the easiest to understand. We are aware that the electrostatic repulsion energy between two electrons is given by the formula $E_{rep} = e^2/4\pi\varepsilon_0 r_{12}$, where r_{12} is the average distance between the electrons. Electrons sharing the same orbital will, on average, be closer together than electrons in separate orbitals. Although the repulsions between all the electrons in the p-shell will increase with the number of electrons, we expect an extra jump in the electrostatic repulsion when orbital sharing starts. If we call the general p_xp_y (different orbital) repulsion energy A, the p_xp_x (same orbital) repulsion energy will be larger than this, by an amount we can call B. The total p_xp_x (same orbital) repulsion energy will thus be $A + B$. We can now calculate the total interelectron repulsion energies for various p^n configurations, and also the loss in repulsion on ionization (Table 1). As we go across the p-group, the energy required for ionization will increase because of the increasing Z_{eff}, but not as much as we might expect, owing to the increasing loss of electron–electron repulsion on ionization (last column in Table 1). This is illustrated in Figure 4.

Thus we can identify the ΔE in Figure 3 and the y in Figure 4 with B, the *extra* electrostatic repulsion between same-orbital electrons. We might expect this to be less for electrons sharing the 3p orbitals because these are larger and more diffuse than the 2p orbitals. On average, two electrons in the same 3p orbital should be further apart and experience less electrostatic repulsion. This is in fact found to be the case: ΔE (3p) < ΔE (2p) (see Fig. 3).

Note that apart from the Pauli stipulation that electrons sharing the same orbital must have opposite spins, the relative spins of the electrons have not been considered in this treatment.

IV. The Parallel Spin Avoidance Factor

The second reason given in section II for the decrease in ionization energy from group V to group VI concerns itself with the different interactions that occur between electrons with parallel and paired spins. The basis for these different interactions is the quantum mechanical antisymmetry requirement, from which can also be deduced the Pauli exclusion principle.

Without delving too deeply into the quantum mechanics of the situation (which can cloud the issue for those who, like me, are not experts in the field), it might appear that the property of electrons with parallel spins tending to avoid each other is almost as mysterious a concept as the supposed half-shell stability mentioned in section II. A complete picture of the situation can be found in books on quantum mechanics (e.g., ref *9*), but the following is offered as a simplified summary.

The total wave function of a system of electrons is made up of two parts: the *space component* of the wave function describes how the behavior of the system depends on the spatial coordinates of the particles, and the *spin component* of the wave function describes how it depends of the spin of each electron.[4] Consider the simplest case of two electrons, labeled (1) and (2), occupying two different orbitals on an atom (represented by wave functions ψ_A and ψ_B). Using these wave functions, we can create new space-component wave functions that will describe the behavior of the new two-electron system. We find that the quantum mechanical requirements of orthogonality, electron indistinguishability, and normalization are satisfied by the following two combinations of ψ_A and ψ_B:

$$\psi_s = (1/\sqrt{2})[\psi_A(1)\psi_B(2)] + (1/\sqrt{2})[\psi_A(2)\psi_B(1)]$$

and

$$\psi_a = (1/\sqrt{2})[\psi_A(1)\psi_B(2)] - (1/\sqrt{2})[\psi_A(2)\psi_B(1)]$$

We now introduce the property of electron spin, and the (Pauli) antisymmetry requirement, which states that *the total wave function must be antisymmetric to the exchange of electrons*. (By antisymmetric, we mean that the total wave function (i.e., including its space and its spin components) should change sign if we substitute electron (2) for electron (1), and vice versa.) If we carry out this operation on the above space-component wave functions, we find that ψ_s does *not* change sign when electrons (1) and (2) are exchanged, whereas ψ_a *does*. The total (space + spin) wave functions are obtained by combining ψ_s and ψ_a with the spin-component functions of the two electrons. Electrons with paired spins have spin-component functions of the *opposite* sign associated with them (σ_+ and σ_-), whereas electrons with parallel spins have spin-component functions of the *same* sign associated with them (either σ_+ and σ_+, or σ_- and σ_-). By inspection, we can deduce that two electrons occupying the state described by ψ_s must have *paired* spins (so that their spin-component wave functions will change sign on exchange), and the two electrons occupying the state described by ψ_a must have *parallel* spins (so that their spin-component wave functions will *not* change sign on exchange). Only by this means will the antisymmetry principle be adhered to.

The significance of this is that we can use the functions ψ_a and ψ_s to calculate the probability of finding each electron at a radius, *r*, from the nucleus, using the relationship

$$P_r = 4\pi r_1^2 \cdot 4\pi r_2^2 \cdot \psi_{A/B}^2$$

Linnett (*10*) plotted P_r for both functions for the case of two s orbitals, and obtained Figure 5. For ψ_a, the parallel spin case, this has a nodal surface along the line $r_1 = r_2$, implying *zero probability of finding the two electrons at the same distance from the nucleus*. By contrast, for ψ_s, the paired spin case, there is a *higher* probability of finding the two electrons at *certain*

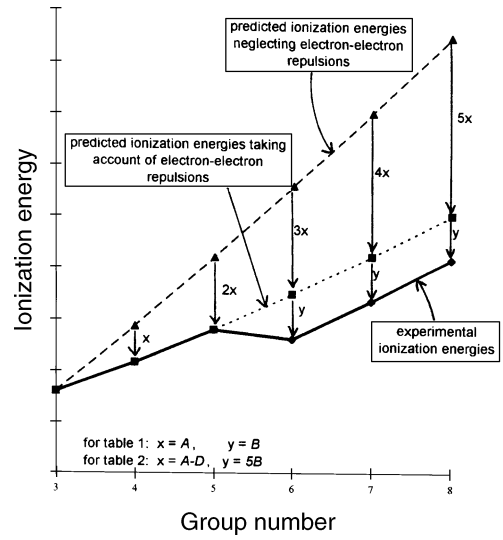

Figure 4. Explanations for the experimental ionization energies.

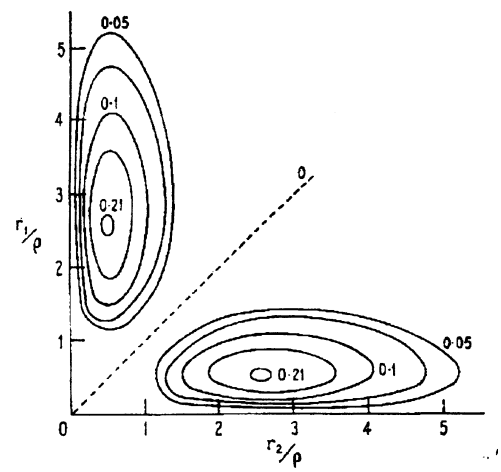

Figure 5a. Plot of P_r as a function of r_1 and r_2 for the parallel spin state of He ($1s^12s^1$) (the antisymmetric wave function ψ_a).

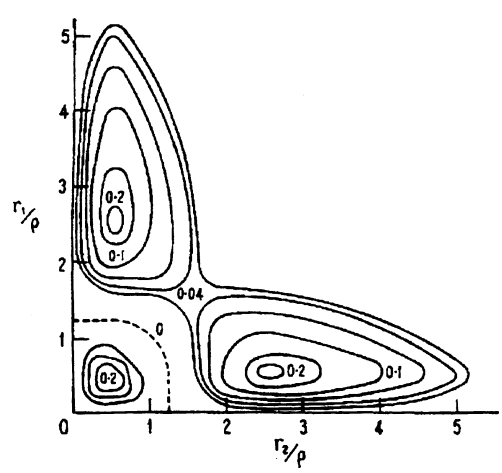

Figure 5b. Plot of P_r as a function of r_1 and r_2 for the paired spin state of He ($1s^12s^1$) (the symmetric wave function ψ_s) (from J. W. Linnett, Wave Mechanics and Valency, Methuen, 1960, p 74)

Table 2. Results of Blake's Calculations (*14*)

No. of p Electrons	Total Coulombic Energy	Total "Exchange" Energy	Total Interelectron Repulsion Energy (E_{tot})	Loss of Interelectron Repulsion on Ionization (δE)[a]	Loss of Interelectron Repulsion in Terms of ($A-D$)
1	0	0	0	0	0
2	A	$-D$	$A-D$	$A-D$	$(A-D)$
3	$3A$	$-3D$	$3A-3D$	$2A-2D$	$2(A-D)$
4	$6A+2D$	$-3D$	$6A-D$	$3A+2D$	$3(A-D)+5D$
5	$10A+4D$	$-4D$	$10A$	$4A+D$	$4(A-D)+5D$
6	$15A+6D$	$-6D$	$15A$	$5A$	$5(A-D)+5D$

[a] $\delta E = E_{tot}(p^n) - E_{tot}(p^{n-1})$.

similar distances from the nucleus (0.5 au in this example). A similar argument can be applied to the p_xp_y case.

Electrons with parallel spins do not physically repel each other any more (or less) than electrons with paired spins (the Coulombic repulsion would be the same for both, if they were separated by the same distance). But because their spatial behavior is described by the antisymmetric wave function ψ_a, the probability of finding two parallel-spin electrons close to each other is much less than is the case with two electrons whose spins are paired, whose spatial behavior is described by the symmetric wave function ψ_s. This lack of same-spin electron density around an electron is called a Fermi hole (*11*), and the mutual avoidance can be predicted to have two effects on the energy of the system: (i) the electrostatic repulsion between parallel-spin electrons should be reduced, and (ii) each electron in a parallel-spin assembly is shielded from the nucleus *less* by its neighbors than is the case with paired electrons.

Each of these effects helps to stabilize a collection of electrons whose spins are parallel. The phenomenon goes by various names: exchange energy, Pauli repulsion energy, spin correlation energy. It is not, though, an energy as such. Rather, it is a factor that can affect the electrostatic energy of the system by the mechanisms described. Perhaps a better term would be "parallel spin avoidance factor".

Strangely, calculations by Boyd (*12*) show that the electrostatic repulsion between parallel-spin electrons is in fact slightly *greater* than that between paired electrons. He therefore suggests that the decrease in the system's energy is entirely due to the increased attraction between the paired electrons and the nucleus.

V. Method B: The Combination of Coulombic Repulsion with the Parallel Spin Avoidance Factor

The treatment described in section III can be extended by incorporating the concept of parallel spin avoidance. Blake (*14*) has performed calculations on both the p^n and d^n systems, which yield values for the Coulomb and "exchange" parts of the electrostatic energy. If we denote the Coulomb repulsion between two electrons in different 2p orbitals by A, as in section III, and the extra repulsion due to their occupancy of the same orbital by $2D$ (this equates to the B of section III), Blake calculates that the exchange energy benefit between two electrons with parallel spins is equal to D. In other words, the reduction of electrostatic repulsion due to parallel spin avoidance in separate 2p orbitals is *half* the extra electrostatic repulsion due to two (paired) electrons sharing the same 2p orbital. His results for the p^n system are shown in Table 2.

This treatment identifies the ΔE in Figure 3 (and the y in Fig. 4) with the value of $5D$, of which $2D$ (40%) comes from "classical" same-orbital repulsion and $3D$ (60%) from "exchange energy". We also identify the constant increment, x, in the electron repulsion (see Fig. 4) with $(A-D)$ rather than with the A in section III. However, when a different set of wave functions is used for the 2p orbitals, Blake's calculations suggest that ΔE is composed of only 20% same-orbital repulsion, and 80% exchange energy. Lennard-Jones and Pople also noted that the relative values of the Coulomb and exchange contributions depended markedly on the form of orbitals they chose for their calculations (*15*). This dependence on seemingly arbitrary assumptions of orbital mix has led some non-quantum chemists to question the reality of exchange energy and the validity of its use in explaining electronic configurations.

VI. Method C: The Stabilizing Effect of Parallel Spins

Sharpe considers that electrons with parallel spins take an *active* role in stabilizing the atom (*13*). His treatment divides the interelectronic energy into two parts: (i) the destabilizing electron–electron repulsions of magnitude $+A$ per two-electron interaction (irrespective of whether the electrons are in the same orbital or different orbitals), and (ii) the *stabilizing* exchange energy between electrons with parallel spins of magnitude $-K$ per two-electron interaction.

This treatment produces the following equation for the change in interelectronic repulsive energy (δE) on ionization:

$$\delta E = (n-1)A - \delta mK$$

where n is the number of p electrons, and δm is the decrease in the number of possible pairs of spin–spin interactions.

Using this equation, a table similar to Table 2 can be drawn up (Table 3). This relationship is illustrated in Figure 6, and the interpretation is as follows: As we go across the p-group, the increase in ionization energy as Z_{eff} increases will be lessened owing to the increasing loss of electron–electron repulsion on ionization (the factor A). This still results in a (small) net steady increase of ionization energy with atomic number (the line ABC in Fig. 6). But for some elements the increase will be *greater*, owing to the loss in stabilization energy (K or $2K$) on ionization. This loss will be greatest for the p^3 and the p^6 cases. In this treatment may be seen the origin of the suggested extra stability of half-filled and filled shells. But the treatment is somewhat misleading, and is also based on an incorrect assumption.

It is misleading in that it suggests that the interaction between electrons of the same spin *stabilizes* a system. This stabilization, however, is only with respect to a (hypothetical) system that has no spin interactions at all. A fuller account might describe a parallel-spin interaction as causing the usual electron–electron repulsion to be *less destabilizing* than expected, owing to the mutual avoidance of the electrons involved.

Its incorrect assumption is that electrons in the same orbital repel each other to the same extent as electrons in different orbitals. Calculations and observations (for example, the progression from high-spin to low-spin configurations on

increasing the strength of the ligand field in transition metal complexes) suggest that double occupancy of an orbital involves more electrostatic repulsion than single occupancy.

VII. Conclusions

All three methods of calculating interelectron repulsions, either including (methods B and C) or not including (method A) the parallel spin avoidance factor and either ignoring (method C) or taking into account (methods A and B) the extra repulsion due to dual occupancy of the same orbital, predict exactly the same shape for the ionization energy–atomic number curve for the $2p^n$ and, by analogy, the $3p^n$ cases. Method C suggests the p^3 or p^6 configurations have a particular stability, whereas the other two do not. Calculation of the exact values for the terms *A*, *B*, *D*, and *K* would enable decisions to be made about which method's results correspond most closely to the experimental values, but the essential parameters are difficult to measure. Oversimplification of the quantum mechanical arguments involved in taking account of the parallel spin avoidance factor seems often to have led to generalizations that can all too easily be interpreted somewhat simplistically and incorrectly.

Conceptually, the approach involving the neglect of the parallel spin avoidance factor (method A) is easier for the pre-university student, who is not versed in quantum mechanics, to comprehend. It is therefore recommended that, at the sixth form/high school stage and also for university students who are not exposed to quantum mechanics, this interpretation be adopted. It is also the most economical theory in terms of the models it uses and the assumptions it makes, and, in the context described, its predictions are no less accurate than those of more sophisticated theories.

Finally, note that a similar treatment can be applied to the *third* ionization energies of the 3d group of transition metals[5] (see Fig. 7). These M^{2+} ions have the d^n configuration (n = 1–10). $\Delta E'$ in Figure 7 (500 kJ mol^{-1}) can be identified either with B' (the extra repulsion that two d electrons experience due to their double occupancy of the same orbital) in the treatment of method A, or with a similar constant to the $5D$ of method C. Blake calculates $\Delta E'$ to be equal to $7D'$, taking the double-occupancy repulsion as equaling $2D'$.

Acknowledgments

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Notes

1. The terms *parallel* and *unpaired* both refer to electrons whose spin vectors are in the same direction. To avoid duplication, in this article they will be referred to as *parallel* spins.

2. Likewise, the term *paired* will be used for electrons whose spin vectors are in opposite directions.

3. Papers by Duke (*7*) and Rich (*8*) comment on this misconception.

4. Like the Born–Oppenheim treatment, which allows us to separate for example electronic, vibrational, and translational en-

Table 3. Calculations Based on Sharpe's Treatment (*13*)

No. of p Electrons	Sum of p_xp_y Repulsion Energies	No. of Pairs of Parallel Spins (m)	Total Inter-electron Repulsion Energy (E_{tot})	Loss of Inter-electron Repulsion on Ionization (δE)[a]
1	0	0	0	0
2	A	1	$A - K$	$A - K$
3	$3A$	3	$3A - 3K$	$2A - 2K$
4	$6A$	3	$6A - 3K$	$3A$
5	$10A$	4	$10A - 4K$	$4A - K$
6	$15A$	6	$15A - 6K$	$5A - 2K$

[a] $\delta E = E_{tot}(p^n) - E_{tot}(p^{n-1})$.

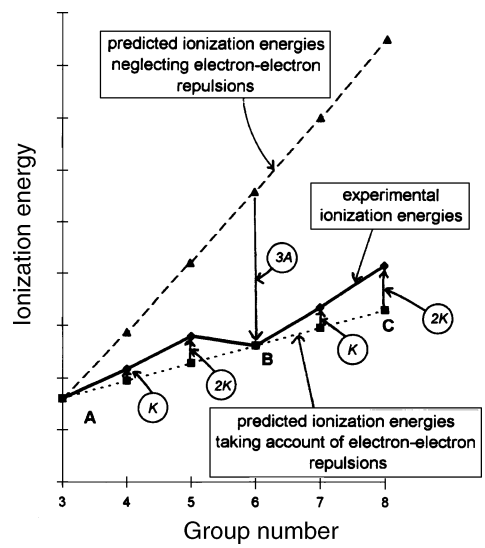

Figure 6. Stabilization by parallel spins.

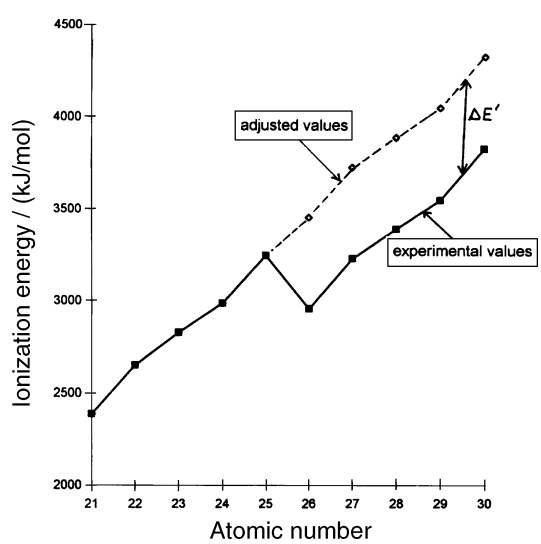

Figure 7. Third ionization energies of the 3d block.

ergies from each other and consider them in isolation, the Pauli treatment of quantum mechanics allows us to factorize ψ_{total} into a product $\psi_{space} \cdot \psi_{spin}$. But as the atom gets larger and the electrons move at close to relativistic speeds, this separation is no longer valid. The Dirac treatment, taking account of relativistic effects, is more appropriate for heavier atoms. It arrives naturally at four quantum numbers, of which the fourth can be associated with the electron's spin.

5. For the reasons given in endnote 4, this treatment is not appropriate for the later transition metal groups.

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