

An Interpretation of Hund's Rule^{*}

J. KATRIEL

Department of Chemistry, Nuclear Research Centre – Negev, P.O.B. 9001, Beer Sheva, Israel

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An interpretation of Hund's rule is presented. The Pauli principle, the variational principle and the virial theorem are shown to be essentially sufficient to account for the roles of the various energetic components in establishing the inter-multiplet separation.

Es wird eine Interpretation der Hund'schen Regel gegeben. Das Pauliprinzip, das Variationsprinzip und das Virialtheorem sind im wesentlichen ausreichend, um die Rollen der verschiedenen energetischen Komponenten beim Zustandekommen der Inter-Multiplett-Separation zu erklären – wie hier gezeigt wird.

1. Introduction

It has been obvious since the early days of quantum mechanics that Hund's rule is closely related to the Pauli principle and should be interpreted in terms of it. The conventional interpretation consists of invoking the Pauli principle to argue that electrons with parallel spins tend to stay further away and therefore repel each other to a lesser extent than electrons with antiparallel spins. The observation made by Davidson [1], Lemberger and Pauncz [2] and Messmer and Birss [3] that in some atomic systems the interelectronic repulsion is higher in the higher multiplicity terms corresponding to a given configuration than in the lower multiplicity terms, has disproved this interpretation. A further analysis [4] resulted in the following conjectures, which are more rigorously established in what follows:

1) The nuclear attraction is always higher in absolute value in the higher multiplicity term. For highly positive atomic ions the interelectronic repulsion is lower in the higher multiplicity term. It may, and usually will, become higher in the higher multiplicity term of the isoelectronic neutral atom.

2) The energy difference between different multiplicity terms is always mainly due to differences in the nuclear attractions and not in the interelectronic repulsions.

A preliminary study of the electronic pair distribution [5] exhibited a dramatic reversal of the commonly expected behaviour. The statement that electrons with parallel spins stay mostly further away than electrons with anti-parallel spins was shown not to apply to light neutral atoms.

A quantum mechanical interpretation of Hund's rule is presented in the concluding section of the present contribution. The energetic ordering of different multiplicity terms is rigorously derived within the Hartree-Fock approximation.

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The disturbing observations concerning the roles of the nuclear attraction and of the interelectronic repulsion are accounted for. A study of the electronic pair distribution and of the role of inner shell electrons precedes the final interpretation and constitutes an essential part of the motivation towards it.

2. The Electronic Pair Distribution

The $(1s, 2p)^{1,3}P$ terms of the He isoelectronic sequence have been studied within the independent particle model with the orbitals represented by linear combinations of Gaussian functions.

$$\phi_{1s} = \sum_{i=1}^N C_i e^{-\alpha_i r^2}; \quad \alpha_i = \alpha \varepsilon^{i-1},$$

$$\phi_{2p} = x \cdot \sum_{i=1}^N D_i e^{-\beta_i r^2}; \quad \beta_i = \beta \delta^{i-1}.$$

The four nonlinear parameters $\alpha, \beta, \varepsilon, \delta$ have been independently optimized for each term, as well as the $2N$ linear coefficients. The results for He are presented in Table 1. An analysis of the high Z behaviour of the parameters is carried out in Fig. 1 for the Gaussian approximation ($N=1$). Each one of the parameters satisfies the asymptotic relation $\eta = Z^2(\eta_0 + \eta_1/Z)$ such that η_0 is the same for both the triplet and the singlet and the difference arises because of η_1 . The asymptotic values of α and β are just the values obtained by Reeves [16] for the $1s$ and $2p$ orbitals of the hydrogen atom. This is in agreement with the perturbation theoretic results which are constructed so that the zero order wavefunctions are the appropriate combinations of the products of unscreened hydrogenic orbitals. The $2p$ orbital is noted to possess a larger parameter in the triplet than in the singlet. It is thus spatially more contracted towards the nucleus. The reverse situation is observed for the inner $1s$ orbital. This observation is in agreement with Eckart's hydrogenic orbital calculations [7] as well as with analogous results in other atoms [2, 4]. The origin of this behaviour and its fundamental significance will be discussed in the concluding section.

A closer observation is enabled by evaluating the pair distribution function $\varrho(r'_{12}) = \langle \Psi | \delta(r_{12} - r'_{12}) | \Psi \rangle$ or rather the pair distribution difference $\Delta(r_{12}) = {}^3\varrho(r_{12}) - {}^1\varrho(r_{12})$. The latter function is plotted in Fig. 2 for $N=2, 3, 4, 5$.

Table 1. Independent particle model results for $1,^3P$ He

N	Energy		Nuclear attraction		Electronic repulsion	
	Triplet	Singlet	Triplet	Singlet	Triplet	Singlet
2	-2.06991	-2.06491	-4.39798	-4.37138	0.25817	0.24156
3	-2.11317	-2.10577	-4.49061	-4.45446	0.26428	0.24293
4	-2.12591	-2.11750	-4.51737	-4.47843	0.26554	0.24343
5	-2.12947	-2.12074	-4.52492	-4.48502	0.26598	0.24355
∞^a	-2.13143	-2.12246			0.2661	0.2436

^a Ref. [1].

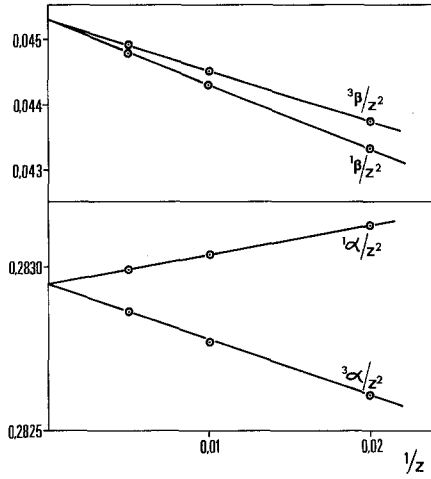


Fig. 1. Asymptotic behaviour of the parameters in the Gaussian approximation

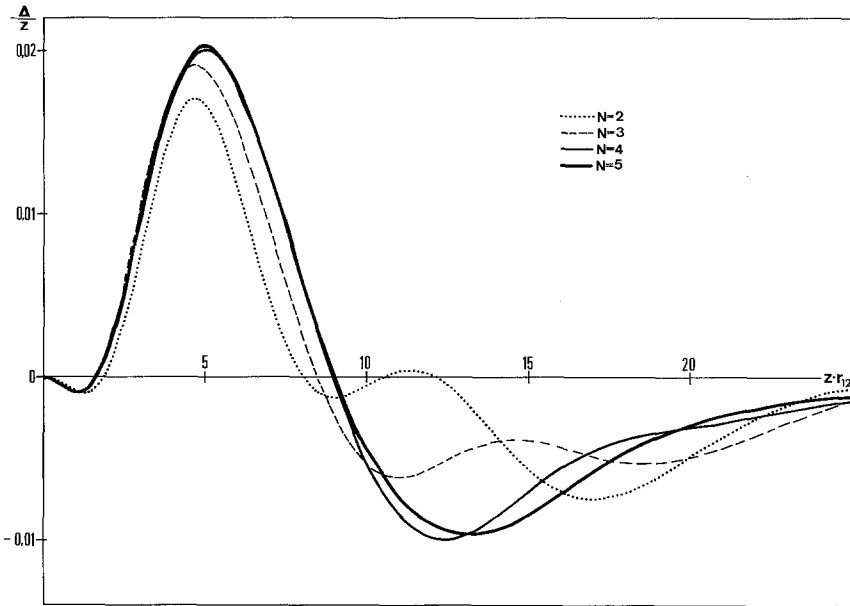


Fig. 2. The pair distribution difference for the ${}^3P - {}^1P$ terms of He

Preliminary results for $N = 1$ have recently been reported [5]. The results are noted to have practically converged for $N = 5$, which therefore essentially represents the Hartree-Fock limit. They indicate that the conventional assertion according to which parallel spin electrons keep further apart than antiparallel spin electrons does not properly describe the situation studied. It still is true that parallel spin electrons, as a consequence of the Pauli principle, do not come close

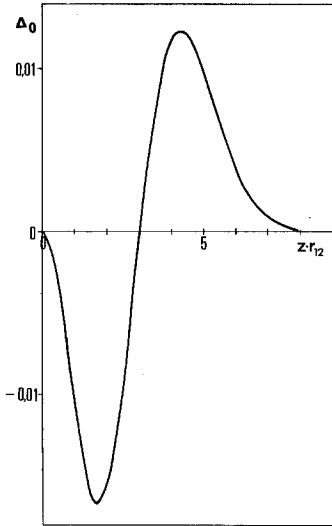


Fig. 3

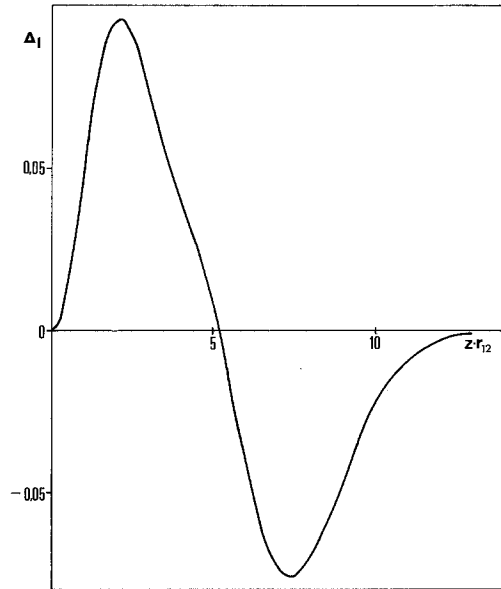


Fig. 4

Fig. 3. The zero order component of the pair distribution difference for the ${}^3P - {}^1P$ terms of the He isoelectronic sequence, in the Gaussian approximation

Fig. 4. The first order component of the pair distribution difference for the ${}^3P - {}^1P$ terms of the He isoelectronic sequence, in the Gaussian approximation

together, but the extrapolation from the local behaviour at $r_{12} \approx 0$ to the whole of space is totally misleading. It has already been observed [5] that for the highly positive isoelectronic ions the pair distribution difference obtains the shape conventionally deduced from the Pauli principle. The asymptotic behaviour of the variational wavefunction as well as the perturbation theoretic expansion suggest that the asymptotic form of the pair distribution difference is

$$\Delta(r_{12})/Z = \Delta_0(r_{12}) + (1/Z) \cdot \Delta_1(r_{12})$$

where $r_{12} = Z \cdot r_{12}$.

$\Delta_0(r_{12})$ represents the pair distribution difference obtained with equal un-screened orbitals for the singlet and the triplet whereas Δ_1 represents the first order correction. Comparing the relation

$$\Delta C = \int_0^{\infty} \Delta(r_{12}) dr_{12}/r_{12} = Z \cdot \int_0^{\infty} \Delta_0(r_{12}) dr_{12}/r_{12} + \int_0^{\infty} \Delta_1(r_{12}) dr_{12}/r_{12}$$

with the perturbation theoretic expression $\Delta C = \alpha(Z - 2Z_0)$ one obtains

$$\int_0^{\infty} \Delta_0(r_{12}) dr_{12}/r_{12} = \alpha < 0 \quad \text{and} \quad \int_0^{\infty} \Delta_1(r_{12}) dr_{12}/r_{12} = -2\alpha Z_0 > 0.$$

From the normalization of the pair distributions it follows that $\int_0^\infty \Delta_0(r_{12}) dr_{12} = 0$ and similarly for $\Delta_1(r_{12})$. $\Delta_0(r_{12})$ is therefore necessarily negative at low r_{12} and positive at higher separation, in accordance with the Pauli principle. This is just the behaviour expected for a pair distribution difference constructed with equal orbitals for both terms. $\Delta_1(r_{12})$ is just reversed, being positive at low interelectronic separations and negative at high ones. The results of a numerical analysis of high Z values of the pair distribution difference in the Gaussian approximation are plotted in Figs. 3 and 4. The qualitative agreement with the discussion just made is entirely satisfactory. The reversal in the interelectronic repulsion as well as in the values of $\langle r_{12} \rangle$ and $\langle r_{12}^2 \rangle$ [5] is therefore accounted for by the first order term in the pair distribution difference. The conventional argument is correct only to zeroth order and therefore fails as the first order correction becomes important, namely at sufficiently high values of the perturbation parameter $1/Z$ (sufficiently low Z).

3. The Role of the Inner Shells

In all the systems hitherto considered in connection with the interpretation of Hund's rule there are at least two occupied major shells. A different situation occurs in autoionizing configurations such as $(2s, 2p)$ and $2p^2$. It has been shown [4] that independent scaling of the wavefunction is sufficient to associate most of the energetic difference between the different multiplicity terms with nuclear attraction rather than with interelectronic repulsion differences. Scaling has further been shown to be incapable of reversing the order of interelectronic repulsions. Independent optimization of the parameters, even with a minimal basis set of Slater or Gaussian functions, is sufficient to give rise to this reversal in those cases in which it is observed in more accurate computations. The discussion in the previous section indicated that the reversal of interelectronic repulsions is due to the first order correction to the wavefunction, in a perturbation theoretic approach. This correction is asymptotically similar to that obtained by variationally optimizing a wavefunction constructed of Slater orbitals which in the limit $Z \rightarrow \infty$ becomes identical with the zero order wavefunction in perturbation theory. The fact that optimized Slater orbital computations lead to the correct qualitative conclusions concerning the relative magnitudes of interelectronic repulsions is thus fairly established. For configurations with only one shell occupied, such as $2p^2$ and essentially also $(2s, 2p)$ there is only one variational parameter in the minimal basis set, and therefore complete optimization is equivalent to simple scaling. For such configurations no reversal of the order of interelectronic repulsions can be effected by the independent optimization of the parameter within the minimal basis set scheme. In view of the comments just made this is sufficient to exclude such reversal even in accurate computations.

Approximate perturbation expansions of the Hartree-Fock solutions for the terms derived from the $2p^2$ configuration of the He isoelectronic sequence are available [8]. The interelectronic repulsion contribution can be obtained by application of the Hellmann-Feynman theorem. The reversal is easily noted

not to occur for $Z > 1$. It therefore seems that the reversal of interelectronic repulsions is closely related to the interrelationship between an inner and an outer shell.

4. An Interpretation of Hund's Rule

A theoretical interpretation of Hund's rule should account for the energetic order of terms corresponding to a given configuration. It should also, desirably, account for the roles of the various energetic components and for the characteristic qualitative features of the wavefunctions corresponding to the different terms.

The energetic aspect of Hund's rule is accounted for as follows. Consider two terms belonging to a certain configuration. For the lower multiplicity term we obtain the best wavefunction within the independent particle model. We shall use the one electron orbitals thus obtained to construct an approximate wavefunction for the higher multiplicity term. The energy corresponding to this wavefunction differs from that of the lower multiplicity term only in the interelectronic repulsion. Due to the Pauli principle, the interelectronic repulsion is lower for the higher multiplicity term if the same one electron orbitals are used. The orbitals are already optimized for the lower multiplicity term, but they may be further improved for the higher multiplicity term. Due to the variational principle this improvement of the orbitals can only lower the energy and thus increase the intermultiplet separation. It is thus shown that within the independent particle model (Hartree-Fock approximation) the higher multiplicity terms is lower in energy, in accordance with Hund's rule. The energetic order is therefore a straightforward consequence of the Pauli principle. The conventional reasoning is an essential part of the argumentation just made. It is incorporated in the particular sequence of arguments in such a way as to provide, in conjunction with the variational principle, a generally valid prediction of the ordering of terms, within the Hartree-Fock approximation. This would have constituted an improvement even if no difficulties had been noted with respect to the conventional interpretation, as the Hartree-Fock approximation is considerably more sophisticated than the approximation conventionally employed in connection with Hund's rule, namely the one in which the same one electron orbitals are used for both terms. It is obvious that the relaxation of the shape of the orbitals in the higher multiplicity term towards their Hartree-Fock shape may result in an extreme change in the roles of the various energetic components, but as far as the total energy is to be accounted for this is of no relevance. Our energetic argument is essentially that a wavefunction can be formed with the lower multiplicity orbitals but with the higher multiplicity symmetry, whose energy is lower than the Hartree-Fock energy of the lower multiplicity term, due to the Pauli principle, but higher than the energy of the higher multiplicity term, due to the variational principle. The philosophy behind this argument is similar to that discussed by Feinberg and Ruedenberg [9] in a different context. The only difficulty which still remains, as far as the energy is concerned, is associated with effect of correlation. Due to the fact that the correlation energy is higher in the lower multiplicity term [10] it is obvious that correlation tends to decrease the energetic difference between the

different multiplicity terms. A satisfactory and general *ab initio* argument which would guarantee that correlation could never reverse the order of terms predicted within the Hartree-Fock approximation is not yet available. One should, however, note that from the point of view of $1/Z$ perturbation theory the intermultiplet separation is a first order effect because even the zero order wavefunction, though not the zero order energy, is different for the different terms. Correlation is a second order effect because both in the Hartree-Fock and in the exact schemes the zero order wavefunction is the same antisymmetrized product of hydrogenic functions. It is therefore highly plausible, though not rigorously guaranteed, that correlation effects are of minor significance as far as the qualitative features of the ordering of the multiplets are considered.

To account for the roles of the various energetic components we note that in the first step we have constructed the higher multiplicity wavefunction using the lower multiplicity Hartree-Fock orbitals. As a consequence of this construction the one electron energy (kinetic and nuclear attraction) is not changed whereas the interelectronic repulsion decreases. The virial theorem, which is satisfied for the lower multiplicity wavefunction, is not satisfied for the one thus obtained for the higher multiplicity term. The most naive improvement, simple scaling, would result in a uniform contraction of the whole wavefunction. This is in only partial agreement with more accurate treatments. If there are two different major shells then the inner orbitals remain essentially hydrogenic, whereas the outer electrons are rather strongly screened by the inner ones. It is therefore obvious that the relaxation necessary for the satisfaction of the virial theorem will mainly affect the outer orbitals. As the kinetic energy has to increase these orbitals ought to contract. As a consequence of the fact that they account for only a small fraction of the total energy the contraction of these orbitals is considerably more significant than the contraction expected assuming uniform scaling. Along with the contraction of the outer orbitals we observe a slight expansion of the inner orbitals which is probably due to the slight screening due to the penetrating part of the contracted outer orbitals. The balance, which occurs so as to satisfy the virial theorem, results in an increase in both the kinetic energy and the nuclear attraction, due to the contraction of the outer orbitals and their approach towards the nucleus. The approach towards the inner electrons results in an increase of the interelectronic repulsion which is more significant than under the assumption of uniform scaling. It is therefore rather plausible that inversion of the order of interelectronic repulsions may occur. The total energy increases quadratically with the nuclear charge whereas the interelectronic repulsion increases only linearly. Thus, upon increasing the nuclear charge, the amount of contraction of the outer orbitals decreases so that the change in the interelectronic repulsion is less significant. It is, however, obvious that the change predicted by the scaling model [4], in which both orbitals contract, is a lower bound to the change observed in the Hartree-Fock approximation in which the much higher contraction of the outer orbitals and the concomitant expansion of the inner orbitals are much more effective in increasing the interelectronic repulsion. It is therefore shown, within the Hartree-Fock approximation, that nuclear attraction differences are always the dominant ones, as this has been shown to be true for the scaling approximation [4].

The fact that for configurations with only one major shell there is no reversal of interelectronic repulsions fits in rather logically at this stage. The only source of increase of the interelectronic repulsion is the contraction of the single shell which is necessary for the kinetic energy to increase so as to satisfy the virial theorem. It is clear that this contraction causes an increase in both the kinetic energy and the nuclear attraction which is more rapid than the increase in the interelectronic repulsion. The whole change essentially necessary in the kinetic energy is of the order of magnitude of the interelectronic repulsion difference before the orbital relaxation was introduced. This change is effected with only a minor change in the interelectronic repulsion. A measure of the relative sensitivity of the interelectronic repulsion and the nuclear attraction to a contraction of the orbitals is the ratio of the screening due to the other electrons and the total nuclear charge. Hence, no reversal of the interelectronic repulsion can be expected without the expansion of an inner shell towards the contracting outer shell.

It seems appropriate at this stage to characterize the difficulties encountered with respect to the interpretation of Hund's rule. It is obvious that the term in the Hamiltonian which is the origin of the energy difference between the different multiplets of a given configuration is the interelectronic repulsion. It is nevertheless observed that the introduction of interelectronic repulsion in the Hamiltonian modifies the wavefunction so as to associate the energetic effect with the one electron part of the Hamiltonian. This is a consequence of the non-commutativity of the interelectronic repulsion with the one electron Hamiltonian. The quantum mechanical origin of Hund's rule is thus more strictly emphasized than in the conventional electrostatic interpretation [11] which takes into account the quantum mechanical nature of the problem by evoking the Pauli principle but disregards the rather surprising dynamic consequences.

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References

1. Davidson, E. R.: J. chem. Physics **42**, 4199 (1965).
2. Lemberger, A., Pauncz, R.: Acta physica hung. **27**, 169 (1969).
3. Messmer, R. P., Birss, F. W.: J. phys. Chem. **73**, 2085 (1969).
4. Katriel, J.: Theoret. chim. Acta (Berl.) **23**, 309 (1972).
5. — Physic. Rev. A (in press).
6. Reeves, C. M.: J. chem. Physics **39**, 1 (1963).
7. Eckart, C.: Physic. Rev. **36**, 878 (1930).
8. Eliezer, I., Moualem, A.: Theoret. chim. Acta (Berl.) **23**, 39 (1971).
9. Feinberg, M. J., Ruedenberg, K.: J. chem. Physics **54**, 1495 (1971).
10. Clementi, E.: J. chem. Physics **38**, 2248 (1963).
11. Condon, E. U., Shortley, G. H.: The theory of atomic spectra. Cambridge: University Press 1935; Koster, G. F.: Physic. Rev. **98**, 514 (1955).

J. Katriel
Nuclear Research Centre-Negev
P.O.B. 9001
Beer Sheva, Israel