Research paper

Singlet *vs.* triplet interelectronic repulsion in confined atoms

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ABSTRACT

Hund's multiplicity rule invariably holds for the ground configurations of few-electron atoms as well as those of multi-electron quantum dots. However, the ordering of the corresponding interelectronic repulsions exhibits a reversal in the former but not in the latter system, upon varying the system parameters. Here, we investigate the transition between these two types of behaviour by studying few-electron atoms confined in spherical cavities. "Counter-intuitive" ordering of the interelectronic repulsions is confirmed when the nuclear charge is low enough and the cavity radius is large enough.

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1. Introduction

Charles Coulson, who as a young scholar maintained that "numerical analysis could solve the basic problems of chemistry" [1], identified, in his Boulder Conference Banquet speech (1959) [2], the widening gap between two distinct ways that theoretical chemistry is being practiced. Group I quantum chemistry, in Coulson's classification, is concerned with highly accurate computations that gradually replace spectroscopy and other experimental techniques, in particular where the latter are not feasible. Group II quantum chemistry is concerned with the development and refinement of concepts, principles and models, aspiring to become relevant to a growing domain of chemistry and biology. Löwdin, in an article marking the centenary of Mendeleev's periodic table [3], that inspired several interesting initiatives, pointed out that while Group I quantum chemistry could confirm the structure of the periodic table box by box, an underlying encompasing principle, grounded in firm quantum mechanics, was (and, we believe, still is) missing. The Madelung $(n + \ell, n)$ rule is arguably such a global principle, but its origins are empirical. None of the several attempts to give it a quantum mechanical justification is entirely satisfactory.

The rules that specify the energetic ordering of distinct atomic states that correspond to a common configuration are arguably the next logical step towards a description of the electronic structure of atoms. Hund's rules, the most familiar statement concerning the relevant observed regularities, have been of ongoing interest for nearly a century, with an emphasis on their limits of validity and conceptual status. These rules were originally proposed by Friedrich Hund [4] entirely empirically, just before the advent of what used to be called the "new" quantum mechanics. Both rules were formulated for the ground state of a system of equivalent electrons, corresponding, in updated notation, to an incomplete common subshell specified by the principal and angular momentum quantum numbers n and ℓ, outside a common closed core. One cannot but admire the depth of understanding of the role of angular momentum coupling in atomic spectroscopy that Hund's article exhibits, although the formalism that we now recognize as giving rise to this coupling was not yet available.

The seminal clue to the quantum–mechanical origins of Hund's rules is due to Heisenberg [5], who elucidated the role of the permutational symmetry of identical particles (a step that Dirac [6] achieved simultaneously in a more explicit form, actually introducing determinantal wave functions, albeit without spin), and derived the exchange term that accounts for singlet–triplet splitting in two-electron systems. Slater [7], the attitude of whose work belongs in Coulson's group I, studied a large number of atomic open-shell configurations, assuming that the different states that each such configuration gives rise to can be treated in terms of a common set of one-electron orbitals. We shall refer to this scheme as the *single-configuration frozen-orbital* (SC-FO) approximation. Within this scheme, the differences among the energies of the different states that a given configuration gives rise to are entirely due to the differences in the magnitudes of the corresponding interelectronic repulsions. The energies of the different terms, within the SC-FO framework, are expressed as linear combinations of a common set of Slater radial integrals. Within the simplest of

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these cases, such as the sp or p^2 configurations, the differences between the energies of pairs of states are given in terms of a single such integral, which is easily shown to be positive. Already for the d^2 configuration these differences depend on linear combinations of two distinct integrals, so that the ordering of terms can only be ascertained if the relative magnitudes of these integrals can be estimated or at least bounded. Slater observed several instances in which his treatment did not agree with Hund's rules. In such cases it is Slater's treatment that is more likely to agree with observed spectra. Indeed, the first instance of this kind discussed by Slater [7] involves the d^2 configuration. Similar multiparameter expressions specify the energies of the $pp\prime$ manifold. A characterization of a class of configurations whose SC-FO treatment suggests violation of Hund's rules was offered by Morgan and Kutzelnigg [8]. Following earlier authors, we refer to the multiplet ordering schemes that the SC-FO analysis produces as the *generalized Hund's rules*. Morgan and Kutzelnigg's remarkable achievement is that they established that such generalized rules can be formulated.

The assumption of a common set of frozen one-electron orbitals leads to an inevitable violation of the virial theorem, since it implies a common kinetic energy but different potential energies for the different states that belong to any given configuration. This assumption was lifted by Eckart [9] for singly-excited helium, and by Hartree and Hartree [10] for carbon, but neither bothered to explicitly examine the effect on the interelectronic repulsion.

Davidson [11] was the first to notice, in a series of Hartree–Fock computations for singly excited helium, that upon allowing the singlet and triplet orbitals to optimize independently, the interelectronic repulsions in the triplet states are higher than those in the corresponding singlets. The triplet is still lower in energy than the corresponding singlet, due to increased nuclear attraction. Several authors reiterated Davidson's observation, studying somewhat heavier atoms, as well as a few light diatomic molecules. Its initial acceptance is conveyed by the concluding sentence in Messmer and Birss' article [12], "The origins of the singlet–triplet splitting . . .need not be amenable to a simple interpretation". However, an interpretation that made this reversal of the interelectronic repulsions plausible, while establishing that, at least within the Hartree–Fock framework, the energetic ordering suggested by the SC-FO approximation remains valid along the whole isoelectronic sequence, was presented in [13] and reviewed in [14].

In [13] the dependence of the difference between the singlet and the triplet interelectronic repulsions was investigated along the isoelectronic sequences of He and C. In both systems the triplet keeps being the lower energy state along the whole isoelectronic sequence. The interelectronic repulsion is lower in the triplet, in agreement with the Heisenberg-Slater interpretation, for most of the isoelectronic sequence, except the first few low Z members, for which it is higher in the triplet. While the plausibility of this behaviour follows from the treatment in [13], its inevitability was only recently established [15].

Quantum dots, sometimes referred to as "artificial atoms", share many features with real atoms. They have been studied both experimentally and theoretically for nearly four decades, obtaining ever increasing technological significance. Quantum dots have been modelled by a variety of potentials, the most common being parabolic (harmonic), rectangular, Gaussian, and various modifications thereof [16,17]. Hund's rules were established to hold in parabolic quantum dots with up to 20 electrons [18]. A theoretical investigation of circular parabolic quantum dots with up to 46 electrons suggests that Hund's first rule holds at least for dots of small sizes [19]. Technologically significant consequences of Hund's rule in more complicated quantum dot arrangements have been reported [20].

Counter-intuitive arrangements of the magnitudes of the interelectronic repulsions in open-shell quantum dots have not been observed. The sign reversal of the difference between the singlet and the triplet interelectronic repulsions in atomic systems, upon raising the nuclear charge, implies that anecdotal evidence, consisting of an isolated computation in which such reversal is not observed in a particular quantum dot [21], cannot shed definitive light on the behaviour of that system upon variation of its defining parameters. Sako et al. [22] established that in an open-shell two-electron parabolic quantum dot the interelectronic repulsion is always lower in the triplet than in the corresponding singlet. Following their earlier work on the open-shell He-like atoms [23,24], these authors provide an illuminating discussion of pertinent features of the corresponding probability distribution functions. Moreover, in analogy with the asymptotic analysis that established the inevitability of the inversion of interelectronic repulsions in the atomic isoelectronic sequences, it was established that no such inversion can take place for harmonic quantum dots, (in which the binding one-particle potential is quadratic) at any value of the force constant [15]. The analysis, in both cases, is based on an application of the Hellmann–Feynman theorem to the singlet–triplet energy difference. The principal feature that is responsible for the distinction between the atomic isoelectronic sequence and the harmonic quantum dot is that in the former the singlet–triplet energy difference vanishes at some positive nuclear charge, below which the outermost electron is not bound. In view of the confining nature of the harmonic potential, the coincidence of the singlet and the triplet energies only takes place when the harmonic force constant vanishes. Since the infinite spherical well is even more remote from the Coulomb potential – more confining – than the harmonic well, it is safe to anticipate no reversal, as a function of the radius of the confining sphere, in the latter system as well.

To understand the transition between these two types of behaviour we consider confined open-shell many-electron atoms. The multiplet structure suggested by the SC-FO treatment of the systems that we actually study agrees with that specified by Hund's rules. Furthermore, we deliberately avoid systems that exhibit asymptotic degeneracies as $\frac{1}{Z} \to 0$. We follow the behaviour of pairs of states that correspond to a common configuration, say, the singlet and triplet states that correspond to the $(1s2p)$ configuration of the two-electron atom. In free space, the interelectronic repulsion is higher in the singlet for higher Z, and higher in the triplet for lower Z. Confining the system into a sphere of radius R and setting $Z = 0$ we still get a singlet–triplet pair, the triplet being lower in energy, but having a lower expectation value of the interelectronic repulsion, for all R. Our aim is to trace the transition between the case $R > 0, Z = 0$ and the case $R = \infty, Z > 1$.

For a pair of singlet–triplet states corresponding to a common configuration of an N-electron atom with nuclear charge Z, confined in a sphere of radius R, let $\Delta E = E(\text{singlet}) - E(\text{triplet})$. It was shown in [15] that the difference between the corresponding interelectronic repulsions is given by

$$\Delta C = 2\Delta E - Z \frac{\partial \Delta E}{\partial Z} + R \frac{\partial \Delta E}{\partial R}. \tag{1}$$

The derivation of Eq. (1) involves the application of the virial theorem and of the Hellmann–Feynman theorem. Both are valid for the exact as well as for the Hartree–Fock energies. It can be written in many equivalent ways, e.g.,

$$\begin{aligned}
\Delta C &= -Z^3 \frac{\partial}{\partial Z} \left(\frac{\Delta E}{Z^2} \right) + R \frac{\partial \Delta E}{\partial R} \\
&= \frac{1}{R} \frac{\partial}{\partial R} \left(R^2 \Delta E \right) - Z \frac{\partial \Delta E}{\partial Z} \\
&= \frac{\partial}{\partial R} (R \Delta E) - Z^2 \frac{\partial}{\partial Z} \left(\frac{\Delta E}{Z} \right).
\end{aligned}$$