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.

keywords: Hund's rule, confined open-shell atoms, interelectronic repulsion.

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)

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[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, corrresponding, 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 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' 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 single-configuration treatment ignores the fact that at infinite Z the configuration of interest may be degenerate with some other configuration that gives rise to terms of common symmetries. A simple illustration is provided by the ground state of the Be-isoelectronic sequence, $1s^2 2s^2\ ^1S$, which is asymptotically degenerate with the state $1s^2 2p^2\ ^1S$. The formal framework for investigating the energetic consequences of such degeneracies was developed by Layzer [9], whose work was extended by Godfredsen [10], and, more recently, by Friesecke and Goddard [11]. Quantitative consequences of this asymptotic degeneracy are widespread, accounting, for example, for the fact that the observed ratio $\frac{E[^1S]-E[^1D]}{E[^1D]-E[^3P]}$ for the terms of the ground configuration of C, $1s^2 2s^2 2p^2$, is 1.127, while the Slater-Condon value is 1.5. First-order perturbation theory, recognizing the asymptotic degeneracy with the $1s^2 2p^4$ configuration, yields for this ratio the value 1.0758 [9] (which is very close to the observed value at the isoelectronic Ca^{+14} [12]). An even more dramatic consequence of asymptotic degeneracy, leading to violation of the level ordering specified by Hund's rule, is illustrated by the Mg $KL3s3d$ configuration (where $K = 1s^2$ and $L = 2s^2 2p^6$). Here, the observed ordering, whose anomaly was pointed out in Moore's introduction to her monumental tabulation of atomic energy levels [13] (of which NIST [12] is a successor) is $E[^1D] < E[^3D]$. Examining the corresponding positive isoelectronic ions we find that their lowest ^1D state is essentially $3p^2$, followed by a ^3D and a ^1D, both nominally labelled as corresponding to the $3s3d$ configuration. The ratio $\frac{E[3s3d\,^1D]-E[3s3d\,^3D]}{E[3s3d\,^1D]-E[3p^2\ ^1D]}$ starts at 0.5908 for Al^+, monotonically decreasing, becoming 0.4278 at K^{+7}. Degenerate first-order perturbation theory, recognizing the asymptotic degeneracy of the $3s3d$ and the $3p^2$ configurations [10], yields for this ratio the value 0.3675, which is consistent with an extrapolation to $\frac{1}{Z} \to 0$ of the ratios mentioned above. For the Mg atom, the corresponding ratio involving the lowest and the next lowest singlets and the triplet that lies between them is 0.7692, which is consistent with the trend suggested by the values corresponding to the positive ions, cited above. It is only the fact that the $(3p^2)^1D$ state is more thinly spread among the $(3snd)^1D$ states that makes the fact that in the Mg atom the lowest ^1D is lower than the lowest ^3D appear odd.

Mixing of configurations that are not asymptotically degenerate with the configuration of interest may play a significant role in atomic spectroscopy, affecting the level ordering in a manner that is less amenable to general considerations. Hence, we do not dwell on this issue in the present paper.

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 [14] for singly-excited helium, and by Hartree and Hartree [15] for carbon, but neither bothered to explicitly examine the effect on the interelectronic repulsion.

Davidson [16] 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 [17], "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 [18] and reviewed in [19].

In [18] 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 [18], its inevitabilty was only recently established [20].

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 [21, 22]. Hund's rules were established to hold in parabolic quantum dots with up to 20 electrons [23]. 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 [24]. Technologically significant consequences of Hund's rule in more complicated quantum dot arrangements have been reported [25].

Couter-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 [26], cannot shed definitive light on the behaviour of that system upon variation of its defining parameters. Sako *et al.* [27] 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 [28, 29], 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 [20]. 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 [20] 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 equation 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.,

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

For $R \to \infty$ ΔE is independent of R, so we obtain

$$\Delta C = -Z^3\frac{\partial}{\partial Z}\left(\frac{\Delta E}{Z^2}\right)\,. \tag{2}$$

Since $\frac{\Delta E}{Z^2}$ vanishes at $Z = Z_c$, the critical charge at which the outer electron ceases to be bound, as well as at $Z \to \infty$, and is positive in between, it must possess a maximum at some intermediate value Z_m. Hence, $\Delta C < 0$ for $Z_c < Z < Z_m$, and $\Delta C > 0$ for $Z > Z_m$.

For $Z = 0$ we obtain

$$\Delta C = \frac{1}{R}\cdot\frac{\partial}{\partial R}(R^2\Delta E)\,. \tag{3}$$

In sections 3 and 4 we consider the $(1s2p)^{1,3}P$ and the $(1s^22s2p)^{1,3}P$ isoelectronic sequences of He and Be, respectively. We obtain near-Hartree-Fock values of the energies and of the interelectronic repulsions. The virial-Hellmann-Feynman relation, equation 1, is verified, mainly to assess the numerical accuracy of our results. This is preceded, in section 2, by a discussion of the computational procedure.

2 The computational procedure

We use the Parameterized Optimized Effective Potential (POEP) method [30, 31] to obtain the wave functions and energies of the confined atoms. The variational wave function for any given state is a single-configuration linear combination of Slater determinants, coupled to the appropriate L and S values. The orbitals are optimized for each state individually, yielding distinctly shaped orbitals for distinct terms of any given configuration. An auxiliary one-body potential (that, following time-honoured practice, we shall refer to as the effective potential) is introduced. This potential, $v(r)$, is specified in terms of a set of parameters that are eventually determined by application of the variational principle to the expectation value of the actual atomic Hamiltonian. It serves as a device for producing a set of convenient atomic orbitals. Its physical significance [32] does not play a role in the present context. However, the order of the corresponding orbital eigenvalues determines the set of occupied orbitals used. The effective potential is written in the form

$$v(r) = -\frac{1}{r}\left(Z - N + 1 + (N-1)\sum_{p=0}^{S}\sum_{k=1}^{n_p} c_{k,p} r^p e^{-\beta_{k,p} r}\right) ,$$

where N is the number of electrons and the constraint $\sum_{k=1}^{n_0} c_{k,0} = 1$ is imposed to satisfy the correct short range behaviour of the potential.

The orbitals are obtained from the single-particle Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + v(r)\right)\phi_\lambda(\vec{r}) = \epsilon_\lambda \phi_\lambda(\vec{r})\,. \tag{4}$$

In order to account for the hard-wall confinement a linear cut-off factor is included in the atomic orbitals, i. e.,

$$\phi_\lambda(\vec{r}) = g(r)\, R_{nl}(r) Y_{lm}(\Omega)\,,$$

with

$$g(r) = 1 - \frac{r}{R}\,.$$

A variational solution of equation 4 is obtained by expressing the radial orbitals as linear combinations of Slater type orbitals, as in the Roothaan-Hartree-Fock method,

$$R_{n\ell}(r) = \sum_{j=1}^{M_\ell} C_{jn\ell} S_{j\ell}(r)\,,$$

where

$$S_{j\ell}(r) = N_{j\ell}\, r^{n_{j\ell}-1} e^{-\alpha_{j\ell} r}\,.$$

$N_{j\ell}$ are the normalization constants. The sets of parameters $\{M_\ell\}$, $\{n_{j\ell}\}$ and $\{\alpha_{j\ell}\}$ specify the basis sets employed for the orbitals (a different basis set for each occupied ℓ value). The form of each basis set (the specification of the $\{n_{j\ell}\}$ values) is adapted for each confined atom to achieve a better performance within the selected basis size (the chosen $\{M_\ell\}$ values), as in Ref. [31]. The coefficients $\{C_{jn\ell}\}$ are obtained by solving Eq. 4 for any given parameterization of the effective potential.

The expectation value of the atomic (electrostatic) Hamiltonian is minimized with respect to the parameters $\{c_{k,p}, \beta_{k,p}\}$ that specify the effective potential. As this minimization proceeds the parameters $\{\alpha_{j\ell}\}$ keep being optimized as well. The size of the expansion (the values S and n_p) is modified until convergence is achieved. This form of the effective potential was demonstrated to work properly for both free and confined atoms (Ref. [31] and references therein).

The derivatives of the total energy with respect to the confinement radius and with respect to the nuclear charge are calculated numerically. The expectation value of the Hamiltonian is obtained for R and for $R \pm \delta R$, and a three point formula is employed to compute the derivative. A value of $\delta R = 0.001$ was shown to be adequate for the accuracy required in the present investigation. The same scheme is employed for the derivative with respect to the nuclear charge.

The results obtained for the total energy, the inter-electronic repulsion energy, the derivative with respect to R and that with respect to Z, were used to evaluate the differences between the inter-electronic repulsion energies of the singlet and the corresponding triplet states, both directly and by using equation 1. Agreement between the two procedures was established, in most cases to three digits. Better agreement could be achieved by more careful optimization and perhaps a more sophisticated estimation of the energy derivatives, but the level of accuracy reported below, typically deviating from the corresponding Hartree-Fock limit by less than a mHartree, is sufficient to clearly illustrate the qualitative behaviour that we are concerned with.

3 The $(1s2p)\,^{1,3}P$ states of the confined He-like atom

Near-Hartree-Fock wavefunctions and energies were obtained for the singly excited pair of states $(1s2p)\,^{1,3}P$, over a range of nuclear charges and confining radii. The results are presented in Table 1, at the bottom of which some free atom data are presented to assess the accuracy of our computations. In all cases, the total energy is lower in the triplet than in the singlet. The most interesting aspect is displayed in Table 2, presenting the difference between the expectation values of the interelectronic repulsion of the singlet and the corresponding triplet states. One notes that the interelectronic repulsion is higher in the singlet except at low Z and high R.

At the bottom of Table 2 we compare the $R = \infty$ results with free atom Hartree-Fock [16] and the exact [33] values, as well as the values extracted from the spectroscopic energy level data [12]. The latter are obtained by evaluating $\frac{E[^1P]-E_{av}[^3P]}{Z^2}$ for $Z = 2, 3, 4, 5, 6$, fitting it to a fourth degree polynomial and using equation 2 to evaluate ΔC. $E_{av}[^3P] = \frac{1}{9}\big(5E[^3P_2] + 3E[^3P_1] + E[^3P_0]\big)$ is the triplet multiplet average.

Further inspection of Table 2 indicates that for low R the difference of the interelectronic repulsions between the singlet and the triplet is a decreasing function of Z. This is a manifestation of the fact that when Z increases for a constant R the wavefunction contracts and the boundary becomes less significant. Since the singlet is more expanded, the boundary affects it more significantly, increasing the singlet-triplet difference of interelectronic repulsions. At high R, including the free atom ($R = \infty$), the difference of interelectronic repulsions increases with increasing Z. This is a trivial consequence of the fact that the difference of interelectronic repulsions is, asymptotically, equal to $2K[1s, 2p]Z$, where $K[1s, 2p]$ is the exchange integral. At intermediate R one notes a minimum in the singlet-triplet difference of interelectroic repulsions, as a function of Z. For Z above this minimum the high R behaviour is manifested, whereas for Z below the minimum one is at the low R regime. The location of the minimum shifts to lower Z upon increase of R. Noticing this trend helps understand what would otherwise look a suspicious sequence of interelectronic repulsion differences at $R = 5$. The difference of interelectronic repulsions is always a decreasing function of R, for constant Z. This trend is due to the fact that the confinement affects the singlet - that is more expanded - more than the triplet, increasing it upon lowering R.

4 The $(1s^2 2s 2p)\,^{1,3}P$ states of the confined Be-like atom

Here, again, the triplet energy is always lower than that of the singlet, *cf.* Table 3. The interelectronic repulsion, presented in Table 4, is lower in the triplet, except at large enough R and low enough Z. At the bottom of the table we compare the $R = \infty$ results with the free atom values extracted from the spectroscopic energy level data [12] in the manner described above. Although the quantitative agreement is modest (due mainly to the numerical limitations of the procedure for extracting the differences of the interelectronic repulsions from the spectral energy data), the trend is clearly displayed.

The topology of the $\Delta C[Z, R]$ surface is somewhat different from that in the two-electron system. ΔC increases with increasing Z at both low and high R, but exhibits a minimum for intermediate R values. Here, at intermediate R the dominant effect is the squeezing of the outermost $2p$ orbital, which is more diffuse in the singlet. At lower R both the $2s$ and the $2p$ orbitals are sequeezed into the core. A detailed interpretation of the consequences of this fact appears more subtle. As a function of R, for constant Z, ΔC decreases just like in the two-electron case.

5 Conclusions

The singlet-triplet splitting was studied for two confined open-shell atomic systems, as a function of the nuclear charge and of the radius of the confining sphere. In all the cases considered the total energy was confirmed to be lower in the triplet. The interelectronic repulsion was found to be lower in the singlet when the nuclear charge is low enough and the confining radius is large enough. The difference of interelectronic repulsions between the singlet and the triplet (denoted ΔC) was found to be a decreasing function of the radius of the confining sphere, at a constant nuclear charge. However, as a function of the nuclear

charge at a constant confining radius, this difference increases for large confining spheres, and exhibits a minimum at intermediate confining spheres. For tightly confining spheres ΔC decrease with increasing nuclear charge in the two-electron $1s2p$ system, but increases with increasing nuclear charge in the four-electron $1s^2 2s2p$ system. This distinction can probably be understood as a consequence of the fact that the $1s$ and the $2p$ orbitals are very differently affected by the confining sphere, which is not the case for the $2s$ and $2p$ orbitals. While the contrast in the behaviour of the difference between the singlet-triplet interelectronic repulsions in the free and in the confined atom follows from the analysis in [20], the transition between these two types of behaviour is now clarified.

In both systems studied $\frac{\partial E}{\partial R} < 0$ (the energy decreases - increasing in absolute value - with increasing R). $\left|\frac{\partial E}{\partial R}\right|$ decreases with increasing R, vanishing at large R. More remarkably, it is higher in the singlet than in the triplet, due to the fact that the triplet wave function is more contracted, hence less affected by the confining sphere. Similarly, $\frac{\partial E}{\partial Z} < 0$. Like the absolute value of the derivative with respect to R, $\left|\frac{\partial E}{\partial Z}\right|$ decreases with increasing R, remaining finite at $R \to \infty$ where it is equal to the expectation value of $\sum_{i=1}^{N} \frac{1}{r_i}$, N being the number of electrons. As a function of Z, $\left|\frac{\partial E}{\partial Z}\right|$ increases. This is obvious, at least at large R, reflecting the contraction of the wave function upon increasing Z. The contraction of the triplet wave function relative to the singlet is also reflected in the fact that $\left|\frac{\partial E}{\partial Z}\right|$ is larger in the former than in the latter.

Investigation of the effects of milder confining potentials, such as a finite spherical square-well or a Gaussian potential, are worth-while extensions of the present study.

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Table 1: Energies of the $(1s2p)^{1,3}P$ states of the confined two-electron atom.

R	He(^{3}P)	He(^{1}P)	Li^+(^{3}P)	Li^+(^{1}P)	Be^{++}(^{3}P)	Be^{++}(^{1}P)	B^{+3}(^{3}P)	B^{+3}(^{1}P)
1.0	7.18908	7.86331	1.99472	2.63051	−3.84255	−3.26322	−10.49949	−9.98074
2.0	−0.56854	−0.28495	−4.07469	−3.85811	−8.62062	−8.45007	−14.28070	−14.12580
3.0	−1.61213	−1.47956	−4.78773	−4.69491	−9.08631	−8.99737	−14.54642	−14.44139
4.0	−1.90428	−1.83691	−4.95696	−4.90144	−9.15898	−9.08855	−14.56781	−14.46968
5.0	−2.01977	−1.98051	−5.00537	−4.96309	−9.16978	−9.10372	−14.56908	−14.47158
6.0	−2.07343	−2.04793	−5.01949	−4.98223	−9.17115	−9.10587	−14.56914	−14.47170
7.0	−2.10049	−2.08193	−5.02338	−4.98795	−9.17126	−9.10613	−14.56914	−14.47170
10.0	−2.12664	−2.11566	−5.02461	−4.99004	−9.17130	−9.10615	−14.56914	−14.47170
∞	−2.131434	−2.122463	−5.024647	−4.990075	−9.171307	−9.106150	−14.569138	−14.471695
HF[34, 35]	−2.131437	−2.122464	−5.024669	−4.990107	−9.171322	−9.106185	−14.569151	−14.471745
NR[36]	−2.133164	−2.123843	−5.027712	−4.993348	−9.174970	−9.110727	−14.573134	−14.477278
exp.[12]	−2.132969	−2.123638	−5.027809	−4.993429	−9.176052	−9.111857	−14.576351	−14.480525

NR=non-relativistic.

Table 2: Difference between the interelectronic repulsions of the $(1s2p)^1P$ and the $(1s2p)^3P$ states of the confined two-electron atom.

R	He	Li^+	Be^{++}	B^{+3}
1.0	0.6699	0.6299	0.5661	0.5003
2.0	0.2734	0.1926	0.1318	0.1077
3.0	0.1057	0.0557	0.0410	0.0459
4.0	0.0368	0.0142	0.0166	0.0331
5.0	0.0103	-0.0019	0.0070	0.0316
6.0	-0.0033	-0.0103	0.0041	0.0313
7.0	-0.0094	-0.0144	0.0039	0.0314
10.0	-0.0180	-0.0176	0.0038	0.0312
∞	-0.0228	-0.0176	0.0036	0.0312
HF [16]	-0.0225			
exact[33]	-0.0216	-0.0161	0.0045	0.0308
exp. [12]	-0.0208	-0.0171	0.0060	0.0273

Table 3: Energies of the $(1s^2 2s2p)^{1,3}P$ states of the confined four-electron atom.

R	Be(^{3}P)	Be(^{1}P)	B^+(^{3}P)	B^+(^{1}P)	C^{++}(^{3}P)	C^{++}(^{1}P)
1.0	4.71081	5.02585	−9.18548	−8.80327	−24.71668	−24.26104
2.0	−11.86665	−11.58512	−22.58383	−22.25490	−35.41652	−35.05414
3.0	−13.84304	−13.60530	−23.86582	−23.60186	−36.16032	−35.86207
4.0	−14.30501	−14.10602	−24.07579	−23.84630	−36.22929	−35.95032
5.0	−14.44274	−14.27074	−24.11235	−23.89792	−36.23485	−35.95938
6.0	−14.48807	−14.33287	−24.11829	−23.90943	−36.23522	−35.96030
7.0	−14.50331	−14.35951	−24.11963	−23.91177		
8.0	−14.50830	−14.37343	−24.11969	−23.91201		
∞	−14.510526	−14.394279	−24.119905	−23.912448	−36.235547	−35.960414
HF[35]	−14.511502	−14.394735	−24.120156	−23.912873	−36.235743	−35.961184
NR[37, 38]	−14.567238	−14.473435	−24.178889	−24.014627	−36.296540	−36.069056
exp.[12]	−14.568293	−14.474500	−24.182968	−24.018728	−36.307075	−36.079565

Table 4: Difference between the interelectronic repulsions of the $(1s^2 2s2p)^1P$ and the $(1s^2 2s2p)^3P$ states of the confined four-electron atom.

R	Be	B^+	C^{++}
1.0	0.2827	0.3473	0.4281
2.0	0.2615	0.3204	0.3518
3.0	0.2295	0.2371	0.2457
4.0	0.1714	0.1656	0.1858
5.0	0.1204	0.1122	0.1653
6.0	0.0736	0.0813	0.1614
7.0	0.0246	0.0660	
8.0	-0.0466	0.0612	
10.0	-0.1946		
∞	-0.2683	0.0584	0.1597
exp.[12]	-0.205	-0.012	0.181