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Citation: *The Journal of Chemical Physics* **128**, 061101 (2008); doi: 10.1063/1.2837456

View online: <http://dx.doi.org/10.1063/1.2837456>

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Hund's multiplicity rule: From atoms to quantum dots

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(Received 19 December 2007; accepted 3 January 2008; published online 11 February 2008)

In 1965, Davidson has shown that the textbook explanation for the Hund's multiplicity rule in atoms, based on the Pauli principle, is wrong. The reason for the failure of the textbook proof, as has been given later by others and as appears today in modern textbooks, it is based on the need to introduce angular electronic correlation into the calculations. Here, we investigate an applicability of this argumentation for helium and for the case of two-electron spherically symmetric rectangular quantum dots (QDs). We show that, for helium and also for the QD, the differences between the singlet and triplet excited states can be explored by calculations within the framework of the mean-field approximation, and, surprisingly, without the need of introducing the angular electronic correlation. Moreover, our calculations have shown that the triplet state of the QD is lower in energy than the corresponding singlet state due to lower electronic repulsion contribution, exactly as being assumed in the oldest explanation of the Hund's rule based on the Pauli principle. © 2008 American Institute of Physics. [DOI: 10.1063/1.2837456]

Low dimensional artificial structures have been the subject of many recent theoretical and experimental investigations.¹⁻³ Of particular interest have been the electronic, structural, and optical properties of few electron quantum dots.¹⁻³ Quantum dots (QDs) are also known as artificial atoms, because like real atoms they confine the motion of the electrons in space, and this results in a discrete energy spectrum. The possibility of fabrication of artificial atoms with tunable properties has opened a wide range of applications and areas of research. The main difference between real atoms and artificial atoms consists in the different nature of the one-electron confining potential. In real atoms the electron-nucleus interaction is a Coulombic long range potential, while in quantum dots the attractive potential of interaction is a soft short ranged potential that is often described as a rectangular potential well. In spite of these differences, many conventional computational approaches of the atomic and molecular quantum physics/chemistry have been successfully applied to calculate the electronic, structural, and spectral properties of the quantum dots.¹⁻³

The original purpose of this letter was to study the Hund's multiplicity rule⁴ for quantum dots. More specifically, we wished to explore whether the well established interpretation of the Hund's rule for atoms⁵⁻⁸ is also applicable for the case of singly excited states of the two-electron quantum dots. To our great surprise, it turned out that even the so-called established interpretation of the Hund's rule for helium atom should be revised as well.

The most restrictive formulation of the Hund's multiplicity rule for atoms states that, for equivalent electronic configurations, the lowest lying state corresponds to the highest possible value of the total spin. Slater's explanation for this behavior was based on the Pauli principle, assuming

(wrongly) that the orbitals are identical for both singlet and triplet states.⁹ According to the Pauli principle, the electrons with parallel spins are kept apart from each other, and therefore the total electron-electron repulsion energy, $V_{ee} = \langle 1/r_{12} \rangle$ (which is a sum of the Coulomb-direct and exchange electron-electron repulsion energy terms), between them can be expected to be *smaller* than for the case of electrons with antiparallel spins. Such an argument would then give an intuitively plausible reason why the triplet states of a two-electron system are lower in energy than their singlet state counterparts. This Slater's explanation for the Hund's multiplicity rule for the atomic states⁹ has been given in textbooks for many years. However, it has serious deficiencies^{5,6,8,10,11} as was first noticed by Davidson for the excited states of He.¹⁰ Numerous calculations on the first members of an isoelectronic sequence of helium (as well as on other isoelectronic sequences) have shown that the states with larger total spin quantum number have higher values of the electron-electron repulsion energy, $V_{ee} = \langle 1/r_{12} \rangle$, in direct contradiction to the above-mentioned Slater's explanation.^{5,6,8,10,11} On the basis of these calculations, correct interpretation of the Hund's rule for atoms has been given by Katriel and Pauncz.^{5,6} Namely, in the higher spin state the electron-nucleus interaction energy, $V_{ne} = \langle -Z/r \rangle$, is more negative than in the associated lower spin state, ${}^3V_{ne} < {}^1V_{ne}$ and ${}^3V_{ne} + {}^3V_{ee} < {}^1V_{ne} + {}^1V_{ee}$, in spite of the fact that ${}^1V_{ee} < {}^3V_{ee}$. However, the Katriel-Pauncz's interpretation^{5,6} raises the following question. What is the role of the angular electronic correlation in Katriel-Pauncz's interpretation of Hund's rule?

Boyd's claim is that the electrons can avoid each other more efficiently and move closer to the nucleus, which *reduces the screening of the nucleus* thus making the electron-nucleus interaction energy more negative in the high spin state.⁸ The logic of this statement is as follows: In helium the

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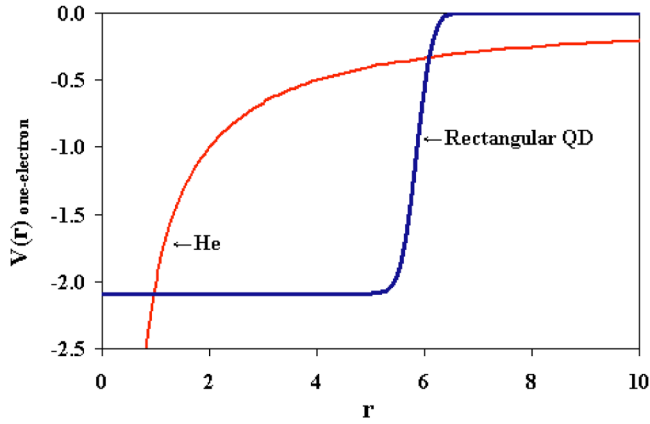


FIG. 1. (Color online) The one-electron confining potential in the helium atom and in the spherically symmetric rectangular quantum dot.

electronic repulsion in 3S state is larger than in 1S state due to the radial-angular correlation (which pushes the electrons to be on the two opposite sides of the nucleus and thereby increases the effective nuclear charge the two electrons feel). This explanation of the Hund's rule appears in modern textbooks. See, for example, one of the best textbooks on quantum chemistry which is used for undergraduate studies in many of the leading universities in the world.¹² However, we will show in the present work that such an explanation needs a substantial revision.

Let us now focus on our numerical investigations of the Hund's multiplicity rule in helium and in the two-electron quantum dots. We have employed a full configuration interaction (FCI) approach which properly covers all the electronic correlation effects and which provides numerically exact benchmark data as long as an appropriate basis set is

used. In Fig. 1, a spherical square well potential well which is a typical potential for the quantum dots is shown, together with the Coulomb attractive potential of He. Both for the helium atom and for the just introduced spherical square well two-electron quantum dot, we have carried out numerical calculations of the singlet and triplet states associated with the excited $S(1s2s)$ electronic configuration. These FCI calculations are performed with the GAMESS(US) quantum chemical package.¹³ In the case of helium atom, we have used a standard optimized d-aug-CC-pVQZ basis set.¹⁴ For the spherical square well quantum dot, we have employed an even-tempered Gaussian basis set whose exponents are calculated from the formula

$$\alpha_i^{s,p,d,f} = \epsilon^{s,p,d,f(1/N^{s,p,d,f})} \alpha_{i-1}^{s,p,d,f}, \quad (1)$$

where

$$\begin{aligned} \alpha_0^s &= 2, & \epsilon^s &= 5 \times 10^{-6}, & N^s &= 30, \\ \alpha_0^p &= 3, & \epsilon^p &= 5 \times 10^{-3}, & N^p &= 5, \\ \alpha_0^d &= 3, & \epsilon^d &= 5 \times 10^{-3}, & N^d &= 2, \\ \alpha_0^f &= 1, & \epsilon^f &= 1, & N^f &= 1. \end{aligned} \quad (2)$$

Numerical tests have shown that these basis set parameters provide stable numerical results for all the QD characteristics under our study. The results of our calculations are displayed in Table I. In addition to these benchmark FCI results, we also present in Table I an outcome of the spin adapted Hartree-Fock calculations for the excited states. Within the spin adapted Hartree-Fock approach, we describe the triplet

TABLE I. The total electronic energy, one-electron potential energy and the two-electron repulsion energy for the lowest lying singly excited states of helium, and for the corresponding states of a two-electron spherical symmetric rectangular quantum dot. Symbol FCI stands for the full CI calculations, whereas symbol HF stands for a spin adapted Hartree-Fock calculation.

System	Method	Total energy (a.u.)	Kinetic energy (a.u.)	One-electron potential energy (a.u.)	Two-electron potential energy (a.u.)
He— $^3(1s2s)$	FCI(<i>spdf</i>)	-2.174 935	2.174 935	-4.618 186	0.268 316
He— $^1(1s2s)$	FCI(<i>spdf</i>)	-2.145 584	2.145 584	-4.540 743	0.249 575
He— $^3(1s2s)$	HF(<i>spdf</i>)	-2.173 960	2.173 960	-4.617 357	0.269 437
He— $^1(1s2s)$	HF(<i>spdf</i>)	-2.143 145	2.143 145	-4.535 592	0.249 302
He— $^3(1s2s)$	FCI(<i>s</i>)	-2.173 841	2.173 841	-4.617 285	0.269 602
He— $^1(1s2s)$	FCI(<i>s</i>)	-2.143 266	2.143 266	-4.537 168	0.250 636
He— $^3(1s2s)$	HF(<i>s</i>)	-2.173 826	2.173 826	-4.617 600	0.269 949
He— $^1(1s2s)$	HF(<i>s</i>)	-2.142 545	2.142 545	-4.535 326	0.250 235
QD— $^3(1s2s)$	FCI(<i>spdf</i>)	-3.314 214	0.551 099	-4.087 051	0.221 741
QD— $^1(1s2s)$	FCI(<i>spdf</i>)	-3.254 452	0.566 812	-4.080 550	0.259 285
QD— $^3(1s2s)$	HF(<i>spdf</i>)	-3.308 536	0.549 765	-4.091 752	0.233 451
QD— $^1(1s2s)$	HF(<i>spdf</i>)	-3.235 523	0.558 053	-4.084 891	0.291 315
QD— $^3(1s2s)$	FCI(<i>s</i>)	-3.309 729	0.549 720	-4.091 610	0.232 160
QD— $^1(1s2s)$	FCI(<i>s</i>)	-3.236 400	0.559 167	-4.086 608	0.291 041
QD— $^3(1s2s)$	HF(<i>s</i>)	-3.309 290	0.550 653	-4.093 215	0.233 273
QD— $^1(1s2s)$	HF(<i>s</i>)	-3.236 263	0.559 017	-4.086 482	0.291 202

and the singlet excited state wavefunctions as in the old textbook formula,

$$|^1S\rangle = 1/\sqrt{2}(\chi_{1s}(\mathbf{r}_1)\chi_{2s}(\mathbf{r}_2) + \chi_{2s}(\mathbf{r}_1)\chi_{1s}(\mathbf{r}_2)) \quad (3)$$

and

$$|^3S\rangle = 1/\sqrt{2}(\chi_{1s}(\mathbf{r}_1)\chi_{2s}(\mathbf{r}_2) - \chi_{2s}(\mathbf{r}_1)\chi_{1s}(\mathbf{r}_2)), \quad (4)$$

with one important difference from the old textbook approach: Rather than using the same $1s$ and $2s$ orbitals for the two spin states, we variationally optimize them by carrying out self-consistent-field calculations similarly as in the conventional Hartree–Fock method. This spin adapted Hartree–Fock method, where the best single configuration is computed, has been taken for the first time for helium by Davidson in 1964.¹⁵ Note that in the Hartree–Fock calculations for the singlet excited states, we follow the iterative method described in Refs. 15 and 16 to avoid the collapse of the excited singlet spin state into the ground state. After carrying out the spin adapted Hartree–Fock calculations using the same (s,p,d,f) -type basis set as taken previously for FCI, we repeat on the FCI and spin adapted Hartree–Fock calculations using the s -type orbitals only. This step is motivated by the fact that, for the s -type basis set, the only included electronic correlation is a radial one, since the FCI(s) and spin adapted Hartree–Fock(s) wavefunctions do not depend on the angle between the two-electronic position vectors.

Comparison between different results presented in Table I clearly shows an excellent agreement between the FCI($spdf$) and the spin adapted Hartree–Fock(s) calculations for all physical characteristics of the singlet and the triplet electronic states, both in the helium and QD cases. In other words, we have found that (i) the spin adapted Hartree–Fock approximation performs remarkably well, and (ii) the obtained results are almost unaffected by removing all the nonvanishing angular momentum basis functions from the calculation. Unlike the s -type basis functions, the angular (pdf) functions are responsible for correlating the angular motions of the two electrons. We therefore conclude that the angular correlation effects play a negligible role. This is a very surprising finding, as it stands in complete contradiction with the explanation given in the literature⁸ and in modern textbooks.¹²

In Fig. 2 we display the radial probability density,

$$|P(r)|^2 = 4\pi r^2 |\Psi_{1s,2s}(r)|^2, \quad (5)$$

corresponding to the $1s$ and the $2s$ orbitals as obtained from our spin adapted Hartree–Fock(s) calculations for the 1S and 3S states of He. Analogical graphs are shown for a QD with the square well potential plotted on Fig. 1. Note that, in the scale of the plots presented in Fig. 2, the same pictures for the $1s$ and the $2s$ orbitals are obtained from spin adapted Hartree–Fock calculations where s,p,d,f -type basis functions are used and for spin adapted Hartree–Fock calculations where only s -type basis functions are used. Let us first focus on the results obtained for helium. Figure 2 shows that the singlet- $1s$ orbital is almost identical with its triplet- $1s$ counterpart. On the other hand, the singlet- $2s$ and the triplet- $2s$ orbitals are considerably different, with the triplet- $2s$ or-

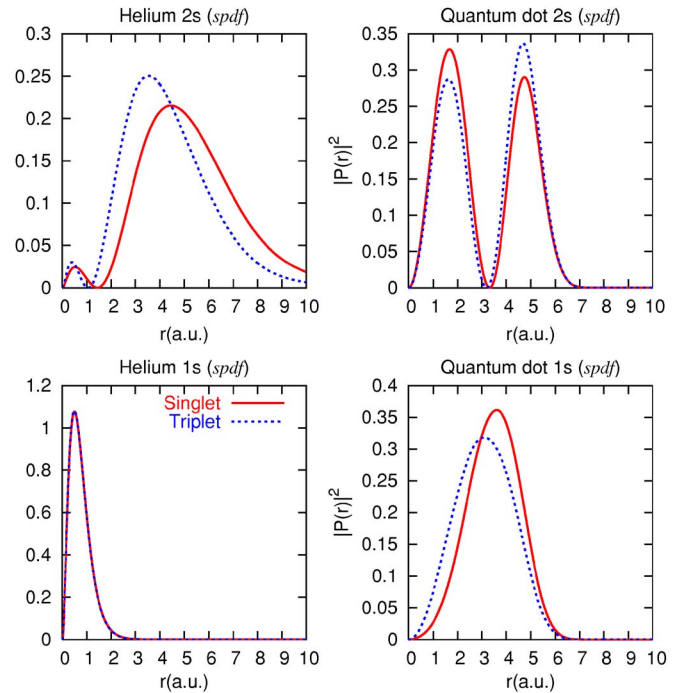


FIG. 2. (Color online) The radial probability densities associated with the $1s$ and $2s$ orbitals of helium and QD systems in the singlet and triplet states. On the scale of the plots shown here, the same results are obtained when spin adapted Hartree–Fock(s) calculations are carried out.

bit being more contracted. The maximum probability to locate the electron in the triplet- $2s$ orbital is on a sphere whose radius is 3.5 a.u., which is about 1 a.u. smaller than the radius of the corresponding singlet- $2s$ orbital. Due to this strong relative contraction of the $2s$ triplet orbital, the contribution of the one-electron energy term (sum of the kinetic energy and the one-electron potential energy presented in Table I) to the total energy of helium is larger than for the singlet. Note also, that electron–electron repulsion energy contribution is considerably smaller than the one-electron contribution energy for both the multiplets.

The results for the QD are very different. As one can see from the plots presented in Fig. 2, not only $2s$ but also the $1s$ orbitals show substantial dissimilarity when a comparison between the singlet and triplet states is made. The maximum probability to find the electron in the triplet- $1s$ orbital is on a sphere whose radius is smaller than the radius of a sphere obtained for the singlet-type $1s$ orbitals. The triplet- $1s$ electron is located closer to the symmetry center (origin) of the rectangular QD potential than the singlet- $1s$ electron. At the same time, the average distance of the electron in the triplet- $2s$ orbital from the origin is larger than for the singlet state $2s$ electron. It is a point of interest that, although the two electrons in the QD avoid being close to one another, the average distance of the electrons in the $1s$ and the $2s$ orbitals from the center is alike. This situation occurs due to the nodal structure of the $2s$ orbital. Namely, the inner and the outer peaks shown in Fig. 2 are located symmetrically on the two different sides of the node. Another point of interest is that the difference between the average distance of the electron in the triplet- $2s$ orbital from the center of the QD, and the average distance of the singlet- $2s$ electron from the cen-

ter results from the differences in the heights of the inner and the outer peaks in the probability distributions shown in Fig. 2. Last but not least, it is interesting to compare the results for the QD presented in Fig. 2 and the shape of the QD potential presented in Fig. 1. It shows that the electron in the $1s$ orbital of QD is mostly located on a sphere whose radius is about equal to the extension of the potential well, whereas the electron in the $2s$ orbital is localized almost in equal probabilities on two spherical shells which are separated by the spherical shell where the $1s$ electron is located.

We can summarize the results obtained in this paper by saying that in two-electron systems, either for a Coulombic potential (helium) or spherically symmetric open square well quantum dot potential (QD), both the singlet and the triplet excited $1s2s$ states (and also the $1s2p$ states which have not been discussed in this text) are very well described by a spin adapted Hartree–Fock ansatz where the best single configuration is calculated. Our calculations show that accurate energies (as well as their single-electron and two-electron components) are obtained within the framework of mean-field theory by optimizing separately the $1s$ and $2s$ orbitals (no angular basis function are included) in the best single-configuration wavefunction. Thus, the angular correlational effects do not play any role for the interpretation of the Hund’s rule. This is the main result of the present work which, in fact, demonstrates the failure of “modern” explanations of the Hund’s rule.^{5–8,12} The main difference between the helium atom and the two-electron QD is that for helium the dominant contribution to the energy (both for the singlet and the triplet states) is coming from the one-electron energy terms (due to presence of the nucleus), whereas in the QD the electronic repulsion is the dominant term. One can argue that, in general, the Hund’s rule is satisfied via lowering the energy term which has the dominant contribution to the total electronic energy of the system. In the case of He, the gain in the negative electron-nucleus energy contribution for the

triplet spin state compensates the accompanying increase of the electronic repulsion. In the QD, on the other hand, one can understand that the Hund’s rule is satisfied via reducing the electronic repulsion for the triplet state in comparison to the electronic repulsion in the corresponding singlet state.

The best single-configuration variational calculations (spin adapted Hartree–Fock) are not restricted to two-electron problems only, but can be easily extended to single-electron excited states of many electron problem, where the ground state is a closed shell, such as, for example, for the excited states of beryllium,

$$\begin{aligned} \Psi = \hat{A} \phi_{1s}(1)\alpha(1)\phi_{1s}(2)\beta(2) & \left(\frac{1}{2}(\phi_{2s}(3)\phi_{3s}(4)) \right. \\ & \pm \phi_{3s}(3)\phi_{2s}(4))(\alpha(3)\beta(4)) \\ & \mp \beta(3)\alpha(4) \left. \right). \end{aligned}$$

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