Origin of the first Hund rule in He-like atoms and 2-electron quantum dots

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   - Hund’s rule - background

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   - Theoretical Model and Computational Method

3 Results
   - Singlet-triplet energy differences
   - Internal wave functions
   - Genuine-and-conjugate-Fermi-holes

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Origin of the first Hund rule
F. Hund (1896-1997)
Hund’s three rules were initially derived empirically in atomic spectroscopy of the pre-quantum-mechanical era. They predict the ordering of the energy levels with different angular momentum and spin quantum numbers.

Friedrich Hund,
Zur Deutung verwickelter Spektren, insbesondere der Elemente Scandium bis Nickel.
Zeitschrift für Physik 33, 345 (1925)
(eingegemgen am 22. Juni 1925)
F. Hund, Linienspekten (1927)

Hund’s rule - background

Hund’s rule - background

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Origin of the first Hund rule
Hund’s rule

Hund’s first rule states

- that among the different spin states belonging to the same orbital configuration the highest spin state has the lowest energy.

Hund’s three rules, in particular the first rule concerning the spin multiplicity, have proved to be almost universally valid for

- atoms,
- molecules (only rule one) and
- artificial atoms (quantum dots)
Interpretation of Hund’s first rule

- Based on Slater’s successful interpretation of complex spectra it was generally assumed that Hund’s first rule is intimately connected with electron correlation.
- It was concluded that in the triplet state the electrons are farther apart on the average than in the corresponding singlet state and that therefore the average electronic repulsion is smaller in the triplet state than in the singlet state.

John C. Slater, Physical Review 34, 1293 (1929)
Interpretation of Hund’s first rule

Davidson was the first to observe that for excited states of He the electron repulsion in the triplet term is consistently larger than in the corresponding singlet term.

... in contradiction to more naïve theories.

As consequence the lower energy of the triplet state as compared to the singlet state must be ascribed to a more compact wavefunction that in turn results in a larger electron repulsion energy but in a much larger energy decrease due to the nuclear attraction potential than in the singlet state.

Ernst R. Davidson, Journal of Chemical Physics 41, 656 (1964); 42, 4199 (1965)
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Origin of the first Hund rule
Theoretical model

- The spatial degrees of freedom of each of the two electrons in both the helium atom and in the quantum dot are confined to a two-dimensional $xy$ plane.
- The *two-dimensional helium model* reproduces all the characteristic features of the energy spectrum of the real 3D helium atom.
- By reducing the dimensionality and thus the number of the degrees of freedom the internal part of the wave functions can be easily visualized.
Hamiltonian

The Hamiltonian for the two-dimensional helium-like systems and for the two-electron two-dimensional quantum dot have the following form, respectively,

\[ H_Z = -\frac{1}{2} \sum_{i=1}^{2} \nabla_i^2 - \sum_{i=1}^{2} \frac{Z_n}{|\vec{r}_i|} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}, \]

\[ H_\omega = -\frac{1}{2} \sum_{i=1}^{2} \nabla_i^2 + \sum_{i=1}^{2} \frac{1}{2} \omega^2 |\vec{r}_i|^2 + \frac{1}{|\vec{r}_1 - \vec{r}_2|}, \]

where \( \omega \) represents the strength of confinement of the quantum dot.
The one-electron part of both Hamiltonians has an analytical solution which yields the following eigenenergies

\[ E^0_Z = \sum_{i=1}^{2} \frac{-Z^2_n}{2(n_i + \frac{1}{2})^2}, \]

\[ E^0_\omega = \sum_{i=1}^{2} \omega(v_i + \frac{1}{2}), \]

where \( n_i \) and \( v_i \) \((i = 1, 2)\) denote the principal and the harmonic-oscillator quantum numbers.
By introducing the $Z_n$- and $\omega$-scaled coordinates

$$\vec{s}_i \equiv Z_n \vec{r}_i \text{ and } \vec{t}_i \equiv \sqrt{\omega} \vec{r}_i \quad (i = 1,2)$$

for the He-like and the quantum dot systems the Hamiltonians take the form

$$\mathcal{H}_{Z/Z_n} = -\frac{1}{2} \sum_{i=1}^{2} \nabla^2_{s,i} - \sum_{i=1}^{2} \frac{1}{|\vec{s}_i|} + \frac{1}{Z_n |\vec{s}_1 - \vec{s}_2|},$$

$$\mathcal{H}_{\omega/\omega} = -\frac{1}{2} \sum_{i=1}^{2} \nabla^2_{t,i} + \sum_{i=1}^{2} \frac{1}{2} |\vec{t}_i|^2 + \frac{1}{\sqrt{\omega} |\vec{t}_1 - \vec{t}_2|}.$$
2D Cartesian Gaussian-type functions

- The one-electron orbitals for the scaled Hamiltonians have been expanded in two-dimensional Cartesian Gaussian-type functions of the form

\[ \chi^{\vec{a},\zeta}(\vec{r}) = x^{a_x} y^{a_y} \exp[-\zeta(x^2 + y^2)]. \]

- Following the quantum chemical convention these functions are classified as

  \[ s-, p-, d\text{-type}, \text{etc. for} \]

  \[ l = a_x + a_y = 0, 1, 2, \text{etc.}, \text{respectively.} \]
Basis sets

- For the He-like systems a [20s10p7d] basis set has been used.
- The exponents of the Gaussian functions have been generated by relying on the geometrical formula

\[ \zeta_{j,l} = \alpha_l \beta_l^{j-1}, j = 1, 2, \ldots, m_l. \]
Basis sets

- For the quantum dot a [1s1p1d1f1g1h1i] basis set with large angular momentum functions has been used.
- All exponents have been chosen as one half of the strength of confinement i.e., $\zeta = 0.5$ in the present case, since the strength of confinement for a harmonic oscillator in the $\omega$-scaled Hamiltonian is unity.
The eigenfunctions and the corresponding energies for the relevant states have been obtained by diagonalizing the full configuration interaction (FCI) scaled Hamiltonian matrix.

The eigenenergies of the unscaled original Hamiltonians can then be obtained by multiplying the calculated energies by $Z_n^2$ and $\omega$, respectively.
The internal space for the two-dimensional two-electron systems with circular symmetry can be described by two radial coordinates and an interelectron angle, i.e.

- \( s_i \equiv |\vec{s}_i| \ (i = 1, 2) \) and \( \phi_- \equiv (\phi_1 - \phi_2)/2 \) for He-like systems
- \( t_i \equiv |\vec{t}_i| \ (i = 1, 2) \) and \( \phi_- \) for quantum dots.

This two-body correlation function in the internal space is called hereafter the \textit{internal wave functions}.
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The lowest singlet-triplet pair of states to which Hund’s multiplicity rule applies is:

- the $^1P - ^3P$ pair of states of the He-like systems with the primary configuration $(1s)(2p)$, and
- the $^1\Pi_u - ^3\Pi_u$ pair of states of the two-dimensional two-electron quantum dot with the primary configuration $(0\sigma_g)(1\pi_u)$. 
Energy differences

**Figure:** Energy differences between the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.
Energy differences between the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.

For large $Z_n$ and $\omega$ values the singlet-triplet energy gap $\Delta E_{\text{tot}}$ is dominated by the two-electron contribution $\Delta E_{\text{two}}$ apparently in accord with the traditional interpretation based on Slater’s paper.

With decreasing $Z_n$ and $\omega$ the two-electron contribution becomes eventually smaller than the one-electron contribution which steadily increases.
Energy differences between the lowest \( P \) singlet-triplet pair of states of He-like systems and of quantum dots.

There exists a fundamental difference between He-like systems and quantum dots apparent from the behavior in the regime of small \( Z_n \) and \( \omega \):

In the case of He-like systems the two-electron contribution does indeed vanish around \( Z_n = 4 \) and becomes significantly negative at \( Z_n = 2 \).

In the case of quantum dots the two-electron contribution \( \Delta E_{\text{two}} \) monotonically decreases with decreasing \( \omega \) and approaches zero in the limit \( \omega \to 0 \).
Traditional interpretation

- Energy differences between the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.

- The traditional interpretation seems to be working in the regime of large $Z_n$ and $\omega$ where the difference in the electron repulsion energy $\Delta E_{\text{two}}$ dominates the singlet-triplet energy gap.

... BUT!
Kinetic and 1e potential energy contributions

Figure: Kinetic energy and one-electron potential energy contributions to the singlet-triplet energy gap for the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.
Kinetic and 1e potential energy contributions analysis

- Kinetic energy and one-electron potential energy contributions to the singlet-triplet energy gap for the lowest \( P \) singlet-triplet pair of states of He-like systems and of quantum dots.

- It is instructive to separate the one-electron energy component \( \Delta E_{\text{one}} \) into its kinetic and one-electron potential components.

- The difference in the kinetic and one-electron potential energies \( \Delta E_T \) and \( \Delta E_V \), respectively, between the singlet and triplet states are plotted in the figure.

- The one- and two-electron energy components \( \Delta E_{\text{one}} \) and \( \Delta E_{\text{two}} \) are plotted for comparison.
Kinetic and 1e potential energy contributions analysis

- Kinetic energy and one-electron potential energy contributions to the singlet-triplet energy gap for the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.

- For He-like systems the nuclear attraction energy component, $\Delta E_V$, is larger than the difference in the electron repulsion energy $\Delta E_{\text{two}}$ even at large $Z_n$ values.

- This positive contribution is almost canceled by the negative contribution of the kinetic energy component $\Delta E_T$ and results in a very small one-electron contribution at large $Z_n$. 
Kinetic and 1e potential energy contributions analysis

- Kinetic energy and one-electron potential energy contributions to the singlet-triplet energy gap for the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.

- For He-like systems the traditional interpretation that ascribes the singlet-triplet energy gap solely to the two-electron contribution fails even in the large $Z_n$ regime.

- For quantum dots in the large $\omega$ regime the one-electron potential contribution $\Delta E_V$ is much smaller than the two-electron energy component $\Delta E_{\text{two}}$, in contrast to the He-like systems.

- Therefore, in case of the quantum dots the traditional interpretation 'works' in the large $\omega$ regime.
Radial electron density distributions

Figure: Radial electron density distributions of the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.
Energy differences between the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.

The radial electron density distribution of the $(1s)(2p)$ and $(0\sigma_g)(1\pi_u)$ singlet-triplet pairs of states is plotted.

The $Z_n$-and $\omega$-scaled radial coordinates $s$ and $t$ are used, respectively, and the electron densities are plotted in a logarithmic scale.
Energy differences between the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots. For small and medium values of $Z_n$ and $\omega$ the singlet and triplet densities are distinct. This is consistent with a significant contribution of the one-electron energy component $\Delta E_{\text{one}}$ in the regime of small and medium $Z_n$ and $\omega$. 

Radial electron density distributions analysis

![Graphs showing radial electron density distributions](image-url)
Energy differences between the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.

For the regime of large $Z_n$ and $\omega$ the electron density distribution of the singlet and triplet states almost coincide with each other.

This is also consistent with the very small one-electron contribution $\Delta E_{\text{one}}$ and the dominating two-electron contribution $\Delta E_{\text{two}}$. 
Energy differences between the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.

In the regime of large $Z_n$ and $\omega$ the small difference in the electron density distribution gives a small difference in the one-electron energy (the two-electron energy dominates the singlet-triplet energy gap).

In the regimes of medium and small $Z_n$ and $\omega$ a large difference in the electron density distributions gives rise to a large difference in the one-electron energy (a breakdown of the traditional interpretation).
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Isosurfaces for the \((1s)(2p)\) singlet-triplet pair

**Figure:** Isosurfaces of the probability density for the internal wave functions for the \((1s)(2p)\) singlet-triplet pair of the helium atom and helium-like ions.
Isosurfaces for the \((0\sigma_g)(1\pi_u)\) singlet-triplet pair

Figure: Isosurfaces of the probability density for the internal wave functions for the \((0\sigma_g)(1\pi_u)\) singlet-triplet pair of a quantum dot.
Isosurfaces for singlet-triplet pairs - analysis

- Isosurfaces for the \(1s(2p)\) singlet-triplet pair of the helium atom and for the \(0\sigma_g(1\pi_u)\) singlet-triplet pair of a quantum dot.

- In the zeroth-order approximation the orbital part of the two-electron wave functions can be expressed as a single determinant

\[
\psi^\pm = \frac{1}{\sqrt{2}} \left[ \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2) \right],
\]
Isosurfaces for singlet-triplet pairs - analysis

- Isosurfaces for the \((1s)(2p)\) singlet-triplet pair of the helium atom and for the \((0\sigma_g)(1\pi_u)\) singlet-triplet pair of a quantum dot.

- Two terms are contributing to the probability densities for He-like systems, namely,
  \[|\psi_{1s}(\vec{r}_1)\psi_{2p}(\vec{r}_2)|^2 + |\psi_{2p}(\vec{r}_1)\psi_{1s}(\vec{r}_2)|^2\]

- Two terms are contributing to the probability densities for quantum, namely,
  \[|\psi_{0\sigma_g}(\vec{r}_1)\psi_{1\pi_u}(\vec{r}_2)|^2 + |\psi_{1\pi_u}(\vec{r}_1)\psi_{0\sigma_g}(\vec{r}_2)|^2\]
Isosurfaces for singlet-triplet pairs - analysis

- Isosurfaces for the \((2p)\) singlet-triplet pair of the helium atom and for the \((0\sigma_g)(1\pi_u)\) singlet-triplet pair of a quantum dot.

- The internal wave functions of the He-like systems have a 'wing' like shape that extents along the \(X\) and \(Y\) axes.

- The internal wave functions of quantum dots have a round shape with a large probability density along the \(Z\) direction.
Isosurfaces for singlet-triplet pairs - analysis

- Isosurfaces for the \((2p)\) singlet-triplet pair of the helium atom and for the \((0\sigma_g)(1\pi_u)\) singlet-triplet pair of a quantum dot.

- In case of He-like systems:
  - The singlet wave function has a larger cross section than the corresponding triplet.
  - The internal wave functions become broader as the nuclear charge \(Z_n\) decreases.
  - The probability density migrates outwards along the \(X\) and \(Y\) axes.
Isosurfaces for singlet-triplet pairs - analysis

- Isosurfaces for the \((2p)\) singlet-triplet pair of the helium atom and for the \((0\sigma_g)(1\pi_u)\) singlet-triplet pair of a quantum dot.

- In case of quantum dots:
  - The size of the internal wave functions becomes larger as \(\omega\) decreases but the difference for different \(\omega\) values is not as large as in the case of He-like systems for different \(Z_n\).
Isosurfaces for singlet-triplet pairs - analysis

- Isosurfaces for the (2p) singlet-triplet pair of the helium atom and for the \((0\sigma_g)(1\pi_u)\) singlet-triplet pair of a quantum dot.

- For both He-like systems and quantum dots the singlet and the corresponding triplet wave internal functions have distinct nodal structures.

- The singlet wave functions have nodes at around \(Z = \pm \pi/2\) while the corresponding triplet wave functions have a node at around \(Z = 0\).

- The difference in the nodal patterns between the singlet and triplet internal wave functions is due to the antisymmetrization of the wave functions.
Isosurfaces for singlet-triplet pairs - analysis

- Isosurfaces for the \((2p)\) singlet-triplet pair of the helium atom and for the \((0\sigma_g)(1\pi_u)\) singlet-triplet pair of a quantum dot.

- The singlet wave function of He-like system with \(Z_n = 20\) and that of quantum dots with \(\omega = 10\) has a large probability density at around \(\phi_- = 0\).

- As \(Z_n\) and \(\omega\) decrease, however, the probability density in this region decreases as well, leading to a clearly visible node for smaller \(Z_n\) and \(\omega\).

- This crucial effect is due to the electron repulsion potential and will be examined in terms of the genuine and conjugate Fermi hole concept.
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Origin of the first Hund rule
Probability density differences in He-like systems

Figure: Difference between the probability density distributions of the (1s)(2p) singlet state $^1P$ and triplet state $^3P$ of He-like systems in the internal space and corresponding electron repulsion potentials.
Probability density differences in quantum dots

Figure: Difference between the probability density distributions of the 
\((0\sigma_g)(1\pi_u)\) singlet \(^1P\) and triplet \(^3P\) states of quantum dots in the 
internal space and corresponding electron repulsion potentials.

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Origin of the first Hund rule
Probability density differences - Analysis

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- In the blue regions the singlet state has a larger probability density than the corresponding triplet.

- In the red regions the triplet state has a larger probability density than the corresponding singlet.
Probability density differences - Analysis

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- The blue regions represent the so-called Fermi holes from which the triplet electrons are repelled.

- The red regions represent the so-called conjugate Fermi holes from which the singlet electrons are repelled.
Probability density differences - Analysis

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- For the $(1s)(2p)$ singlet-triplet pair the zero-order wave function can be written as

\[
\psi^\pm = \frac{1}{\sqrt{4\pi}} \exp(i\phi_+) \left[ \psi_{1s}(r_1)\psi_{2p}(r_2) \exp(-i\phi_-) \pm \psi_{2p}(r_1)\psi_{1s}(r_2) \exp(i\phi_-) \right].
\]
Probability density differences - Analysis

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- For the spatial configuration defined by $r_1 = r_2$ and $\phi = 0, \pm \pi$, that correspond to the case when the electron repulsion potential diverges, the triplet wave function $\Psi^-$ vanishes.

- For the spatial configuration defined by $r_1 = r_2$ and $\phi = \pm \pi/2$, the singlet wave function $\Psi^-$ vanishes.
Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

The appearance of the conjugate Fermi hole is not limited to the \((1s)(2p)\) configuration considered here but represents a general feature in the sense that genuine and conjugate Fermi holes always appear as a pair.
Probability density differences - Analysis

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- The electron repulsion potential penetrates precisely into the Fermi holes.

- Therefore the singlet state is more effected by the electron repulsion potential than the triplet state.
Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

In the regime of large $Z_n$ values the electron repulsion potential is small and a large singlet probability density is found in the vicinity of regions characterized by Fermi holes where $X = Y$ and $Z = 0$ while the triplet density is rather insignificant.
Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

In the regime of small $Z_n$ values the electron repulsion potential is large and in the case of He most of the singlet probability density in the vicinity of the Fermi holes has to migrate into regions where the $X$ and $Y$ coordinates are independently large.
Probability density differences - Analysis

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- Historically, it has been often argued that the outer electron of the triplet state shrinks toward the nucleus yielding a more compact electron density distribution in the triplet state relative to the corresponding singlet state.
Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

However, it is actually the singlet state rather than the triplet one that is responsible for the complexity that is associated with a proper understanding of the origin of Hund’s multiplicity rule:

For small nuclear charges $Z_n$ the electron density distribution in the singlet state *extends* over a much broader region than does the corresponding triplet distribution due to the existence of conjugate Fermi holes.
Probability density differences - Analysis

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- In the case of quantum dots the singlet probability that is located in the vicinity of the Fermi holes migrates out of these regions but there appear no 'wings' for large X and Y that characterize He-like atomic systems.
Figure: Projection of the internal wave functions onto the $XY$ plane for the $(1s)(2p)$ singlet state of He-like systems and for the $(\sigma_g)(\pi_u)$ singlet state of quantum dots. Along the dotted line the electron repulsion potential diverges.
Projection of the internal wave functions - analysis

- Projection of the internal wave functions onto the $XY$ plane for the $(1s)(2p)$ singlet state of He-like systems and for the $(\sigma_g)(\pi_u)$ singlet state of quantum dots.

- In the case of He-like systems this singlet probability density migrates along the $s_1$ and $s_2$ axes.

- In the case of quantum dots the singlet probability density located originally along the line $t_1 = t_2$ migrates out of this region towards both sides of this line.
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Origin of the first Hund rule
The present study focuses on the origin of their differences between He-like systems and quantum dots. It is the concept of genuine and *conjugate* Fermi holes as well as their structure in the internal space that represents the key to an understanding of these differences.
Energy differences between the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.

For large $Z_n$ and $\omega$ values the singlet-triplet energy gap $\Delta E_{\text{tot}}$ is dominated by the two-electron contribution $\Delta E_{\text{two}}$ apparently in accord with the traditional interpretation based on Slater’s paper.

With decreasing $Z_n$ and $\omega$ the two-electron contribution becomes eventually smaller than the one-electron contribution which steadily increases.
There exists a fundamental difference between He-like systems and quantum dots apparent from the behavior in the regime of small $Z_n$ and $ω$:

- In the case of He-like systems the two-electron contribution does indeed vanish around $Z_n = 4$ and becomes significantly negative at $Z_n = 2$.
- In the case of quantum dots the two-electron contribution $ΔE_{two}$ monotonically decreases with decreasing $ω$ and approaches zero in the limit $ω → 0$. 
Traditional interpretation

- Energy differences between the lowest $P$ singlet-triplet pair of states of He-like systems and of quantum dots.

- The traditional interpretation seems to be working in the regime of large $Z_n$ and $\omega$ where the difference in the electron repulsion energy $\Delta E_{\text{two}}$ dominates the singlet-triplet energy gap.

... BUT!
Genuine and conjugate Fermi holes

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- The structure of genuine and conjugate Fermi holes and of the poles of the electron repulsion potential in the internal space explain the difference between the He-like and quantum dot systems:

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Origin of the first Hund rule
Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

In the regime of large $Z_n$ and $\omega$ the singlet wave function has a large probability density in regions defined by the Fermi holes.

Since the poles of the electron repulsion potential penetrate into the Fermi holes, the singlet state is characterized by a larger electron repulsion than the triplet thus supporting the traditional interpretation of Hund’s multiplicity rule.
Genuine and conjugate Fermi holes

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- In the regime of large $Z_n$ and $\omega$ the electron repulsion potential becomes stronger at its poles and pushes the singlet probability density out of the Fermi holes.

- This effects the singlet singlet probability more strongly than the corresponding triplet.

- Therefore the one-body electron density distribution in the singlet and triplet states become increasingly distinct.
Genuine and conjugate Fermi holes

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- In the case of He-like systems the singlet probability density migrates towards the regions of large $r_1$ and large $r_2$ while in the case of quantum dots it stays around the poles of the electron repulsion potential.

- This difference in the spatial distribution of the migrated singlet probability density in these systems originates from the difference in the shell structure of the Coulomb-type and harmonic-oscillator-type orbitals.
Genuine and conjugate Fermi holes

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- For He-like systems this results in a smaller electron repulsion and a smaller decrease of the nuclear attraction energy for the singlet state relative to the triplet state.

- For quantum dots this results in a larger electron repulsion of the singlet state relative to the triplet state.
Understanding the origin of Hund’s rule

- Difference between the probability density distributions of the singlet-triplet pair of states of He-like systems and quantum dots in the internal space and corresponding electron repulsion potentials.

- Historically, it has been often argued that the outer electron of the triplet state shrinks toward the nucleus yielding a more compact electron density distribution in the triplet state relative to the corresponding singlet state.

- However, it is actually the singlet state rather than the triplet one that is responsible for the complexity that is associated with a proper understanding of the origin of Hund’s multiplicity rule:
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   - Theoretical Model and Computational Method

3. Results
   - Singlet-triplet energy differences
   - Internal wave functions
   - Genuine-and-conjugate-Fermi-holes

4. Summary and Acknowledgement
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   - Acknowledgement
   - Reference
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T Sako, A Ichimura, J Paldus and GHF Diercksen

Origin of the first Hund rule
Outline

1. Background
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The lecture is based on the following publication:

T Sako, J Paldus, A Ichimura, and GHF Diercksen
*Origin of the first Hund rule and the structure of Fermi holes in two-dimensional He-like atoms and two-electron quantum dots*
Doi:10.1088/0953-4075/45/23/235001

The lecture is available at (the spoken word prevails):

http://www.mpa-garching.mpg.de/mol_physics/lectures.shtml