Origin of Hund's multiplicity rule in quasi-two-dimensional two-electron quantum dots

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Outline

1. Background
2. Model
   - Theoretical Model and Computational Method
3. Results
   - 2eQD: Spectrum and HF orbitals
   - 2eQD: Normal-mode assignments
   - 2eQD: Origin of Hunds rule in QD's
4. Summary and Acknowledgement
   - Summary
   - Acknowledgement
   - Reference

F. Hund (1896-1997)

- Friedrich Hund in the 1920th

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Quantum dots

- Finite many-body quantum systems consisting of a small number of electrons bound in a fabricated nano-scale potential are referred to as
  - quantum dots or
  - artificial atoms.
- As in usual atoms, the electronic configurations of artificial atoms follow Hund's multiplicity rule.

F. Hund, Z. Physik (1925)

Zur Deutung verwickelter Spektren, insbesondere der Elemente Scandium bis Nickel.

Von **F. Hund** in Göttingen.

Mit drei Abbildungen. (Eingegangen am 22. Juni 1925.)

Auf Grund der Vorstellungen von Russell und Saunders, Pauli und Heisenberg über das Zusammenwirken mehrerer Elektronen bei der Aussendung von Spektrallinien werden die Spektralterme einiger Elemente auf ganz bestimmte, durch Quantenzahlen gekennzeichnete Anordnungen von Elektronen zurückgeführt. Insbesondere werden bei den Elementen Sc bis Ni für die Normalzustände der Elemente und (soweit bekannt) ihrer positiven Ionen, ferner für die übrigen tiefen Terme der Elemente die Quantenzahlen aller Elektronen angegeben. Damit ist der Zusammenhang hergestellt zwischen dem Bau dieser verwickelten Spektren und der Stellung der Elemente im periodischen System.

Man kann mehrere Stufen der Erklärung eines empirisch bekannten Spektrums unterscheiden. Beim Wasserstoff liefert die Bohrsche Quantentheorie mehrfach periodischer Systeme eine quantitativ genaue Festlegung der Spektralterme. Für die übrigen Elemente gibt es keine entsprechende strenge Theorie. Bei einer Anzahl von Elementen, im wesentlichen bei den in den ersten drei Spalten des periodischen Systems stehenden, lassen sich die Spektralterme bestimmten Quantenbahnen eines Elektrons (des Leuchtelektrons) zuordnen (Bohr, Sommerfeld) und die Energiewerte wenigstens angenähert abschätzen. Noch weniger war bisher bei den verwickelteren Spektren, z. B. bei Sc bis Ni möglich. Catalan und die ihm gefolgten Forscher[1]),

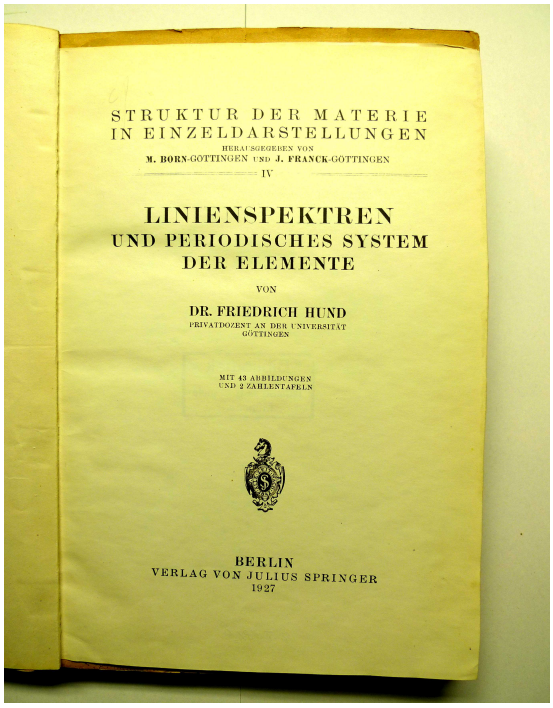
[1]) Über Elemente der mit K beginnenden Periode: Ca: H. N. Russell und F. A. Saunders, Astrophys. Journ. **61**, 38, 1925. Sc: M. A. Catalan, An. Soc. Esp. d. Fis. y Quim. **20**, 606, 1922; **21**, 464, 1923. Ti: C. C. Kiess und H. K. Kiess, Journ. Washington Acad. Sc. **13**, 270, 1923; Journ. Opt. Soc. Amer. **8**, 607, 1924. V: W. F. Meggers, Journ. Washington Acad. Sc. **13**, 317, 1923; O. Laporte, Naturwissensch. **11**, 779, 1923; Phys. ZS. **24**, 510, 1923; M. A. Catalan, An. Soc. Esp. d. Fis. y Quim. **22**, 72, 1924; H. Gieseler und W. Grotrian, ZS. f. Phys. **25**, 342, 1924; K. Bechert und L. A. Sommer, ZS. f. Phys. **31**, 145, 1925. Cr: M. A. Catalan, Phil. Trans. Roy. Soc. London (A) **223**, 127, 1922; H. Gieseler, Ann. d. Phys. **69**, 147, 1922; C. C. und H. K. Kiess, Science **56**, 666, 1922, Nr. 1458; M. A. Catalan, An. Soc. Esp. d. Fis. y Quim. **21**, 84, 1923. Mn: M. A. Catalan, Phil. Trans. Roy. Soc. London (A) **223**, 127, 1922; A. Sommerfeld, Ann. d. Phys. **70**, 32, 1923; E. Back, ZS. f. Phys. **15**, 206, 1923. Fe: F. M. Walters jr., Journ. Washington Acad. Sc. **13**, 243, 1923; H. Gieseler und W. Grotrian, ZS. f. Phys. **22**, 245, 1924; **25**, 243, 1924; E. v. Angerer und G. Joos, Naturwissensch. **12**, 140, 1924; Ann. d. Phys. **74**, 743, 1924; O. Laporte, ZS. f. Phys. **23**, 135, 1924; **26**, 1, 1924. Co: F. M. Walters jr.,

Hund's three rules were initially derived empirically in atomic spectroscopy of the pre-quantum-mechanical era.

- Friedrich Hund, Zeitschrift für Physik **33**, 345 (1925)

They predict the ordering of the energy levels with different angular momentum and spin quantum numbers.

F. Hund, Linienspekten (1927)



STRUKTUR DER MATERIE
IN EINZELDARSTELLUNGEN
HERAUSGEGEBEN VON
M. BORN-GÖTTINGEN UND J. FRANCK-GÖTTINGEN
IV

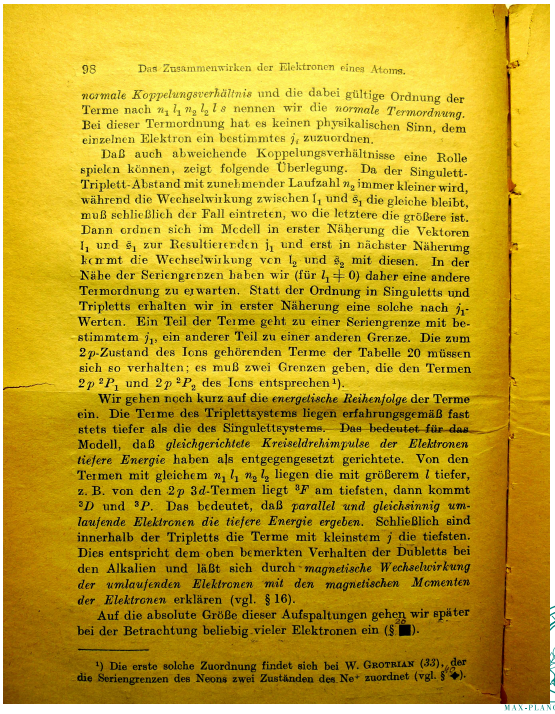
LINIENSPEKTREN
UND PERIODISCHES SYSTEM
DER ELEMENTE

VON

DR. FRIEDRICH HUND
PRIVATDOZENT AN DER UNIVERSITÄT
GÖTTINGEN

MIT 43 ABBILDUNGEN
UND 2 ZAHLENTAFELN

BERLIN
VERLAG VON JULIUS SPRINGER
1927



98 Das Zusammenwirken der Elektronen eines Atoms.

normale Koppelungsverhältnis und die dabei gültige Ordnung der Terme nach $n_1\, l_1\, n_2\, l_2\, l\, s$ nennen wir die *normale Termordnung*. Bei dieser Termordnung hat es keinen physikalischen Sinn, dem einzelnen Elektron ein bestimmtes j_i zuzuordnen.

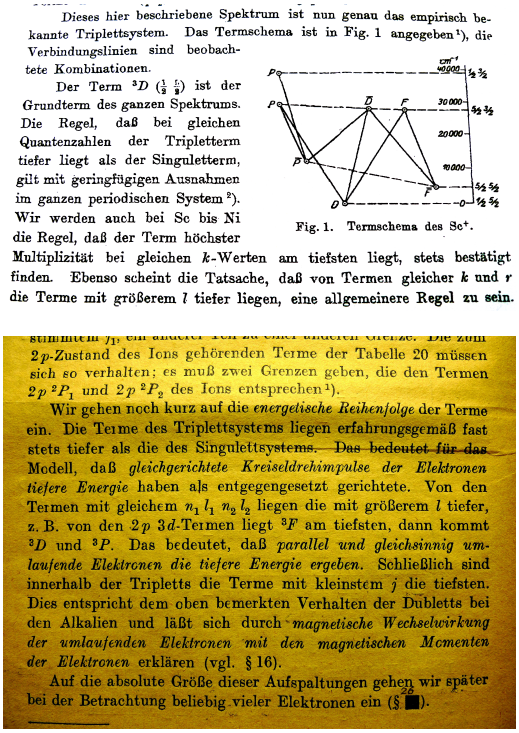
Daß auch abweichende Koppelungsverhältnisse eine Rolle spielen können, zeigt folgende Überlegung. Da der Singulett-Triplett-Abstand mit zunehmender Laufzahl n_2 immer kleiner wird, während die Wechselwirkung zwischen l_i und $\mathfrak{s}_i$ die gleiche bleibt, muß schließlich der Fall eintreten, wo die letztere die größere ist. Dann ordnen sich im Modell in erster Näherung die Vektoren l_1 und $\mathfrak{s}_1$ zur Resultierenden j_1 und erst in nächster Näherung kommt die Wechselwirkung von l_2 und $\mathfrak{s}_2$ mit diesen. In der Nähe der Seriengrenzen haben wir (für $l_1 \neq 0$) daher eine andere Termordnung zu erwarten. Statt der Ordnung in Singuletts und Tripletts erhalten wir in erster Näherung eine solche nach j_1-Werten. Ein Teil der Terme geht zu einer Seriengrenze mit bestimmtem j_1, ein anderer Teil zu einer anderen Grenze. Die zum $2p$-Zustand des Ions gehörenden Terme der Tabelle 20 müssen sich so verhalten; es muß zwei Grenzen geben, die den Termen $2p\,{}^2P_1$ und $2p\,{}^2P_2$ des Ions entsprechen[1]).

Wir gehen noch kurz auf die *energetische Reihenfolge* der Terme ein. Die Terme des Triplettsystems liegen erfahrungsgemäß fast stets tiefer als die des Singulettsystems. Das bedeutet für das Modell, daß *gleichgerichtete Kreiseldrehimpulse der Elektronen tiefere Energie* haben als entgegengesetzt gerichtete. Von den Termen mit gleichem $n_1\, l_1\, n_2\, l_2$ liegen die mit größerem l tiefer, z. B. von den $2p\,3d$-Termen liegt ${}^3F$ am tiefsten, dann kommt ${}^3D$ und ${}^3P$. Das bedeutet, daß *parallel und gleichsinnig umlaufende Elektronen die tiefere Energie ergeben*. Schließlich sind innerhalb der Tripletts die Terme mit kleinstem j die tiefsten. Dies entspricht dem oben bemerkten Verhalten der Dubletts bei den Alkalien und läßt sich durch *magnetische Wechselwirkung der umlaufenden Elektronen mit den magnetischen Momenten der Elektronen* erklären (vgl. § 16).

Auf die absolute Größe dieser Aufspaltungen gehen wir später bei der Betrachtung beliebig vieler Elektronen ein (§ ■).

[1]) Die erste solche Zuordnung findet sich bei W. Grotrian (33), der die Seriengrenzen des Neons zwei Zuständen des Ne^+ zuordnet (vgl. § ◆).

Hund's first rule



Dieses hier beschriebene Spektrum ist nun genau das empirisch bekannte Triplettsystem. Das Termschema ist in Fig. 1 angegeben[1]), die Verbindungslinien sind beobachtete Kombinationen.

Der Term ^3D ($\frac{1}{2}$ $\frac{5}{2}$) ist der Grundterm des ganzen Spektrums. Die Regel, daß bei gleichen Quantenzahlen der Tripletterm tiefer liegt als der Singuletterm, gilt mit geringfügigen Ausnahmen im ganzen periodischen System[2]). Wir werden auch bei Sc bis Ni die Regel, daß der Term höchster Multiplizität bei gleichen k-Werten am tiefsten liegt, stets bestätigt finden. Ebenso scheint die Tatsache, daß von Termen gleicher k und r die Terme mit größerem l tiefer liegen, eine allgemeinere Regel zu sein.

Fig. 1. Termschema des Sc^+.

stimmtem j_1, ein anderer Teil zu einer anderen Grenze. Die zum $2p$-Zustand des Ions gehörenden Terme der Tabelle 20 müssen sich so verhalten; es muß zwei Grenzen geben, die den Termen $2p\,^2P_1$ und $2p\,^2P_2$ des Ions entsprechen[1]).

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Auf die absolute Größe dieser Aufspaltungen gehen wir später bei der Betrachtung beliebig vieler Elektronen ein (§ 26).

Hund's first rule states

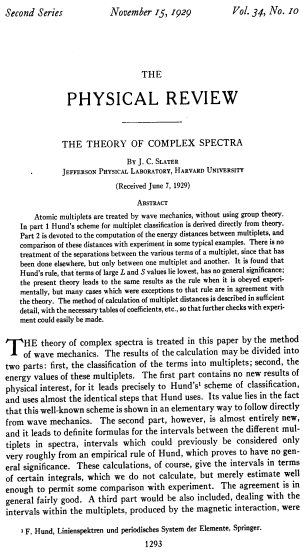
- that among the different spin states belonging to the same orbital configuration
- the highest spin state has the lowest energy.

Validity of Hund's rules

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)

JC Slater, Physical Review (1929)



Second Series *November 15, 1929* *Vol. 34, No. 10*

THE
PHYSICAL REVIEW

THE THEORY OF COMPLEX SPECTRA

By J. C. Slater
Jefferson Physical Laboratory, Harvard University

(Received June 7, 1929)

Abstract

Atomic multiplets are treated by wave mechanics, without using group theory. In part I Hund's scheme for multiplet classification is derived directly from theory. Part 2 is devoted to the computation of the energy distances between multiplets, and comparison of these distances with experiment in some typical examples. There is no treatment of the separations between the various terms of a multiplet, since that has been done elsewhere, but only between one multiplet and another. It is found that Hund's rule, that terms of large L and S values lie lowest, has no general significance; the present theory leads to the same results as the rule when it is obeyed experimentally, but many cases which were exceptions to that rule are in agreement with the theory. The method of calculation of multiplet distances is described in sufficient detail, with the necessary tables of coefficients, etc., so that further checks with experiment could easily be made.

THE theory of complex spectra is treated in this paper by the method of wave mechanics. The results of the calculation may be divided into two parts: first, the classification of the terms into multiplets; second, the energy values of these multiplets. The first part contains no new results of physical interest, for it leads precisely to Hund's[1] scheme of classification, and uses almost the identical steps that Hund uses. Its value lies in the fact that this well-known scheme is shown in an elementary way to follow directly from wave mechanics. The second part, however, is almost entirely new, and it leads to definite formulas for the intervals between the different multiplets in spectra, intervals which could previously be considered only very roughly from an empirical rule of Hund, which proves to have no general significance. These calculations, of course, give the intervals in terms of certain integrals, which we do not calculate, but merely estimate well enough to permit some comparison with experiment. The agreement is in general fairly good. A third part would be also included, dealing with the intervals within the multiplets, produced by the magnetic interaction, were

[1] F. Hund, Linienspektren und periodisches System der Elemente, Springer.

1293

Slater was the first to develop a theory of complex spectra on a quantum mechanical basis.

- John C. Slater, Physical Review **34**, 1293 (1929)

Early interpretation of Hund's first rule

Based on Slater's succesful interpretation of complex spectra it was generally assumed that Hund's first rule is intimitely connected with

- electronic correlation.

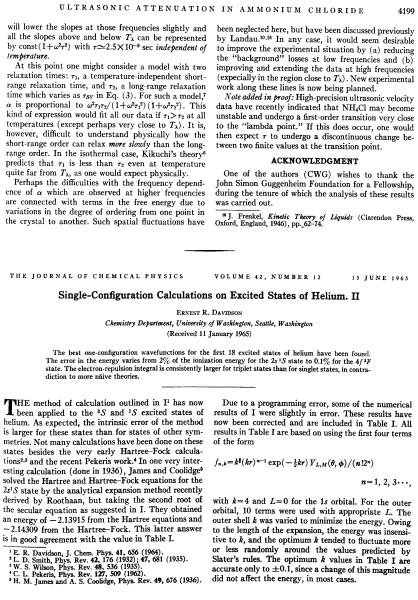
It was concluded

- that in the triplet state the lectrons 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.

WRONG !

... and this is **WRONG !**

ER Davidson, Journal of Chemical Physics (1964/5)



ULTRASONIC ATTENUATION IN AMMONIUM CHLORIDE 4199

will lower the slopes at those frequencies slightly and all the slopes above and below T_λ can be represented by const$\times(1+\omega^2\tau^2)$ with $\tau \simeq 2.5\times10^{-9}$ sec *independent of temperature*.

At this point one might consider a model with two relaxation times: τ_1, a temperature-independent short-range relaxation time, and τ_2, a long-range relaxation time which varies as τ_{RP} in Eq. (3). For such a model,[7] α is proportional to $\omega^2\tau_1\tau_2/(1+\omega^2\tau_2^2)(1+\omega^2\tau_1^2)$. This kind of expression would fit all our data if $\tau_1 \gg \tau_2$ at all temperatures (except perhaps very close to T_λ). It is, however, difficult to understand physically how the short-range order can relax *more slowly* than the long-range order. In the isothermal case, Kikuchi's theory[6] predicts that τ_1 is less than τ_2 even at temperature quite far from T_λ, as one would expect physically.

Perhaps the difficulties with the frequency dependence of α which are observed at higher frequencies are connected with terms in the free energy due to variations in the degree of ordering from one point in the crystal to another. Such spatial fluctuations have been neglected here, but have been discussed previously by Landau.[10,20] In any case, it would seem desirable to improve the experimental situation by (a) reducing the "background"[1] losses at low frequencies and (b) improving and extending the data at high frequencies (especially in the region close to T_λ). New experimental work along these lines is now being planned.

Note added in proof: High-precision ultrasonic velocity data have recently indicated that NH_4Cl may become unstable and undergo a first-order transition very close to the "lambda point." If this does occur, one would then expect τ to undergo a discontinuous change between two finite values at the transition point.

ACKNOWLEDGMENT

One of the authors (CWG) wishes to thank the John Simon Guggenheim Foundation for a Fellowship, during the tenure of which the analysis of these results was carried out.

[20] J. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford, England, 1946), pp. 62-74.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 42, NUMBER 12 15 JUNE 1965

Single-Configuration Calculations on Excited States of Helium. II

ERNEST R. DAVIDSON
Chemistry Department, University of Washington, Seattle, Washington
(Received 11 January 1965)

The best one-configuration wavefunctions for the first 18 excited states of helium have been found. The error in the energy varies from 2% of the ionization energy for the $2s\,^1S$ state to 0.1% for the $4f\,^{1,3}F$ state. The electron-repulsion integral is consistently larger for triplet states than for singlet states, in contradiction to more naïve theories.

THE method of calculation outlined in I[1] has now been applied to the ^1S and ^3S excited states of helium. As expected, the intrinsic error of the method is larger for these states than for states of other symmetries. Not many calculations have been done on these states besides the very early Hartree–Fock calculations[2,3] and the recent Pekeris work.[4] In one very interesting calculation (done in 1936), James and Coolidge[3] solved the Hartree and Hartree–Fock equations for the $2s^1S$ state by the analytical expansion method recently derived by Roothaan, but taking the second root of the secular equation as suggested in I. They obtained an energy of -2.13915 from the Hartree equations and -2.14309 from the Hartree–Fock. This latter answer is in good agreement with the value in Table I.

Due to a programming error, some of the numerical results of I were slightly in error. These results have now been corrected and are included in Table I. All results in Table I are based on using the first four terms of the form

$$f_{n,k}=\phi^k(kr)^{n-1}\exp(-\tfrac{1}{2}kr)\,Y_{L,M}(\theta,\phi)/(n!2^n)^{\frac{1}{2}}$$
$$n=1,\,2,\,3\cdots,$$

with $k=4$ and $L=0$ for the $1s$ orbital. For the outer orbital, 10 terms were used with appropriate L. The outer shell k was varied to minimize the energy. Owing to the length of the expansion, the energy was insensitive to k, and the optimum k tended to fluctuate more or less randomly around the values predicted by Slater's rules. The optimum k values in Table I are accurate only to ±0.1, since a change of this magnitude did not affect the energy, in most cases.

[1] E. R. Davidson, J. Chem. Phys. **41**, 656 (1964).
[2] L. D. Smith, Phys. Rev. **42**, 176 (1932); **47**, 681 (1935).
[3] W. S. Wilson, Phys. Rev. **48**, 536 (1935).
[4] C. L. Pekeris, Phys. Rev. **127**, 509 (1962).
[5] H. M. James and A. S. Coolidge, Phys. Rev. **49**, 676 (1936).

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 näive theories.

- Ernst R. Davidson, Journal of Chemical Physics **41**, 656 (1964); **42**, 4199 (1965)

Consequence of Davidson's study

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

- much larger energy decrease

due to the nuclear attraction potential.

The Origin ?

Although this is a reasonable explanation of Hund's first rule its

ORIGIN

is still unclear.

The Origin ?

In order to understand the origin of Hund's multiplicity rule for artificial atoms,

- a full configuration interaction (CI) calculation

has been carried out for a system of

- a quasi-two-dimensional isotropic harmonic-oscillator quantum dot

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Hamiltonian

The Hamiltonian operator used in the present study for a model of quasi-two-dimensional two-electron quantum dots is given by

$$\mathcal{H} = \sum_{i=1}^{2} \left[-\tfrac{1}{2}\nabla_i^2 \right] + \sum_{i=1}^{2} w_{\mathrm{q2D}}(\mathbf{r}_i) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

where the one-electron confining potential w_{q2D} has the form

$$w_{\mathrm{q2D}}(\boldsymbol{r}) = \tfrac{1}{2}\omega_{xy}^2(x^2 + y^2) + \tfrac{1}{2}\omega_z^2 z^2.$$

One-electron confining potential

$$w_{\mathrm{q2D}}(\boldsymbol{r}) = \tfrac{1}{2}\omega_{xy}^2(x^2 + y^2) + \tfrac{1}{2}\omega_z^2 z^2$$

- For sufficiently large values of ω_z ($\omega_z >> \omega_{xy}$) electrons bound by the above one-electron confining potential are
  - strongly compressed along the z direction and represent
  - a quasi-two-dimensional harmonic-oscillator quantum dot with an oblate-top, disk-like shape within the xy plane.
- In the present study ω_z has been chosen to be 100 times larger than ω_{xy}, i.e., ω_z = 100$\times\omega_{xy}$.

Quantum Mechanical Method

The Schrödinger equation for the Hamiltonian is solved by using the

- *full configuration interaction (CI)* method employing
- closed-shell Hartree-Fock orbitals.

Cartesian anisotropic Gaussian-type orbitals

- The one-electron Hartree-Fock orbitals are expanded in Cartesian anisotropic Gaussian-type orbitals (C-aniGTO's) centered at (b_x, b_y, b_z):

$$\chi_{ani}^{\vec{a},\vec{\zeta}}(\vec{r};\vec{b}) = x_{b_x}^{a_x} y_{b_y}^{a_y} z_{b_z}^{a_z} \exp(-\zeta_x x_{b_x}^2 - \zeta_y y_{b_y}^2 - \zeta_z z_{b_z}^2),$$

$x_{b_x} = (x - b_x)$, etc.

Cartesian anisotropic Gaussian-type orbitals

- Following the quantum chemical convention the orbitals are classified as s-type, p-type, ... for $a = a_x + a_y + a_z = 0$, 1, ..., respectively.
- The (b_x, b_y, b_z) parameters are chosen in general to coincide with the center of the confining potential, i.e. the origin of the Cartesian coordinate system.
- The optimal orbital exponents $(\zeta_x, \zeta_y, \zeta_z)$ are chosen to be $(\omega_x/2, \omega_y/2, \omega_z/2)$.

Basi set

As basis set a total of 66 C-aniGTO's are used sharing the common exponents

- $(\omega_{xy}/2, \omega_{xy}/2, \omega_z/2)$

and designated

- (1s1p1d1f1g1h1i1j1k1l1m]

Reason for the Model

The two-electron nature of the model permits

- the separation of the orbital and spin degrees of freedom.

The harmonic nature of the confining potential permits

- the separation of the center-of-mass and internal degrees of freedom.

The low dimensionality of the model reduces the dimension of the internal space to two and permits

- the direct visualisation of the internal wavefunctions within a plane.

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Energy spectrum

- Two-electron He-like atoms involve only one-electron excitations from the singlet ground state $(1s)^2\ ^1S$.
- In two-electron quantum dots, multiple excitations play a fundamental role in the understanding of their complex energy spectra.

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Energy spectrum

- The analysis of the excitation spectra of two-electron quantum dots is simplyfied for strong confinement strength ω_{xy}, since in this case the complexity of the corresponding spectra is considerably reduced.
- The energy spectrum of two electrons confined by a quasi-two-dimensional harmonic potential with (ω_{xy}, ω_z) = (10.0,1000.0) relative to the ground state energy is displayed in the following figure.

2eQD: Energy spectrum

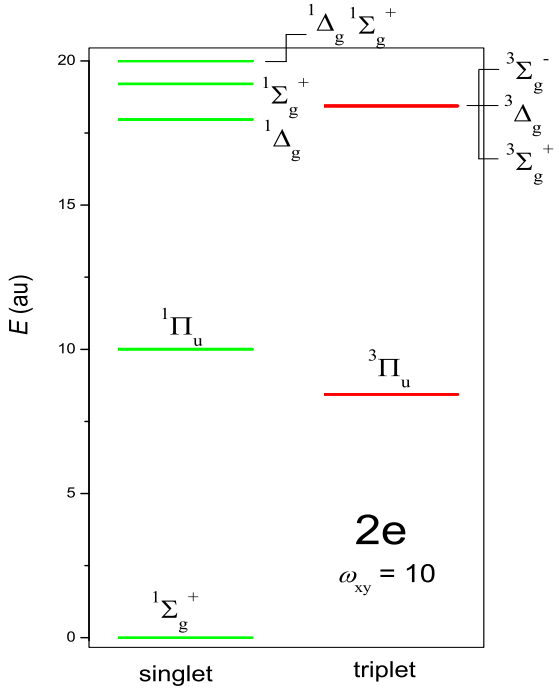
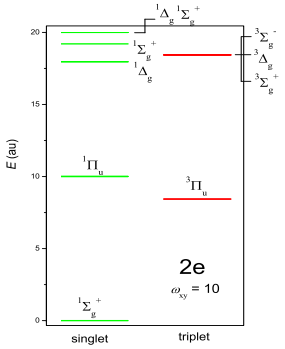


Figure: Energy spectrum of two electrons confined by a quasi two-dimensional harmonic potential relative to the ground state energy.

2eQD: Energy spectrum - analysis

- Energy spectrum.

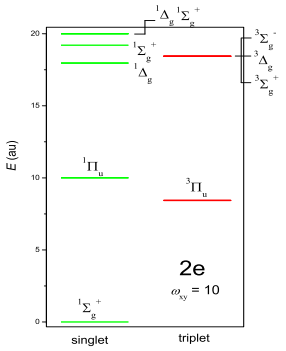


- The symbol ^{2S+1}A represents
  - the spin multiplicity $2S + 1$ and
  - the spatial symmetry label A

  in the $D_{\infty,h}$ symmetry group.
- Energy levels of singlet and triplet states are rendered in green and red, respectively.
- The *polyad quantum number* v_p is defined by
  - the total number of nodes of the leading configuration in the CI wave functions

2eQD: Energy spectrum - analysis

- Energy spectrum



- The energy spectrum displayed in the figure shows a harmonic band structure, in which the energy levels with the same value of v_p are close together, while those having a different value of v_p are separated by multiples of ω_{xy}.
- The 5th level in the singlet manifold is doubly degenerate and the 2nd level in the triplet manifold is triply degenerate.

2eQD: Wavefunction

- The low-lying closed-shell Hartree-Fock orbitals are displayed in the following figure in the order of increasing orbital energies.
- The orbitals are labeled by the symbol $[v_{xy}, v_z]a$ with
  - v_{xy} representing the number of nodes within the xy plane,
  - v_z representing the number of nodes along the z axis and
  - a representing the spatial symmetry label.

2eQD: Wavefunction

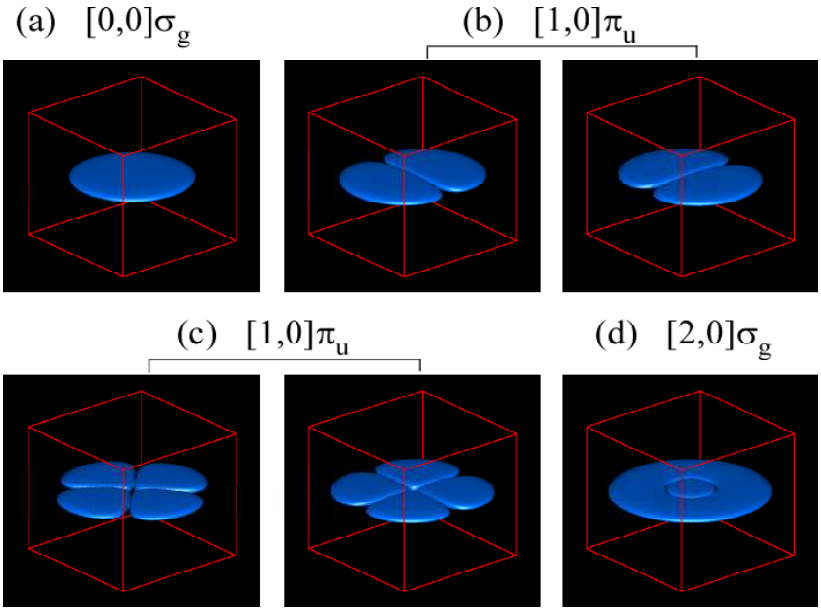
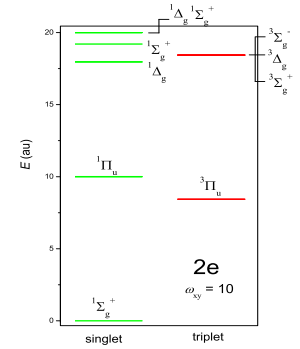
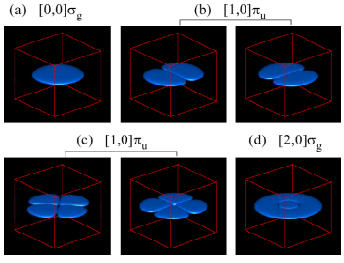


Figure: Closed-shell HF orbitals. The orbitals are labeled by $[v_{xy}, v_z]a$.

2eQD: Wavefunction - analysis

- Energy spectrum & HF orbitals





- Two types of nodes are observed in the *xy* plane:
  - *angular nodes* originating from the angular momentum with respect to the *z* axis and
  - circular *radial nodes* cutting the orbital circularly about the *z* axis.
- The number of angular and radial nodes is designated by $|l_z|$ and n_r, respectively.

2eQD: Leading configurations

- Energy spectrum & HF orbitals

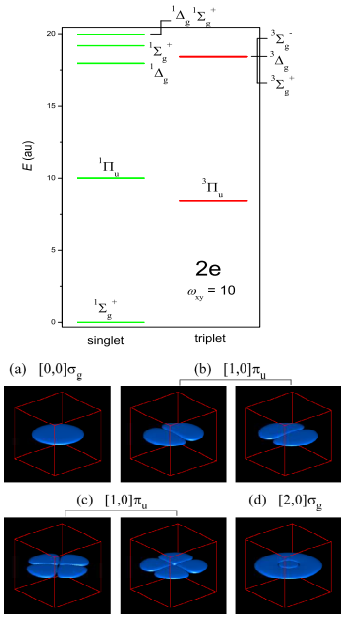
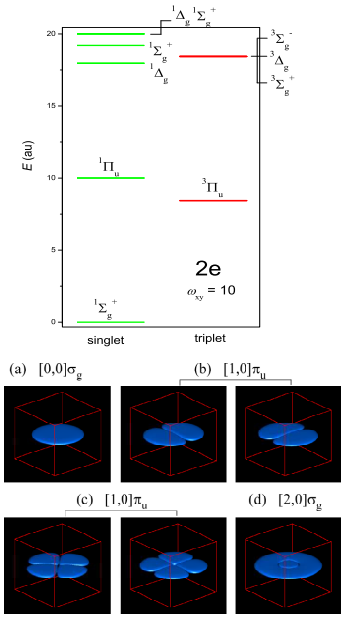


Table: Leading configurations in the CI wave functions.

v_p	E	state	configuration	coef.
0	0.000	$^1\Sigma_g^+$	$([0,0]\sigma_g)^2$	0.995
1	8.437	$^3\Pi_u$	$([0,0]\sigma_g)([1,0]\pi_u)$	0.998
1	10.002	$^1\Pi_u$	$([0,0]\sigma_g)([1,0]\pi_u)$	0.993
2	17.968	$^1\Delta_g$	$([0,0]\sigma_g)([2,0]\delta_g)$	0.499
			$([1,0]\pi_u)^2$	0.498
2	18.437	$^3\Sigma_g^+$	$([0,0]\sigma_g)([2,0]\sigma_g)$	0.997
2	18.438	$^3\Delta_g$	$([0,0]\sigma_g)([2,0]\delta_g)$	0.997
2	18.438	$^3\Sigma_g^-$	$([1,0]\pi_u)([1,0]\pi_u)$	0.996
2	19.208	$^1\Sigma_g^+$	$([0,0]\sigma_g)([2,0]\sigma_g)$	0.498
			$([1,0]\pi_u)^2$	0.498
2	20.003	$^1\Sigma_g^+$	$([0,0]\sigma_g)([2,0]\sigma_g)$	0.498
			$([1,0]\pi_u)^2$	0.490
2	20.004	$^1\Delta_g$	$([0,0]\sigma_g)([2,0]\delta_g)$	0.495
			$([1,0]\pi_u)^2$	0.496

2eQD: Leading configurations -analysis

- Energy spectrum & HF orbitals



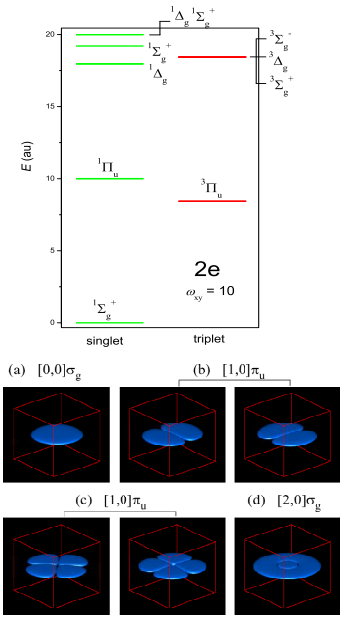
- Leading configurations in the CI wave functions.

v_p	E	state	configuration	coef.
0	0.000	$^1\Sigma_g^+$	$([0,0]\sigma_g)^2$	0.995
1	8.437	$^3\Pi_u$	$([0,0]\sigma_g)([1,0]\pi_u)$	0.998
1	10.002	$^1\Pi_u$	$([0,0]\sigma_g)([1,0]\pi_u)$	0.993

- The $^1\Sigma_g^+$ ground state has the leading configuration $([0,0]\sigma_g)^2$ with the weight 0.995
- The first excited $^1\Pi$ singlet state and the lowest $^3\Pi$ triplet state have the same leading configuration $([0,0]\sigma_g)([1,0]\pi_u)$ with the weights 0.993 and 0.998, respectively. This implies that they form a singlet-triplet pair to which the Hund multiplicity rule applies.

2eQD: Leading configurations - analysis

- Energy spectrum & HF orbitals



- Leading configurations in the CI wave functions.

v_p	E	state	configuration	coef.
2	17.968	$^1\Delta_g$	$([0,0]\sigma_g)([2,0]\delta_g)$	0.499
			$([1,0]\pi_u)^2$	0.498
2	19.208	$^1\Sigma_g^+$	$([0,0]\sigma_g)([2,0]\sigma_g)$	0.498
			$([1,0]\pi_u)^2$	0.498
2	20.003	$^1\Sigma_g^+$	$([0,0]\sigma_g)([2,0]\sigma_g)$	0.498
			$([1,0]\pi_u)^2$	0.490
2	20.004	$^1\Delta_g$	$([0,0]\sigma_g)([2,0]\delta_g)$	0.495
			$([1,0]\pi_u)^2$	0.496

- In the singlet manifold with $v_p = 2$,
  - all three states involve two leading configurations with almost the same weights, indicating a strong configuration mixing, and
  - the two $^1\Sigma_g^+$ singlet states share the same set of two leading configurations $([0,0]\sigma_g)([2,0]\sigma_g)$ and $([1,0]\pi_u)^2$

Outline

1 Background

2 Model
- Theoretical Model and Computational Method

3 Results
- 2eQD: Spectrum and HF orbitals
- 2eQD: Normal-mode assignments
- 2eQD: Origin of Hunds rule in QD's

4 Summary and Acknowledgement
- Summary
- Acknowledgement
- Reference

2eQD: Normal coordinates

$$
\begin{aligned}
x_s &= \frac{1}{\sqrt{2}}[x_1 + x_2], \\
y_s &= \frac{1}{\sqrt{2}}[y_1 + y_2], \\
x_a &= \frac{1}{\sqrt{2}}[x_1 - x_2], \\
y_a &= \frac{1}{\sqrt{2}}[y_1 - y_2],
\end{aligned}
$$

2eQD: Hamiltonian in normal coordinates

- The symmetric coordinates x_s and y_s represent the center-of-mass degrees of freedom, while the anti-symmetric coordinates x_a and y_a represent the internal degrees of freedom.
- Using these symmetric coordinates and neglecting the dependence on the z coordinate, the Hamiltonian separates into the sum of two contributions, depending either on the coordinates (x_s, y_s) or (x_a, y_a),

$$\mathcal{H}_{\mathrm{2D}} = \mathcal{H}_{\mathrm{c.o.m}}(x_s, y_s) + \mathcal{H}_{\mathrm{int}}(x_a, y_a),$$

2eQD: Center-of-mass and internal Hamiltonian

$$\mathcal{H}_{\mathrm{c.o.m}} = -\frac{1}{2}\left[\frac{\partial^2}{\partial x_s^2} + \frac{\partial^2}{\partial y_s^2}\right] + \frac{1}{2}\omega_{xy}^2\left[x_s^2 + y_s^2\right],$$

$$\begin{aligned}\mathcal{H}_{\mathrm{int}} &= -\frac{1}{2}\left[\frac{\partial^2}{\partial x_a^2} + \frac{\partial^2}{\partial y_a^2}\right] + \frac{1}{2}\omega_{xy}^2\left[x_a^2 + y_a^2\right] \\ &\quad + \frac{1}{\sqrt{2(x_a^2 + y_a^2)}}. \end{aligned} \tag{1}$$

2eQD: Center-of-mass Hamiltonian

$$\mathcal{H}_{\mathrm{c.o.m}} = -\frac{1}{2}\left[\frac{\partial^2}{\partial x_s^2} + \frac{\partial^2}{\partial y_s^2}\right] + \frac{1}{2}\omega_{xy}^2\left[x_s^2 + y_s^2\right],$$

- The Hamiltonian $\mathcal{H}_{\mathrm{c.o.m}}$ is the Hamiltonian for a two-dimensional isotropic harmonic oscillator.
- The eigenstates $\Psi_{\mathrm{c.o.m}}^{n_s,l_s}$ of $\mathcal{H}_{\mathrm{c.o.m}}$ are labelled by the two quantum numbers n_s and l_s as representing the number of radial nodes and the angular momentum about the z axis.
- The eigenenergy $E_{c.o.m}$ is represented in terms of these quantum numbers as $E_{c.o.m} = \omega_{xy}[2n_s + l_s + 2]$.

2eQD: Internal Hamiltonian

$$\mathcal{H}_{\rm int} = -\frac{1}{2}\left[\frac{\partial^2}{\partial x_a^2} + \frac{\partial^2}{\partial y_a^2}\right] + \frac{1}{2}\omega_{xy}^2\left[x_a^2 + y_a^2\right] + \frac{1}{\sqrt{2(x_a^2 + y_a^2)}}.$$

- The Hamiltonian $\mathcal{H}_{\rm int}$ is the sum of a two-dimensional isotropic harmonic-oscillator Hamiltonian and of a singular potential that has an axial symmetry about the origin.
- The eigenstates $\Psi_{\rm int}^{n_a,l_a}$ are labelled by the radial quantum number n_a and the angular momentum quantum number l_a.
- The eigenstates of the total Hamiltonian are labeled by the set of four normal-mode quantum numbers (n_s, l_s, n_a, l_a).

2eQD: Energies and densities for the i-Hamiltonian

- The eigenenergy $E_{\rm int}^{n_a,l_a}$ of the internal Hamiltonian relative to the energy of the lowest state and the plot of the square-density of the internal eigenfunction $\Psi_{\rm int}^{n_a,l_a}$ are displayed in the following figure.
- The ω_{xy}-scaled dimensionless internal coordinates $(x_a\sqrt{\omega_{xy}}, y_a\sqrt{\omega_{xy}})$ have been used in the density plots for convenience in the later discussion concerning the dependence of the results on the confinement strength.
- For comparison, the spectrum of the total energy has also been plotted on the left hand side of the figure.

2eQD: Energies and densities for the i-Hamiltonian

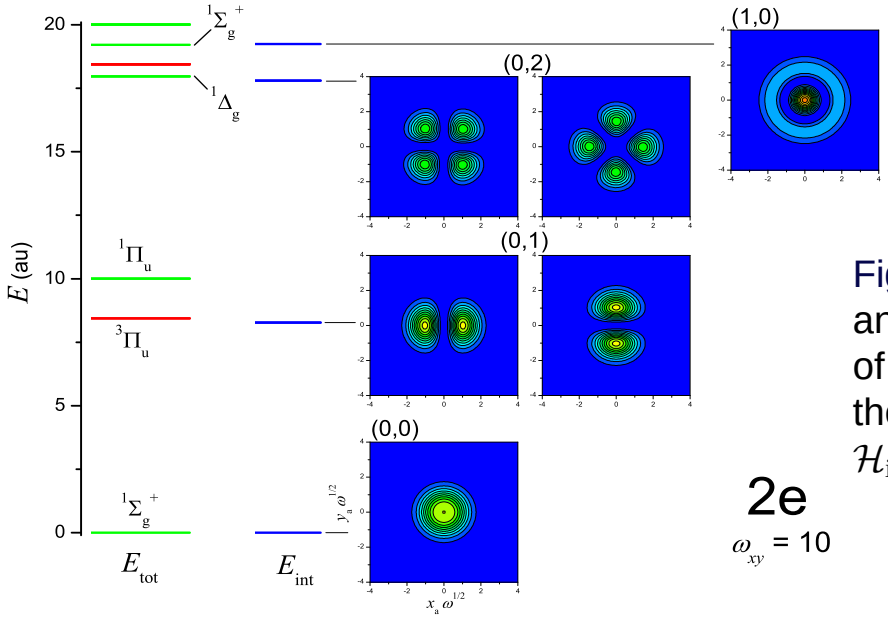
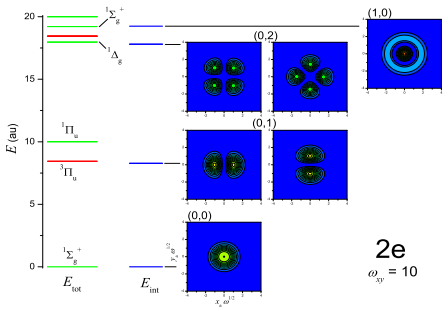


Figure: Eigenenergies and square-density plot of the eigenfunctions for the internal Hamiltonian $\mathcal{H}_{\text{int}}$

2eQD: Energies and square-densities - analysis

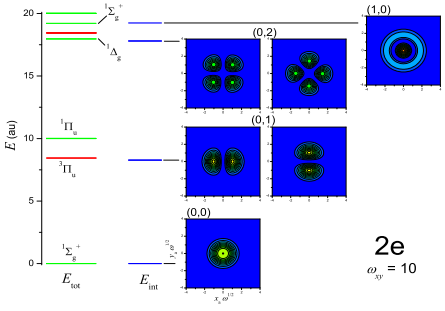
- Energy spectrum & density plot



- Some levels in the total energy spectrum have a corresponding level in the internal energy spectrum at nearly the same height, others not.

2eQD: Energies and square-densities - analysis

- Energy spectrum & density plot



- Levels having a corresponding counterpart in the internal energy spectrum are associated with the states that have no excitation into the center-of-mass degrees of freedom.
- Levels having no counterpart in the internal energy spectrum are generated by excitation into the center-of-mass modes, and their energy is given by the sum of the internal energy and of a multiple of ω_{xy}.

2eQD: Assignment by normal-mode q-numbers

- Energy spectrum

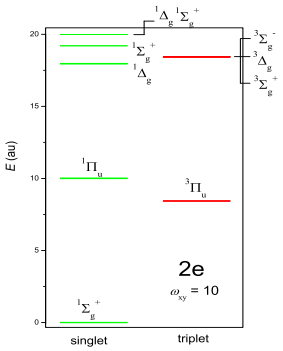
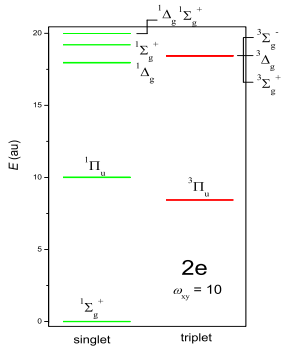


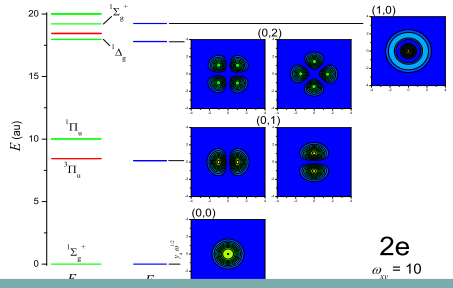
Table: Assignments based on the normal-mode quantum numbers (n_s, l_s, n_a, l_a) for the low-lying states.

v_p	E	state	n_s	l_s	n_a	l_a	$\lvert l_s + l_a \rvert$
0	0.000	$^1\Sigma_g^+$	0	0	0	0	0
1	8.437	$^3\Pi_u$	0	0	0	±1	1
1	10.002	$^1\Pi_u$	0	±1	0	0	1
2	17.968	$^1\Delta_g$	0	0	0	±2	2
2	18.437	$^3\Sigma_g^+$	0	+1	0	-1	0
			0	-1	0	+1	0
2	18.438	$^3\Delta_g$	0	+1	0	+1	2
			0	-1	0	-1	2
2	18.438	$^3\Sigma_g^-$	0	+1	0	-1	0
			0	-1	0	+1	0
2	19.208	$^1\Sigma_g^+$	0	0	1	0	0
2	20.003	$^1\Sigma_g^+$	1	0	0	0	0
2	20.004	$^1\Delta_g$	0	±2	0	0	2

2eQD: $v_p = 1$ manifold - analysis

- Energy spectrum & density plot





- Assignments based on the normal-mode quantum numbers (n_s, l_s, n_a, l_a) for the low-lying states.

v_p	E	state	n_s	l_s	n_a	l_a	$\lvert l_s + l_a \rvert$
0	0.000	$^1\Sigma_g^+$	0	0	0	0	0
1	8.437	$^3\Pi_u$	0	0	0	± 1	1
1	10.002	$^1\Pi_u$	0	± 1	0	0	1

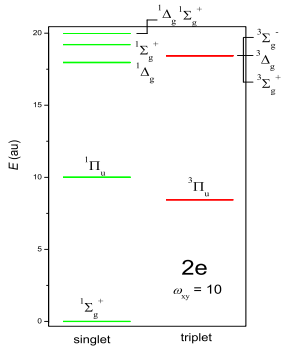
- The $^1\Sigma_g^+$ ground state involves neither an excitation into the center-of-mass mode nor into the internal mode.
- The lowest $^3\Pi_u$ triplet state involves an excitation of one quantum into the angular mode of the internal degrees of freedom, as can be seen from the density plot.

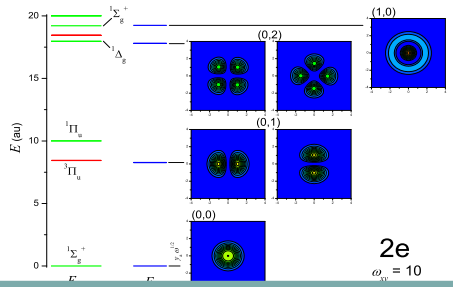
Background
Model
Results
Summary and Acknowledgement

2eQD: Spectrum and HF orbitals
2eQD: Normal-mode assignments
2eQD: Origin of Hunds rule in QD's

2eQD: $v_p = 1$ manifold - analysis

Energy spectrum & density plot





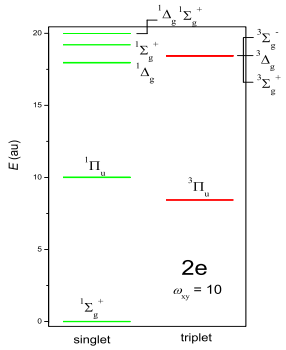
Assignments based on the normal-mode quantum numbers (n_s, l_s, n_a, l_a) for the low-lying states.

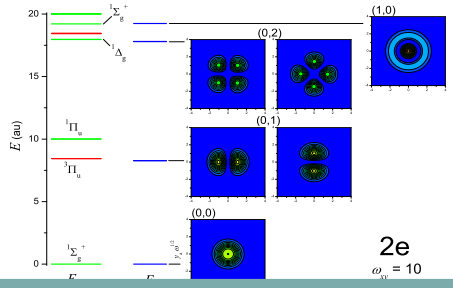
v_p	E	state	n_s	l_s	n_a	l_a	$\lvert l_s + l_a \rvert$
0	0.000	$^1\Sigma_g^+$	0	0	0	0	0
1	8.437	$^3\Pi_u$	0	0	0	± 1	1
1	10.002	$^1\Pi_u$	0	± 1	0	0	1

- The first excited $^1\Pi_u$ singlet state is the singlet counterpart to the $^3\Pi_u$ triplet state according to Hund's multiplicity rule.
- It has no excitation into the internal degrees of freedom but instead has an excitation of one quantum into the angular mode of the center-of-mass degree of freedom.

2eQD: $v_p = 1$ manifold - analysis

- Energy spectrum & density plot





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v_p	E	state	n_s	l_s	n_a	l_a	$\lvert l_s + l_a \rvert$
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1	8.437	$^3\Pi_u$	0	0	0	± 1	1
1	10.002	$^1\Pi_u$	0	± 1	0	0	1

- This singlet-triplet pair of states has the same orbital configuration in terms of Hartree-Fock orbitals. But there is a significant difference in terms of the normal-mode description.

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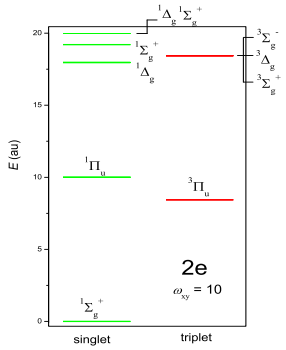
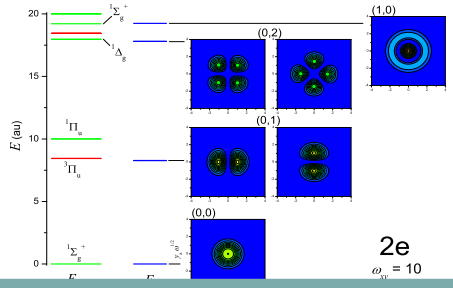
Model
Results
Summary and Acknowledgement

2eQD: Spectrum and HF orbitals
2eQD: Normal-mode assignments
2eQD: Origin of Hunds rule in QD's

2eQD: $v_p = 1$ manifold - analysis

Energy spectrum & density plot





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v_p	E	state	n_s	l_s	n_a	l_a	$\lvert l_s + l_a \rvert$
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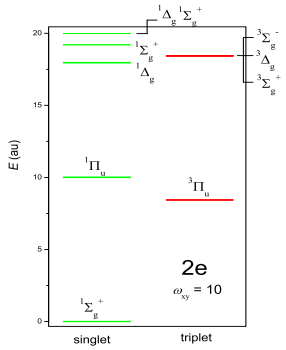
1	8.437	$^3\Pi_u$	0	0	0	± 1	1
1	10.002	$^1\Pi_u$	0	± 1	0	0	1

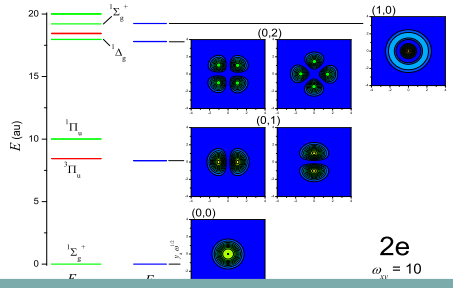
These singlet and triplet states involve an excitation into different degrees of freedom:

- the singlet state into the center-of-mass degree of freedom and
- the triplet state into the internal angular degree of freedom.

2eQD: $v_p = 2$ manifold - analysis

- Energy spectrum & density plot





- Assignments based on the normal-mode quantum numbers (n_s, l_s, n_a, l_a) for the low-lying states.

v_p	E	state	n_s	l_s	n_a	l_a	$\lvert l_s + l_a \rvert$
2	17.968	$^1\Delta_g$	0	0	0	± 2	2
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			0	-1	0	+1	0
2	18.438	$^3\Delta_g$	0	+1	0	+1	2
			0	-1	0	-1	2
2	18.438	$^3\Sigma_g^-$	0	+1	0	-1	0
			0	-1	0	+1	0

- The lowest energy $^1\Delta_g$ state in this manifold arises by the excitation of two quanta into the internal angular mode.
- There is no counterpart triplet state to this singlet state.

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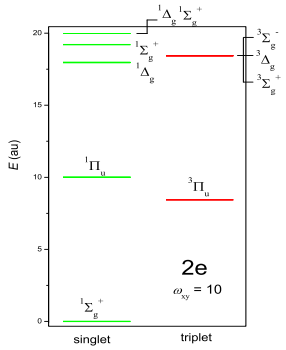
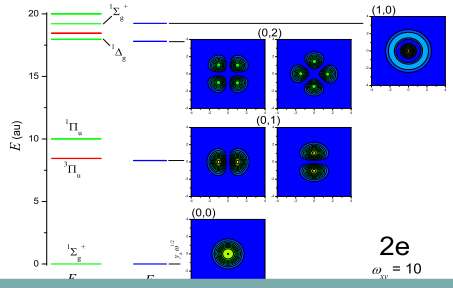
Energy spectrum & density plot





Assignments based on the normal-mode quantum numbers (n_s, l_s, n_a, l_a) for the low-lying states.

v_p	E	state	n_s	l_s	n_a	l_a	$\lvert l_s + l_a \rvert$
2	17.968	$^1\Delta_g$	0	0	0	± 2	2
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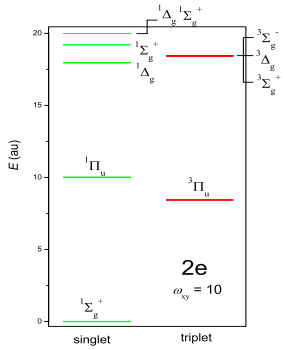
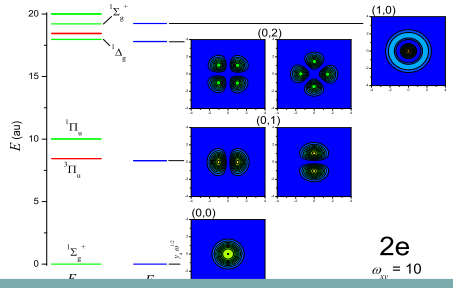
			0	-1	0	-1	2
2	18.438	$^3\Sigma_g^-$	0	+1	0	-1	0
			0	-1	0	+1	0

- The three triplet states of this manifold, $^3\Sigma_g^+$, $^3\Delta_g$ and $^3\Sigma_g^-$, have practically the same energy
- Their excitation energies relative to the lowest $^3\Pi_u$ triplet state equal ω_{xy} within an accuracy of 1×10^{-3} a.u.
- This implies that they are dipole-allowed from the $^3\Pi_u$ state

2eQD: $v_p = 2$ manifold - analysis

- Energy spectrum & density plot





- Assignments based on the normal-mode quantum numbers (n_s, l_s, n_a, l_a) for the low-lying states.

v_p	E	state	n_s	l_s	n_a	l_a	$\lvert l_s + l_a \rvert$
2	19.208	$^1\Sigma_g^+$	0	0	1	0	0
2	20.003	$^1\Sigma_g^+$	1	0	0	0	0
2	20.004	$^1\Delta_g$	0	± 2	0	0	2

- In the $^1\Sigma_g$ state at E = 19.208 a.u. the internal radial mode is excited for the first time with one quantum.
- For the two singlet states, $^1\Sigma_g^+$ and $^1\Delta_g$, the excitation energy relative to the $^1\Pi_u$ state almost equals ω_{xy}.
- This implies that they are the dipole-allowed states from the $^1\Pi_u$ state.

Outline

1 Background

2 Model
- Theoretical Model and Computational Method

3 Results
- 2eQD: Spectrum and HF orbitals
- 2eQD: Normal-mode assignments
- 2eQD: Origin of Hunds rule in QD's

4 Summary and Acknowledgement
- Summary
- Acknowledgement
- Reference

2eQD: Energies and energy differences

- There are two candidates for singlet-triplet pairs in the energy spectrum that should obey Hund's multiplicity rule:
  - The pair $^1\Pi_u$-$^3\Pi_u$ in the v_p = 1 manifold and
  - the degenerate pair $^1\Delta_g$-$^3\Delta_g$ and $^1\Sigma_g^+$-$^3\Sigma_g^+$ in the v_p = 2 manifold.

Background
Model
Results
Summary and Acknowledgement
2eQD: Spectrum and HF orbitals
2eQD: Normal-mode assignments
2eQD: Origin of Hunds rule in QD's

2eQD: Energies and energy differences

- Three energy differences of one-electron energy ΔE_1, the two-electron energy ΔE_2, and the total energy ΔE between the $^1\Pi_u$ and $^3\Pi_u$ states for different ω_{xy} values are displayed in the folowing figure.
- The one-electron energy E_1 has been calculated by evaluating the expectation value of the sum of one-electron operators in the corresponding Hamiltonianover the CI eigenfunctions.
- Two-electron energy E_2 has been obtained by subtracting E_1 from the total energy E.

2eQD: Energies and energy differences

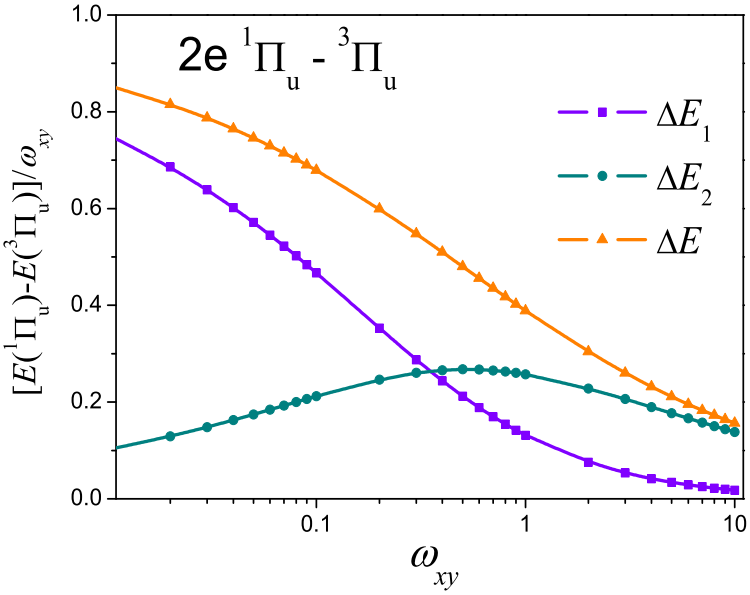
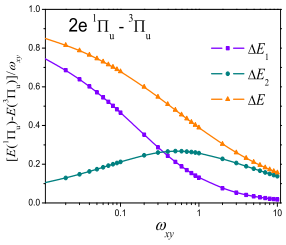


Figure: Energy differences between the lowest singlet-triplet pair of states

2eQD: Energies and energy differences - analysis

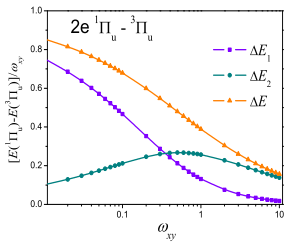
- Energy differences



- The energy splitting between the singlet and triplet levels is larger for smaller ω_{xy} than for the larger ω_{xy}.
- For large values of ω_{xy} the relative contribution of ΔE_1 and ΔE_2 to the total energy difference ΔE is almost exclusively due to ΔE_2 .
- This implies that for large ω_{xy} the interpretation of the energy difference between different spin multiplets is close to that based on Slaters study.

2eQD: Energies and energy differences - analysis

- Energy differences



- As ω_{xy} decreases, so does ΔE_2, while ΔE_1 increases.
- For small values of ω_{xy} the relative contribution of ΔE_1 and ΔE_2 to the total energy difference ΔE is mostly due to ΔE_1 .
- This implies that for small ω_{xy} the interpretation of the energy difference between different spin multiplets is close to that of Davidson found for the helium case.

He: Square radial electron density distribution

- For comparison the square electron density distributions of the corresponding states of the helium atom, $(2p)\ ^1P$ and $(2p)\ ^3P$ have been computed.
- The electron density distributions of He are calculated using a full CI wave function of the He atom obtained by employing the even-tempered uncontracted Cartesian basis set [10*s*7*p*5*d*].

He: Square radial electron density distribution

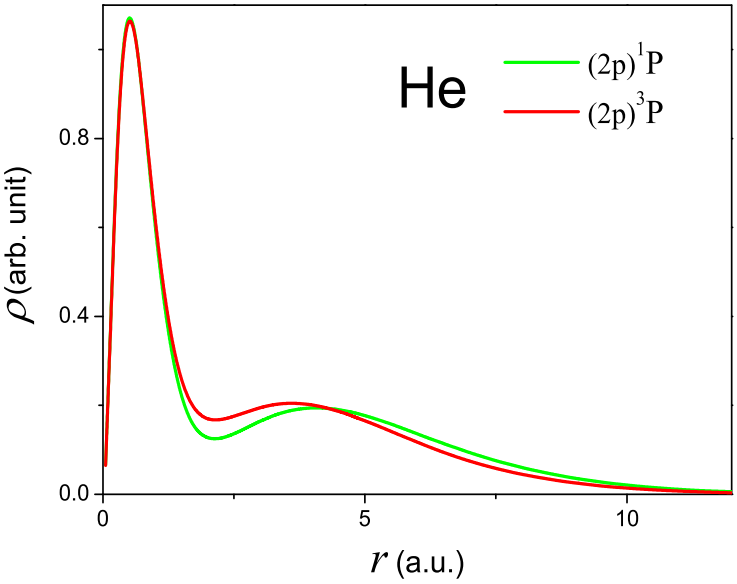
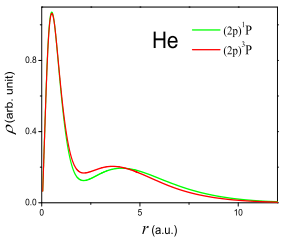


Figure: Square electron density distributions of the $(2p)\ ^1P\ -\ (2p)\ ^3P$ singlet-triplet pair of states.

He: Density distribution - analysis

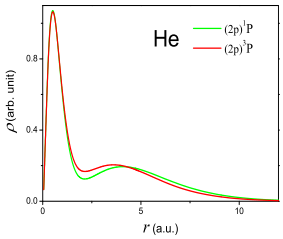
- Electron density



- The inner part of the density distribution is almost the same for the $(2p)\ ^1P$ and $(2p)\ ^3P$ states and has a sharp peak at around $r = 0.5$.
- In the outer tail for $r > 5$ the density distribution for the singlet (green curve in the figure) is larger than that of the triplet state (red curve).
- The deficient density of the triplet state in this region reappears in the inner region around $r = 2.2$.
- The density distribution of the triplet state is on the average closer to the nucleus than that of the singlet state.

He: Density distribution - analysis

- Electron density



- This compact density distribution of the triplet state results in a larger energy *increase* in the electron repulsion potential, yet a much larger energy *decrease* in the nuclear attraction potential than is the case for the corresponding singlet state.
- These two opposite contributions to the total energy result in the lowering of the triplet level relative to the singlet one, even though a simple origin the compact density distribution of the triplet state is still lacking.

2eQD: Radial electron density distribution

- The square radial electron density distribution of the singlet-triplet pair of the $^1\Pi_u$ and $^3\Pi_u$ states of the two-electron quantum dot for ω_{xy} = 10, 1, and 0.1, as a function of the dimensionless scaled radial coordinate $r\sqrt{\omega_{xy}}$ are shown in the following figure.

2eQD: Radial electron density distribution

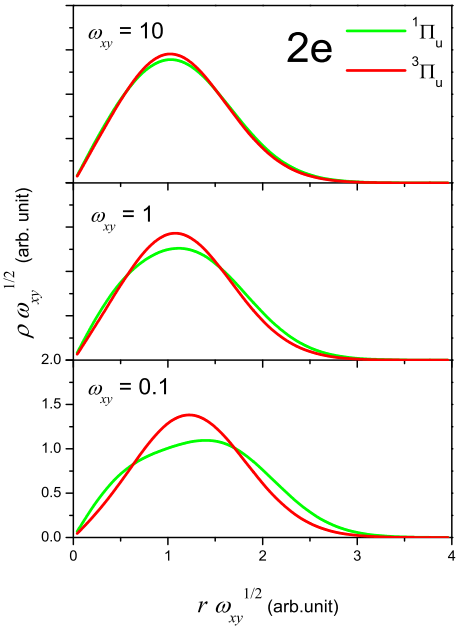
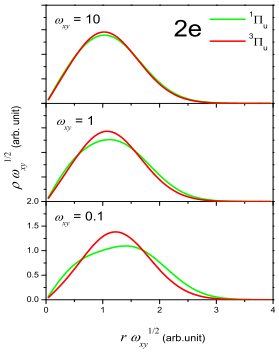
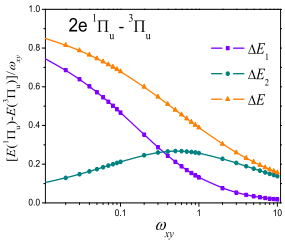


Figure: Square radial electron density distributions of the $^1\Pi_u$-$^3\Pi_u$ singlet-triplet pair of states

2eQD: Electron density distribution - analysis

- Electron density & energy differences

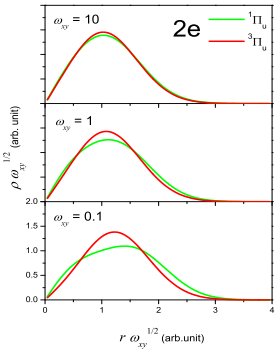


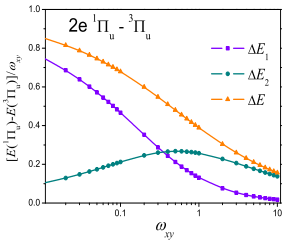


- For ω_{xy} = 10 the electron density distributions for the $^1\Pi_u$ and $^3\Pi_u$ states are almost identical.
- This agrees with the energy differences previously where the one-electron energy difference ΔE_1 is very small while the difference in the two-electron energy ΔE_2 is primarily responsible for the singlet-triplet energy gap.

2eQD: Electron density distribution - analysis

- Electron density & energy differences





- For ω_{xy} = 1.0 the density distribution of the singlet state peaks at a slightly larger value of $r\sqrt{\omega_{xy}}$ and becomes slightly broader while that of the triplet state remains almost the same as in the ω_{xy} = 10 a.u. case.
- For ω_{xy} = 0.1 the density distribution of the singlet state become even broader with the peak position shifted strongly towards larger r values, while that of the triplet state preserves almost the same shape with a slightly shifted peak position toward the region of larger r values.

2eQD: Potential energy function

- In order understand the mechanism of why the
  - triplet $^3\Pi_u$ state has always a **lower energy** than
  - the singlet $^1\Pi_u$ state

  in the whole range of ω_{xy}
  - the *potential energy function*

  defined by a sum of one-electron and two-electron potentials within the internal space, namely, the potential part of the internal Hamiltonian $\mathcal{H}_{\rm int}$ has been plotted for both the large and small confinement with ω_{xy} = 10 and 0.1, respectively.

2eQD: Potential energy function

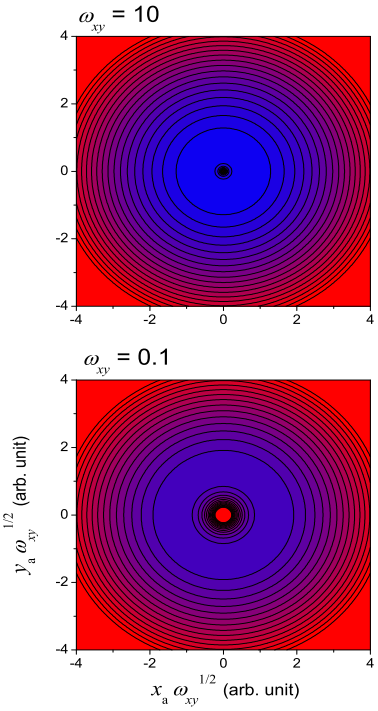
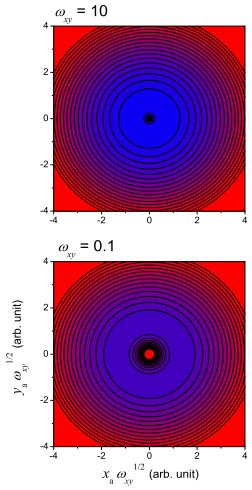


Figure: Contour plot of the potential energy function defined by the sum of the one- and two-electron potentials within the internal space for ω_{xy} = 10 (upper figure) and 0.1 (lower figure).

2eQD: Potential energy function - analysis

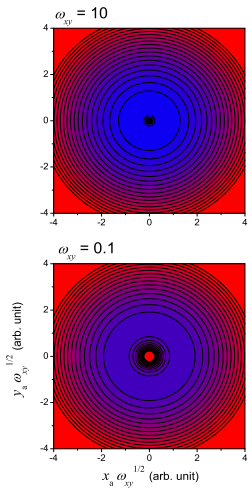
- Potential energy function



- The potential part of the internal Hamiltonian $\mathcal{H}_{\rm int}$ has been plotted for both the large and small confinement regimes of ω_{xy} = 10 and 0.1.
- The energy function is represented in the ω_{xy}-scaled dimensionless internal coordinates $x_a\sqrt{\omega_{xy}}$ and $y_a\sqrt{\omega_{xy}}$.
- The maximum energy of contours plotted figure amounts to $20\times\omega_{xy}$.

2eQD: Potential energy function - analysis

- Potential energy function



- The electron repulsion potential appears only in the internal space and is characterized by a sharp pole-like singularity in the potential energy.
- The pole becomes larger as ω_{xy} decreases from 10 to 0.1.
- This implies that the effect of the electron-electron interaction becomes stronger as the confinement strength ω_{xy} becomes smaller.

2eQD: Square-density plot of the wave function

- The total wave function, i.e., both of the center-of-mass component $\Psi_{\mathrm{c.o.m}}$ and the internal part Ψ_{int} of the $^1\Pi_u$ singlet and $^3\Pi_u$ triplet states for ω_{xy} = 10 and 0.1 is shown in the following figure.
- By relying on the potential energy function and the square-density plot of the wave function the
  - **origin of Hund′s multiplicity rule**

  in the quasi-two-dimensional quantum dots can be rationalized.

2eQD: Square-density plot of the wave function

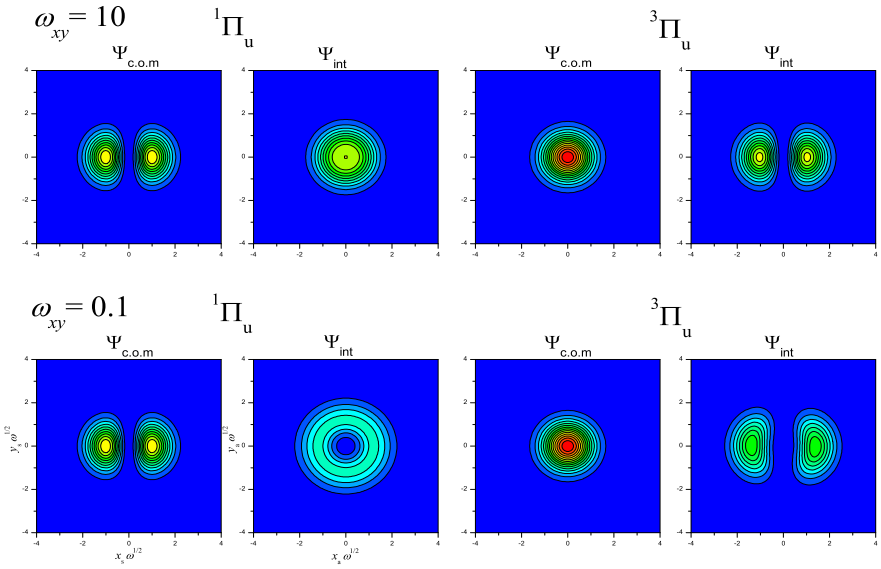
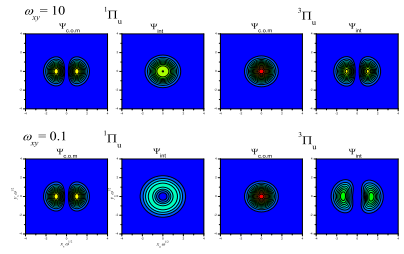
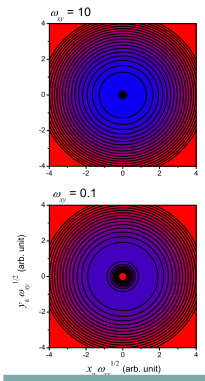


Figure: Square-density plot of the center-of-mass and internal parts of wave function of the $^1\Pi_u$ singlet state and of the $^3\Pi_u$ triplet state.

2eQD: Density plot of the wave function - analysis

- Electron density & potential energy

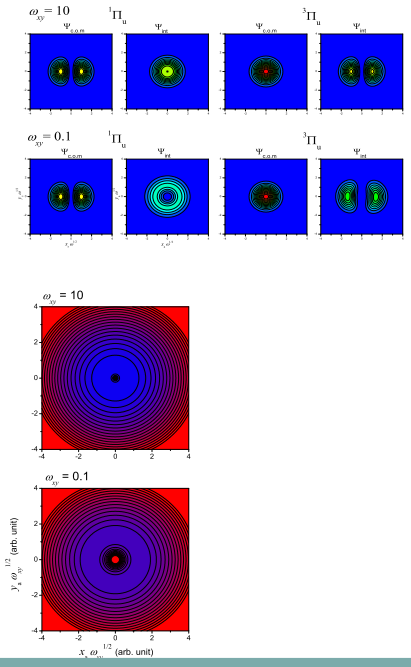




- For the large confinement strength ω_{xy} = 10 the internal wave function Ψ_{int} of the $^3\Pi_u$ triplet state is only insignificantly influenced by this pole since its density in the neighborhood of this singularity is negligible
- In the case of the $^1\Pi_u$ singlet state the internal wave function is significantly influenced by the pole since it has a finite density at the singularity region.

2eQD: Density plot of the wave function - analysis

- Electron density & potential energy



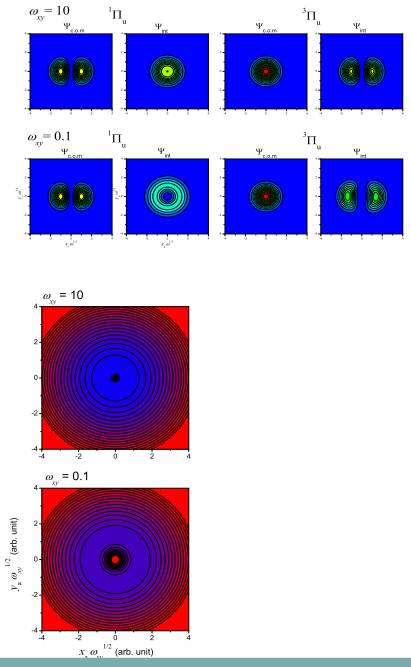
- For the small confinement strength ω_{xy} = 0.1 the electron-electron interaction potential becomes stronger and the pole at the center of the potential energy function significantly increases in size.
- In the case of the $^3\Pi_u$ triplet state the internal wave function Ψ_{int} can still avoid the effect of the singularity at the pole due to the presence of its nodal line.
- The width of the nodal region is, however, larger than in case of ω_{xy} = 10.

Background
Model
Results
Summary and Acknowledgement

2eQD: Spectrum and HF orbitals
2eQD: Normal-mode assignments
2eQD: Origin of Hunds rule in QD's

2eQD: Density plot of the wave function - analysis

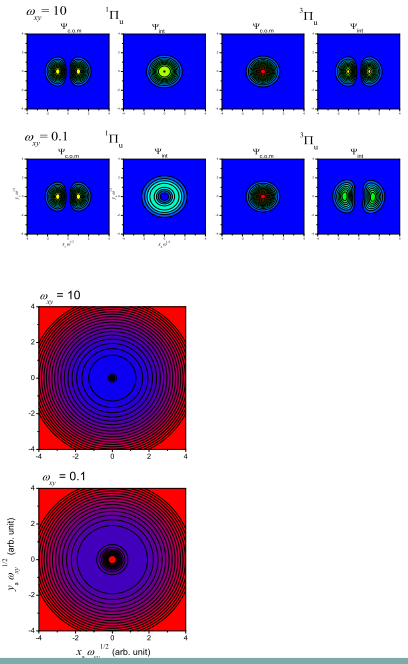
- Electron density & potential energy



- For ω_{xy} = 0.1 the internal wave function of the $^1\Pi_u$ singlet state has a hole at the center where the electron density practically vanishes.
- This low-density region is created by the large singular region in the neighborhood of the potential pole.
- The electron density distribution of the internal wave function becomes expanded.

2eQD: Density plot of the wave function - analysis

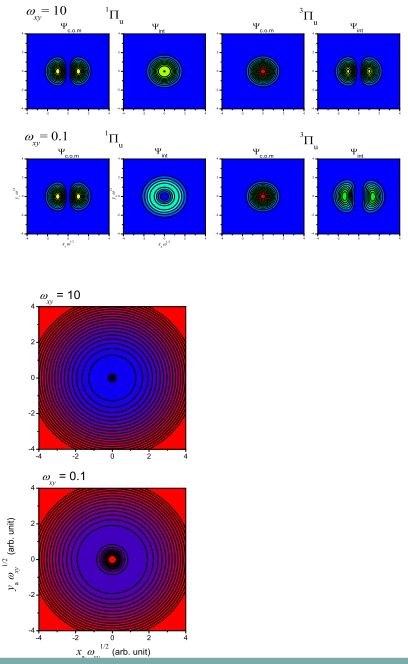
- Electron density & potential energy



- For small ω_{xy} the large difference in the electron density distributions between the singlet and triplet states results in a significant difference in their one-electron energies.
- This explains why for smaller ω_{xy} the partition of the total energy difference into the one- and two-electron contributions becomes close to that proposed for the helium case.

2eQD: Density plot of the wave function - analysis

- Electron density & potential energy



- The singlet and triplet states of the the Hund multiplicity pairs are characterized by the normal-mode quantum numbers (n_s, l_s, n_a, l_a) for the former and by $(n_s, l_s - 1, n_a, l_a + 1)$ or $(n_s - 1, l_s + 1, n_a, l_a + 1)$ for the latter.
- The larger quantum number in the internal angular mode for triple states enables them to avoid efficiently the singularity in the electron repulsion potential
- Therefore the triplet states have a lower energy than the singlet states

Outline

1 Background

2 Model
- Theoretical Model and Computational Method

3 Results
- 2eQD: Spectrum and HF orbitals
- 2eQD: Normal-mode assignments
- 2eQD: Origin of Hunds rule in QD's

4 Summary and Acknowledgement
- Summary
- Acknowledgement
- Reference

The $^1\Pi_u$ singlet and $^3\Pi_u$ triplet states as example

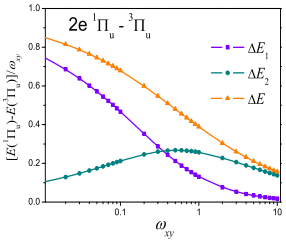
As a typical example to study Hund's multiplicity rule in quasi-two-dimensional two-electron quantum dots the

- $^1\Pi_u$ singlet and $^3\Pi_u$ triplet states in the $v_p = 1$ manifold

have been chosen.

Energy difference as function of ω_{xy}

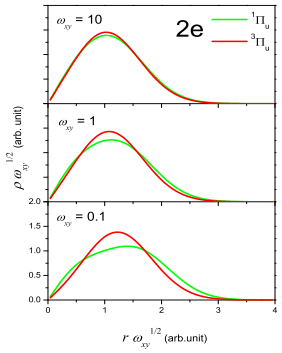
- Energy differences



- The energy separation characterizing this lowest singlet-triplet pair significantly increases in terms of the normalized energy unit as the confinement strength ω_{xy} decreases.
- This energy separation is shown to be primarily due to the difference in the two-electron energy for large ω_{xy}.
- As ω_{xy} decreases the contribution of the
  - one-electron energy becomes larger while that of the
  - two-electron energy becomes smaller.

Radial electron density distribution

- Electron density



- For large ω_{xy} = 10 the radial electron density distributions in the singlet and triplet states are almost identical.
- For smaller ω_{xy} they increasingly differ.
- As ω_{xy} decreases the singlet state electron density distribution becomes broader and its shape becomes gradually deformed.
- The triplet state density distribution remains almost the same except for a small shift of the peak position towards the region of larger r values.

Examination of the nodal pattern

In order to rationalize the observed energy differences and electron density distributions of the singlet-triplet pair

- the nodal pattern of
  the *center-of-mass* and of the *internal* wave functions

have been examined.

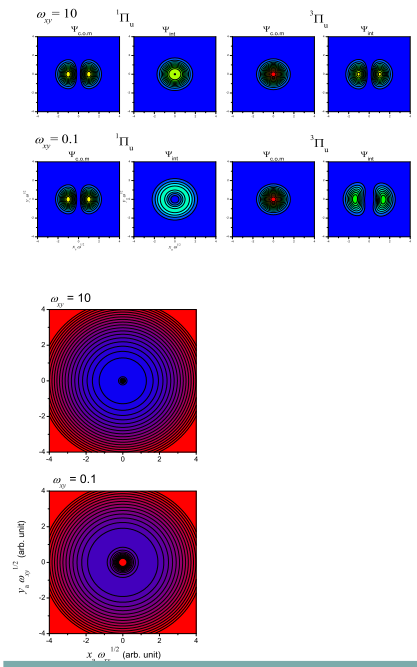
Exitation into different modes

It is observed that the singlet-triplet pair of states having the same orbital configuration in terms of Hartree-Fock orbitals, involves an excitation into different degrees of freedom, namely,

- the center-of-mass angular mode for the singlet and
- the internal angular mode for the triplet.

State density at the origin

- Electron density & potential function

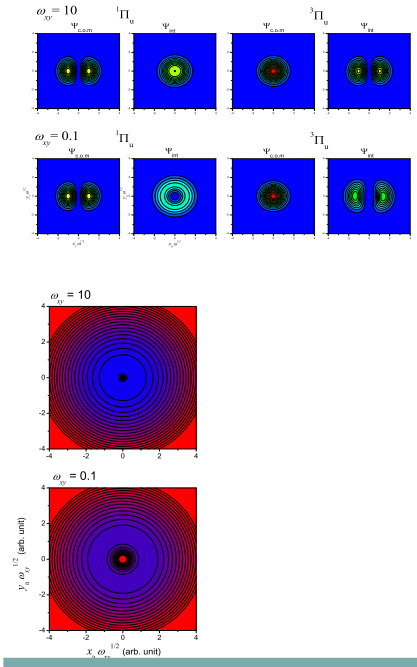


Due to a nonzero angular momentum in the internal degree of freedom:

- The internal wave function of the $^3\Pi_u$ triplet state avoids the singularity of the electron repulsion potential,since the angular nodal line passes through the origin.
- The internal wave function of the $^1\Pi_u$ singlet state has no node and thus a finite density in the region of singularity.

Conclusion

- Electron density & potential function



Consequently,

- **the triplet state has always a lower energy than the counterpart singlet state.**
- This is true for all ω_{xy} values.

Outline

1 Background

2 Model
- Theoretical Model and Computational Method

3 Results
- 2eQD: Spectrum and HF orbitals
- 2eQD: Normal-mode assignments
- 2eQD: Origin of Hunds rule in QD's

4 Summary and Acknowledgement
- Summary
- Acknowledgement
- Reference

Acknowledgement: Institutions

Outline

1 Background

2 Model
- Theoretical Model and Computational Method

3 Results
- 2eQD: Spectrum and HF orbitals
- 2eQD: Normal-mode assignments
- 2eQD: Origin of Hunds rule in QD's

4 Summary and Acknowledgement
- Summary
- Acknowledgement
- Reference

Reference

- The lecture is based on the following paper:

T Sako, J Paldus and GHF Diercksen
The origin of Hund's multiplicity rule in quasi-two-dimensional two-electron quantum dots.
Phys. Rev. A **81**, 022501 (2010)
Doi:10.1103/PhysRevA.81.022501

- The lecture is available at:

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