Quantum Chemistry of Confined Systems

Tokuei Sako
sako@chem.s.u-tokyo.ac.jp
Department of Chemistry, The University of Tokyo
Tokyo, Japan

and

Geerd HF Diercksen
ghd@MPA-Garching.MPG.de
Max-Planck-Institut für Astrophysik
Garching, Germany

http://www.MPA-Garching.MPG.de
Overview

- Spectral properties of two-electron quantum dots

- A comparison of the spectral properties of the two-electron quantum dot, the negative hydrogen ion and the helium atom

- Dipole polarizability of the 2-electron quantum dot, the hydrogen negative ion and the helium atom
Spectral properties of 2-electron quantum dots
Computational Methodology

The Schrödinger equation for $N$ electrons confined by a potential $\mathcal{W}$ is given by (in atomic units):

$$[\mathcal{H}(\mathbf{r}) + \mathcal{W}(\mathbf{r})] \psi(1, 2, \ldots, N) = E \psi(1, 2, \ldots, N),$$

(1)
where the set $(1, 2, \ldots, N)$ denotes the orbital and the spin coordinates of the electrons. The $N$-electron operators $\mathcal{H}$ represents the kinetic energy and the electron interaction described by

$$\mathcal{H}(\mathbf{r}) = \sum_{i=1}^{N} \left[ -\frac{1}{2} \nabla_{i}^{2} \right] + \sum_{i>j}^{N} \left[ \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} \right],$$

(2)
where $\mathbf{r} \equiv \{\mathbf{r}_{1}, \mathbf{r}_{2}, \ldots, \mathbf{r}_{N}\}$ denotes the spatial coordinates of the electrons. The $N$-electron interaction potential $\mathcal{W}$ is defined as the sum of one-electron contributions:

$$\mathcal{W}(\mathbf{r}) = \sum_{i=1}^{N} w(r_{i}).$$

(3)
Spectral properties of 2-electron quantum dots
Computational Methodology

The one-particle confining potential \( w(r_i) \) is written as a linear combination of powers of electron coordinates:

\[
 w(r_i) = \frac{1}{2} \left[ \omega_x^{n_x+1} x_i^{2n_x} + \omega_y^{n_y+1} y_i^{2n_y} + \omega_z^{n_z+1} z_i^{2n_z} \right], \tag{4}
\]

where \( r_i = \{x_i, y_i, z_i\} \). The special case of an anisotropic harmonic oscillator potential centered at the origin of the coordinate system (\( n_x = n_y = n_z = 1 \)) is written as:

\[
 V_\omega(r) = \frac{1}{2} (\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2). \tag{5}
\]
Spectral properties of 2-electron quantum dots

Computational Methodology

For an electron confined in a harmonic oscillator potential the Schrödinger equation has a well known analytical solution. The eigenvalues are given by

\[ E_0^\omega = \omega_x (\nu_x + 1/2) + \omega_y (\nu_y + 1/2) + \omega_z (\nu_z + 1/2). \tag{6} \]

The eigenstates are labeled by a set of three harmonic oscillator quantum numbers \((\nu_x, \nu_y, \nu_z)\).

The eigenfunctions are given by a product of three Hermite-Gaussian functions

\[ \chi_{\nu_x \nu_y \nu_z}^{\omega}(\vec{r}) = N_{\nu_x \nu_y \nu_z}^{\omega} H_{\nu_x}(x) H_{\nu_y}(y) H_{\nu_z}(z) \exp \left[ -\frac{1}{2}(\omega_x x^2 + \omega_y y^2 + \omega_z z^2) \right], \tag{7} \]

where \( N_{\nu_x \nu_y \nu_z}^{\omega} \) is a normalization constant and \( H_{\nu}(x) \), etc., stands for a Hermite polynomial. The lowest order Hermite polynomials are:

\[ H_0(x) = 1, \tag{8} \]
\[ H_1(x) = 2x, \tag{9} \]
\[ H_2(x) = 4x^2 - 2, \tag{10} \]
\[ H_3(x) = 8x^3 - 12x, \tag{11} \]
\[ H_4(x) = 16x^4 - 48x^2 + 12. \tag{12} \]
Spectral properties of 2-electron quantum dots
Computational Methodology

The eigenvalues for an electron confined in a spherical harmonic oscillator potential \( \omega_x = \omega_y = \omega_z = \omega \) are given by

\[
E_0^\omega = \omega(2\nu + \ell + 3/2).
\] (14)

The eigenstates are labeled by the principal quantum number \( \nu \) and the one-electron angular momentum quantum number \( \ell \) with \( \nu = 0,1,2, \ldots \) and \( \ell = 0,1,2, \ldots \). It is noted that the one-electron orbitals are not ordered in the hydrogen-like but in the following sequence:

\[
E_0^\omega[0s] = (3/2)\omega, \quad E_0^\omega[0p] = (5/2)\omega, \quad E_0^\omega[0d] = E_0^\omega[1s] = (7/2)\omega, \quad E_0^\omega[0f] = E_0^\omega[1p] = (9/2)\omega, \quad E_0^\omega[0g] = E_0^\omega[1d] = E_0^\omega[3s] = (11/2)\omega, \ldots.
\] (15-19)
Spectral properties of 2-electron quantum dots

Computational Methodology

The consecutive configuration energies $E_0^{\nu}[\nu_1\ell_1\nu_2\ell_2]$ for two non-interacting electrons are:

\[
\begin{align*}
E_0^{\omega}[(0s)^2] &= 3\omega, (20) \\
E_0^{\omega}[0s0p] &= 4\omega, (21) \\
E_0^{\omega}[0s1s] &= E_0^{\omega}[0s0d] = E_0^{\omega}[(0p)^2] = 5\omega, (22) \\
E_0^{\omega}[0s1p] &= E_0^{\omega}[1s0p] = E_0^{\omega}[0s0f] = E_0^{\omega}[0p0d] = 6\omega, \ldots (23)
\end{align*}
\]

The degenerate energy levels are split due to the electron interaction. If this splitting is smaller than that due to the Hooke’s law potential (i.e. if the separation between the extreme energies of the terms related to the same configuration is smaller than $\omega$), then the consecutive singlet energies are:

\[
\begin{align*}
E^{\omega}[S(0s)^2] &< E^{\omega}[P(0s0p)] < E^{\omega}[D(0s0d)] < \\
E^{\omega}[S(0s1s)] &< E^{\omega}[S(0p)^2] < E^{\omega}[D(0p)^2] < \ldots (24)
\end{align*}
\]
Spectral properties of 2-electron quantum dots
Computational Methodology

The eigenvalues for an electron confined in an \textit{elliptical} harmonic oscillator potential are given by

\[ E^\omega_0 = \omega(\nu_x + \nu_y + 1) + \omega_z(\nu_z + 1/2). \quad (25) \]

The eigenstates are labeled by a set of three harmonic oscillator quantum numbers \((\nu_x, \nu_y, \nu_z)\), or equivalently, by specifying the \(z\) component of the one-electron angular momentum quantum numbers as \((\nu, l_z, \nu_z)\), where \(\nu = \nu_x + \nu_y\) and \(l_z = \nu, \nu - 2, \ldots, 0\) or \(1\) for \(\nu = \text{even or odd}\).

The orbital energies are expressed as a combination of two harmonic oscillator sequences of \(\omega\) and \(\omega_z\), and orbitals belonging to the same \((\nu, \nu_z)\) manifold with different values of \(l_z\) are degenerate. Two different types of elliptical confinement can be distinguished: prolate-type \((\omega_x = \omega_y > \omega_z)\) and oblate-type \((\omega_x = \omega_y < \omega_z)\).
Spectral properties of 2-electron quantum dots

Basis Sets

It is noted that a quantum chemical standard spherical or cartesian gaussian basis set is not the most appropriate choice to expand the eigenfunctions of an electron in an anisotropic harmonic oscillator potential given by the equation

\[ V_\omega(r) = \frac{1}{2}(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2). \]  

The inspection of the explicit form of the eigenfunctions suggests to expand them in a properly constructed set of cartesian anisotropic Gaussian-type orbitals.

The following four types of basis sets have been explored in an attempt to find the most suitable basis set for expanding the eigenfunctions of an electron in an anisotropic harmonic oscillator potential:
Spectral properties of 2-electron quantum dots

Basis Sets

- A basis set of cartesian anisotropic Gaussian-type orbitals \((c\text{-aniGTO})\) with one function for each type of orbital of the following general form

\[
\chi_{ani}(\vec{r}) = x^{a_x}y^{a_y}z^{a_z} \exp(-\zeta_x x^2 - \zeta_y y^2 - \zeta_z z^2). \tag{27}
\]

The orbital exponents are chosen to be \((\zeta_x, \zeta_y, \zeta_z) = (\omega_x/2, \omega_y/2, \omega_z/2)\). Following the quantum chemical convention, these orbitals are classified as \(s\)-, \(p\)-, \(d\)-type, ... for \(a = a_x + a_y + a_z = 0, 1, 2, ...\), respectively.
Spectral properties of 2-electron quantum dots

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<tr>
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Figure 1

Spectrum of one electron confined by a prolate-type elliptical harmonic oscillator potential with \((\omega_x, \omega_y, \omega_z) = (0.5, 0.5, 0.25)\) for different cartesian anisotropic Gaussian basis sets. The analytical spectrum labeled by the harmonic oscillator quantum numbers \((\nu_x, \nu_y, \nu_z)\) is shown at the right hand side. The states are labeled by their degeneracy in square brackets. The total number of basis functions is given in round brackets.
Spectral properties of 2-electron quantum dots

Figure 2

Spectrum of one electron confined by a prolate-type elliptical harmonic oscillator potential with \((\omega_x, \omega_y, \omega_z) = (0.5, 0.5, 0.25)\) for different spherical anisotropic Gaussian basis sets. The analytical spectrum labeled by the harmonic oscillator quantum numbers \((\nu_x, \nu_y, \nu_z)\) is shown at the right hand side. The states are labeled by their degeneracy in square brackets. The total number of basis functions is given in round brackets.
Spectral properties of 2-electron quantum dots

Figure 4

Spectrum of one electron confined by a prolate-type elliptical harmonic oscillator potential with \((\omega_x, \omega_y, \omega_z) = (0.5, 0.5, 0.25)\) for different conventional spherical Gaussian basis sets. The analytical spectrum labeled by the harmonic oscillator quantum numbers \((\nu_x, \nu_y, \nu_z)\) is shown at the right hand side. The states are labeled by their degeneracy in square brackets. The total number of basis functions is given in round brackets.
Spectral properties of 2-electron quantum dots

Figure 8
Correlation between the Hartree-Fock orbitals of a spherical, a prolate and an oblate quantum dot.
Spectral properties of 2-electron quantum dots

Figure 10
Spectra of two electrons confined by a spherical harmonic oscillator potential with $\omega = 0.1, 0.2, 0.3, 0.4,$ and $0.5$. 
Spectral properties of 2-electron quantum dots

Figure 11
Electron density distribution and energy diagram for two electrons confined by a spherical harmonic oscillator potential with $\omega = 0.1$ (left) and $0.5$ (right).
Spectral properties of 2-electron quantum dots

Figure 14
Spectrum of two electrons confined by an oblate-type elliptical harmonic oscillator potential with $\omega = 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5$. 
Spectral properties of 2-electron quantum dots

Figure 15

Electron density distribution for two electrons confined by an oblate-type elliptical harmonic oscillator potential with \( \omega = 0.1 \) (left) and 0.5 (right).
Spectral properties of 2-electron quantum dots

Figure 16
Correlation energy of a spherical, a prolate, and an oblate quantum dot as function of $\omega$. 
Spectral properties of highly anisotropic 2, 3, and 4-electron quantum dots

Figure 1

HF orbital density distribution and their orbital energies for two electrons confined by an oblate harmonic oscillator potential with \((\omega_x, \omega_y, \omega_z) = (0.01, 0.01, 0.1)\). The density at the surface is \(1.0 \times 10^{-4}\). The side length of the cubes is 48 au.
Spectral properties of highly anisotropic 2, 3, and 4-electron quantum dots

Electron density distribution of singlet states for two electrons confined by an oblate harmonic oscillator potential with $(\omega_x, \omega_y, \omega_z) = (0.01, 0.01, 0.1)$. The density at the surface is $1.0 \times 10^{-4}$. The side length of the cubes is 48 au.
Spectral properties of highly anisotropic 2, 3, and 4-electron quantum dots

Figure 5

Electron density distribution of doublet states for three electrons confined by an oblate harmonic oscillator potential with \((\omega_x, \omega_y, \omega_z) = (0.01, 0.01, 0.1)\). The density at the surface shown is \(1.0 \times 10^{-4}\). The side length of the cube is 48 au.
Spectral properties
of highly anisotropic 2, 3, and 4-electron quantum dots

Electron density distribution of singlet states for four electrons confined by an oblate harmonic oscillator potential with \((\omega_x, \omega_y, \omega_z) = (0.01, 0.01, 0.1)\). The density at the surface is \(1.0 \times 10^{-4}\). The side length of the cubes is 48 au.
Spectral properties of the 2-electron quantum dot, the hydrogen negative ion and the helium atom

Figure 6
Spectrum of the He atom, the hydrogen negative ion and two electrons confined by a spherical harmonic oscillator potential with $(\omega_x, \omega_y, \omega_z) = (0.1, 0.1, 0.1)$ (left fig.) and $(0.5, 0.5, 0.5)$ (right fig.).
Spectral properties of the 2-electron quantum dot, the hydrogen negative ion and the helium atom

Figure 7
Electron density distributions for the He atom, the hydrogen negative ion and two electrons confined by a spherical harmonic oscillator potential with \((\omega_x, \omega_y, \omega_z) = (0.5, 0.5, 0.5)\).
Spectral properties of the 2-electron quantum dot, the hydrogen negative ion and the helium atom

Figure 10

Spectrum of the He atom, the hydrogen negative ion and two electrons confined by an oblate-type elliptical harmonic oscillator potential with \((\omega_x, \omega_y, \omega_z) = (0.5\omega, 0.5\omega, \omega)\), \(0.1 \leq \omega \leq 0.5\).
Spectral properties of the 2-electron quantum dot, the hydrogen negative ion and the helium atom

Figure 11

Electron density distributions for the He atom, the hydrogen negativ ion and two electrons confined by a oblate-type elliptical harmonic oscillator potential with \((\omega_x, \omega_y, \omega_z) = (0.25, 0.25, 0.5)\).
Dipole polarizability of the 2-electron quantum dot, the hydrogen negative ion and the helium atom
Computational Methodology

The Schrödinger equation for an $N$-electron molecule confined by a potential $\mathcal{W}$ is given by (in atomic units):

$$[\mathcal{H}(r) + \mathcal{W}(r)] \psi(1, 2, \ldots, N) = E \psi(1, 2, \ldots, N),$$  \hspace{1cm} (28)

where the set $(1, 2, \ldots, N)$ denotes the orbital and the spin coordinates of the electrons. The Hamilton operator $\mathcal{H}$ represents the $N$-electron operators describing the kinetic energy, the nuclear attraction, and the electron interaction potentials:

$$\mathcal{H}(r) = \sum_{i=1}^{N} \left[ -\frac{1}{2} \nabla_i^2 \right] + \sum_{i=1}^{N} \sum_{\alpha=1}^{M} \left[ -\frac{Z_\alpha}{|r_i - R_\alpha|} \right] + \sum_{i>j}^{N} \left[ \frac{1}{|r_i - r_j|} \right] ,$$  \hspace{1cm} (29)

where $r \equiv \{r_1, r_2, \ldots, r_N\}$ stands for the spatial coordinates of the electrons.
The $N$-electron interaction potential is defined as the sum of one-electron contributions:

$$\mathcal{W}(\mathbf{r}) = \sum_{i=1}^{N} w(\mathbf{r}_i).$$ \hspace{1cm} (30)

The one-particle confining potential $w(\mathbf{r}_i)$ is written as a linear combination of powers of electron coordinates:

$$w(\mathbf{r}_i) = \frac{1}{2} \left[ \omega_x^{n_x+1}(x_i - b_x)^{2n_x} + \omega_y^{n_y+1}(y_i - b_y)^{2n_y} + \omega_z^{n_z+1}(z_i - b_z)^{2n_z} \right],$$ \hspace{1cm} (31)

where $\mathbf{r}_i = \{x_i, y_i, z_i\}$. The anisotropic harmonic oscillator potential centered at the origin of the coordinate system ($n_x = n_y = n_z = n = 1$, $b_x = b_y = b_z = 0$) is defined as:

$$V_\omega(\mathbf{r}) = \frac{1}{2} \left[ \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2 \right].$$ \hspace{1cm} (32)
Applying a finite electric field to a quantum system confined by the *anisotropic* harmonic oscillator potential will change the one-electron potential (32) to

\[
\tilde{V}_\omega(r) = \frac{1}{2} \left[ \omega_x^2 \left( x_i - \frac{F_x}{\omega_x^2} \right)^2 + \omega_y^2 \left( y_i - \frac{F_y}{\omega_y^2} \right)^2 + \omega_z^2 \left( z_i - \frac{F_z}{\omega_z^2} \right)^2 \right]
\]

\[
-\frac{1}{2} \left[ \frac{F_x^2}{\omega_x^2} + \frac{F_y^2}{\omega_y^2} + \frac{F_z^2}{\omega_z^2} \right],
\]

where \((F_x, F_y, F_z)\) denote the electric field strength. From the previous equations it follows that the contribution of the electric field to the energy of a quantum dot with nuclear charge \(Z=0\) is a constant

\[
E(F) = E(0) - \frac{1}{2} \sum_{i=1}^{N} \left[ \frac{F_x^2}{\omega_x^2} + \frac{F_y^2}{\omega_y^2} + \frac{F_z^2}{\omega_z^2} \right].
\]
Dipole polarizability of the 2-electron quantum dot, the hydrogen negative ion and the helium atom
Computational Methodology

Therefore, the dipole polarizability of the harmonic oscillator quantum dot is determined by the analytically expression

\[
\alpha_{xx} = - \left[ \frac{\partial^2 E(F_x)}{\partial F_x^2} \right]_{F_x=0} = \frac{N}{\omega_x^2}, \quad (35)
\]

\[
\alpha_{yy} = - \left[ \frac{\partial^2 E(F_y)}{\partial F_y^2} \right]_{F_y=0} = \frac{N}{\omega_y^2}, \quad (36)
\]

\[
\alpha_{zz} = - \left[ \frac{\partial^2 E(F_z)}{\partial F_z^2} \right]_{F_z=0} = \frac{N}{\omega_z^2}. \quad (37)
\]
Dipole polarizability of
the 2-electron quantum dot,
the hydrogen negative ion and the helium atom

Computational Methodology

- The dipole polarizability of the harmonic oscillator quantum dot is proportional to the number of electrons and inverse proportional to the square of \( \omega \). This relation is valid for all states including excited states.

- There is no higher order contribution of the electric field to the total energy. Therefore the harmonic-oscillator quantum dot has no hyperpolarizability.

- For an anisotropic harmonic oscillator quantum dot the polarizability along any of the axes is independent of that along the other axes.

- The polarizability of the harmonic-oscillator quantum dot is purely a one-electron property and there is no electron correlation contribution.
Dipole polarizability of the 2-electron quantum dot, the hydrogen negative ion and the helium atom

Computational Methodology

The numerical differentiation required in the calculation of the dipole polarizability has been performed by using the finite difference approximation

\[
\left[ \frac{\partial^2 E(F_\beta)}{\partial F^2_\beta} \right]_{F_\beta=0} = \frac{E(+F_\beta) + E(-F_\beta) - 2E(0)}{F^2_\beta}. \quad (38)
\]

The field strength \( F_\beta \) has been tested within the range \( 0.001 < F_\beta < 0.01 \) and the value 0.005 has been chosen.
Dipole polarizability of 
the 2-electron quantum dot, 
the hydrogen negative ion and the helium atom

Figure 2

Dipole polarizability (upper fig.) and electron correlation contribution (lower fig.) of the lowest singlet $1^1\Sigma^+_g$ state of He and H− confined by a spherical harmonic oscillator potential with $(\omega_x, \omega_y, \omega_z) = (\omega, \omega, \omega)$, $\omega = 0.1 - 1.2$. 
Dipole polarizability of the 2-electron quantum dot, the hydrogen negative ion and the helium atom

Figure 4

Dipole polarizability of the lowest singlet $1^1\Sigma_g^+$ state of He and H$^-$ confined by a prolate-type harmonic oscillator potential with $(\omega_x, \omega_y, \omega_z) = (\omega, \omega, 0.1)$, $\omega = 0.1 - 1.2$. 

35
Dipole polarizability of the 2-electron quantum dot, the hydrogen negative ion and the helium atom

![Graphs showing dipole polarizability of H^- and He](image)

**Figure 5**

Electron correlation contribution to the dipole polarizability of the lowest singlet $^1\Sigma_g^+$ state of He and H^- confined by a prolate-type harmonic oscillator potential with $(\omega_x, \omega_y, \omega_z) = (\omega, \omega, 0.1)$, $\omega = 0.1 - 1.2$. 
References
Computational Methodology

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  Confined quantum systems: spectral properties of the atoms helium and lithium in a power series potential

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  Confined quantum systems: a comparison of the spectral properties of the two-electron quantum dot, the negative hydrogen ion and the helium atom

- Sako, T and Diercksen, G H F
  Confined quantum systems: spectral properties of two-electron quantum dots

- Sako, T and Diercksen, G H F
  Confined quantum systems: dipole polarizability of the 2-electron quantum dot, the hydrogen negative ion and the helium atom