

INVITED ARTICLE

Excited states of spherium

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We report analytic solutions of a recently discovered quasi-exactly solvable model consisting of two electrons, interacting via a Coulomb potential, but restricted to remain on the surface of a \mathcal{D} -dimensional sphere. Polynomial solutions are found for the ground state, and for some higher ($L \leq 3$) states. Kato cusp conditions and interdimensional degeneracies are discussed.

Keywords: exact solution; excited states; spherium; cusp condition; interdimensional degeneracies

1. Introduction

A quasi-exactly solvable model is one for which it is possible to solve the Schrödinger equation exactly for a finite portion of the energy spectrum [1]. In quantum chemistry, a famous example of this is the Hooke's law atom [2–5], which consists of a pair of electrons, repelling Coulombically but trapped in a harmonic external potential. This model and others [6–12] have been used extensively to test various approximations [13–20] within density functional theory (DFT) [21–23] and explicitly correlated methods [24–28].

We have recently discovered [29] that a pair electrons, repelling Coulombically but constrained to remain on the surface of a \mathcal{D} -sphere of radius R [17,30–37] is also quasi-exactly solvable and we have called this system \mathcal{D} -spherium. (We adopt the convention that a \mathcal{D} -sphere is the surface of a $(\mathcal{D} + 1)$ -dimensional ball.) We have shown that the Schrödinger equation for the 1S and the 3P states of \mathcal{D} -spherium can be solved exactly for a countably infinite set of R values and that the resulting wave functions are polynomials in the interelectronic distance $0 \leq u \equiv |\mathbf{r}_1 - \mathbf{r}_2| \leq 2R$.

In this article, we extend our earlier results [29] to higher angular momentum (up to $L = 3$) states of \mathcal{D} -spherium ($\mathcal{D} \geq 2$) for both the singlet and triplet manifolds. The $\mathcal{D} = 1$ case is anomalous and, for brevity, is not discussed here. We use atomic units throughout.

2. Wave function

The Hamiltonian of \mathcal{D} -spherium is

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{1}{u}, \quad (1)$$

where the two first terms represent the kinetic contribution of each electron, and u^{-1} is the Coulomb operator.

Following Breit [38], we write the total wave function as the product

$$\Phi(\{s_1, s_2\}, \{\Omega_1, \Omega_2\}, u) = \Xi(s_1, s_2)\chi(\Omega_1, \Omega_2)\Psi(u), \quad (2)$$

where Ξ , χ and Ψ are the spin, angular and interparticle wave functions, respectively, and s_i and Ω_i are the spin and hyperspherical coordinates [39] of the i th electron. The singlet and triplet wave functions are given by the familiar [40] forms

$$^1\Xi(s_1, s_2) = \frac{1}{2^{1/2}}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)], \quad (3)$$

$$^3\Xi(s_1, s_2) = \begin{cases} \alpha(s_1)\alpha(s_2), \\ \frac{1}{2^{1/2}}[\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)], \\ \beta(s_1)\beta(s_2). \end{cases} \quad (4)$$

The angular part is associated with an energy

$$E_\chi = \frac{A}{R^2}, \quad (5)$$

$$A = \frac{\ell_1(\ell_1 + \mathcal{D} - 1)}{2} + \frac{\ell_2(\ell_2 + \mathcal{D} - 1)}{2}, \quad (6)$$

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Table 1. Ground state and excited states of \mathcal{D} -spherium.

State	Configuration	$\chi(\Omega_1, \Omega_2)$	δ	γ^{-1}	A	κ	Transformation
$^1S^e$	s^2	1	$2\mathcal{D}-1$	$\mathcal{D}-1$	0	0	$^3P^e$
$^3P^o$	sp	$\cos \theta_1 - \cos \theta_2$	$2\mathcal{D}+1$	$\mathcal{D}+1$	$\mathcal{D}/2$	1	$^1D^o$
$^1P^o$	sp	$\cos \theta_1 + \cos \theta_2$	$2\mathcal{D}+1$	$\mathcal{D}-1$	$\mathcal{D}/2$	0	$^3D^o$
$^3P^e$	p^2	$\sin \theta_1 \sin \theta_2 \sin(\phi_1 - \phi_2)$	$2\mathcal{D}+3$	$\mathcal{D}+1$	\mathcal{D}	1	
$^3D^e$	sd	$\chi^3_{p^o} \cdot \chi^1_{p^o}$	$2\mathcal{D}+3$	$\mathcal{D}+1$	$\mathcal{D}+1$	1	$^1F^e$
$^1D^o$	pd	$\chi^3_{p^o} \cdot \chi^3_{p^e}$	$2\mathcal{D}+5$	$\mathcal{D}+3$	$3\mathcal{D}/2+1$	2	
$^3D^o$	pd	$\chi^1_{p^o} \cdot \chi^3_{p^e}$	$2\mathcal{D}+5$	$\mathcal{D}+1$	$3\mathcal{D}/2+1$	1	
$^1F^e$	pf	$\chi^3_{p^e} \cdot \chi^3_{D^e}$	$2\mathcal{D}+7$	$\mathcal{D}+3$	$2\mathcal{D}+3$	2	

where ℓ_1 and ℓ_2 are the angular momentum quantum numbers of the corresponding one-electron configuration ($s=0$, $p=1$, $d=2$, $f=3, \dots$). The functions χ , which are dependent on the nature of the state considered [38,41], are gathered in Table 1, where $\theta_i \in [0, \pi]$ and $\phi_i \in [0, 2\pi]$ are the $(\mathcal{D}-1)$ th and \mathcal{D} th hyperspherical angles of the electron i . The corresponding one-electron configurations are also reported. In Table 1, the suffixes e (even) and o (odd) are related to the parity of the states, which is given by $(-1)^{\ell_1+\ell_2}$. Hence, we label the states with the notation $^{1,3}L^{e,o}$, where $L=S, P, D, F, \dots$

3. Polynomial solutions

Substituting the ansatz (2) into the Hamiltonian (1) yields the Schrödinger equation

$$\left(\frac{u^2}{4R^2} - 1\right) \frac{d^2\Psi}{du^2} + \left(\frac{\delta u}{4R^2} - \frac{1}{\gamma u}\right) \frac{d\Psi}{du} + \frac{\Psi}{u} = E\Psi, \quad (7)$$

where the parameters δ and γ are tabulated for each state in Table 1.

By introducing the dimensionless variable $x = u/2R$, Equation (7) can be recast as a Heun's differential equation [42] with singular points at $x = -1, 0, +1$. Following the known solutions of this equation [43], we seek wave functions of the form

$$\Psi(u) = \sum_{k=0}^{\infty} a_k u^k, \quad (8)$$

and substitution into (7) yields the three-step recurrence relation

$$a_{k+2} = \frac{\gamma}{(k+2)[(k+1)\gamma+1]} \times \left\{ a_{k+1} + \left[\frac{k(k+\delta-1)}{4R^2} - E \right] a_k \right\}, \quad (9)$$

with the starting values $a_0 = 1$ and $a_1 = \gamma$.

If the series (8) terminates at a certain $k=n$, we obtain the exact wave function

$$\Psi_{n,m}(u) = \sum_{k=0}^n a_k u^k, \quad (10)$$

for a particular radius $R_{n,m}$ and energy $E_{n,m}$. This is an n th degree polynomial with m nodes between 0 and $2R$ ($0 \leq m \leq \lfloor (n+1)/2 \rfloor$) and requires that a_{n+1} and a_{n+2} vanish. If $a_{n+1} = 0$, the relation

$$R_{n,m}^2 E_{n,m} = \frac{n}{2} \left(\frac{n}{2} + \frac{\delta-1}{2} \right) \quad (11)$$

ensures that $a_{n+2} = 0$. For a given n , the energies are thus determined by finding the roots of the equation $a_{n+1} = 0$, which is a polynomial in E , of degree $\lfloor (n+1)/2 \rfloor$.

For the $^1D^e$ state, we have not been able to obtain polynomial solutions because the Hamiltonian (1) is not separable using the ansatz (2) and the wave function satisfies exchange coupled equations [44]. This applies also to some other states of higher angular momentum.

4. Results and discussion

Numerical values of the energies and radii for the $^1P^o$ and $^3P^e$ states are reported in Tables 2 and 3. Tables containing results for the $^1S^e$ and $^3P^o$ states can be found in [29]. Numerical values of the energies and radii for the higher angular momentum states can be determined using the interdimensional degeneracies (see Section 4.5).

For any given state, as n increases, the radius increases and the energy decreases. The opposite behaviour is observed with respect to m . Furthermore, as R (or, equivalently, n) increases, the electrons tend to localize on opposite sides of the sphere due to the dominance of the Coulomb interaction as the density decreases [34,35]. Such Wigner crystallization [45] has also been observed in other systems [5,10,46].

Table 2. Radii $R_{n,m}$ and energies $E_{n,m}$ for $^1P^o$ states of two electrons on a \mathcal{D} -sphere ($\mathcal{D}=2, 3, 4$).

n/m	$\mathcal{D}=2$				$\mathcal{D}=3$				$\mathcal{D}=4$			
	0	1	2	3	0	1	2	3	0	1	2	3
Radius												
1	1.118				1.871				2.598			
2	3.162				4.637				6.083			
3	6.226	1.656			8.376	2.520			10.52	3.303		
4	10.30	4.232			13.11	5.888			15.93	7.440		
5	15.38	7.847	2.159		18.84	10.21	3.127		22.32	12.49	3.966	
6	21.46	12.49	5.246		25.57	15.53	7.077		29.72	18.51	8.732	
7	28.54	18.14	9.397	2.639	33.30	21.84	11.97	3.707	38.11	25.51	14.39	4.599
8	36.63	24.80	14.59	6.222	42.03	29.15	17.86	8.220	47.49	33.49	21.01	9.976
Energy												
1	1.000				0.5000				0.3333			
2	0.3000				0.1860				0.1351			
3	0.1355	1.914			0.09622	1.063			0.07460	0.7562		
4	0.07541	0.4467			0.05820	0.2884			0.04731	0.2168		
5	0.04757	0.1827	2.414		0.03874	0.1319	1.406		0.03260	0.1041	1.033	
6	0.03257	0.09620	0.5450		0.02753	0.07468	0.3594		0.02378	0.06129	0.2754	
7	0.02363	0.05851	0.2180	2.764	0.02051	0.04771	0.1587	1.656	0.01808	0.04035	0.1267	1.241
8	0.01789	0.03903	0.1127	0.6200	0.01585	0.03295	0.08781	0.4144	0.01419	0.02853	0.07252	0.3215

Table 3. Radii $R_{n,m}$ and energies $E_{n,m}$ for $^3P^e$ states of two electrons on a \mathcal{D} -sphere ($\mathcal{D}=2, 3, 4$).

n/m	$\mathcal{D}=2$				$\mathcal{D}=3$				$\mathcal{D}=4$			
	0	1	2	3	0	1	2	3	0	1	2	3
Radius												
1	2.291				3.000				3.708			
2	5.477				6.892				8.307			
3	9.616	3.006			11.72	3.748			13.84	4.478		
4	14.73	6.851			17.52	8.334			20.32	9.797		
5	20.84	11.62	3.676		24.30	13.82	4.453		27.78	16.01	5.208	
6	27.94	17.35	8.156		32.07	20.26	9.708		36.22	23.15	11.22	
7	36.04	24.05	13.54	4.315	40.83	27.66	15.84	5.128	45.65	31.25	18.10	5.909
8	45.13	31.75	19.86	9.412	50.58	36.04	22.90	11.03	56.07	40.32	25.89	12.60
Energy												
1	0.3333				0.2500				0.2000			
2	0.1333				0.1053				0.08696			
3	0.07300	0.7472			0.06002	0.5874			0.05093	0.4862		
4	0.04607	0.2131			0.03908	0.1728			0.03390	0.1459		
5	0.03166	0.1019	1.018		0.02752	0.08503	0.8196		0.02429	0.07315	0.6913	
6	0.02306	0.05983	0.2706		0.02042	0.05117	0.2228		0.01829	0.04477	0.1906	
7	0.01752	0.03932	0.1242	1.222	0.01575	0.03432	0.1046	0.9983	0.01428	0.03046	0.09079	0.8522
8	0.01375	0.02778	0.07096	0.3161	0.01251	0.02464	0.06102	0.2629	0.01145	0.02215	0.05370	0.2269

The energies of the S , P and D states ($m=0$) for 3-spherium are plotted in Figure 1 (the quasi-exact solutions are indicated by markers), while density plots of 2-spherium ($n=1$ and $m=0$) are represented on Figure 2.

4.1. Natural/unnatural parity

In attempting to explain Hund's rules [47] and the 'alternating' rule [48,49] (see also [50,51]), Morgan and

Kutzelnigg [52–54] have proposed that the two-electron atomic states be classified thus: a two-electron state, composed of one-electron spatial orbitals with individual parities $(-1)^{\ell_1}$ and $(-1)^{\ell_2}$ and hence with overall parities $(-1)^{\ell_1+\ell_2}$, is said to have natural parity if its parity is $(-1)^L$. [...] If the parity of the two-electron state is $-(-1)^L$, the state is said to be of unnatural parity. [54].

After introducing spin, three classes emerge. In a three-dimensional space, the states with a cusp

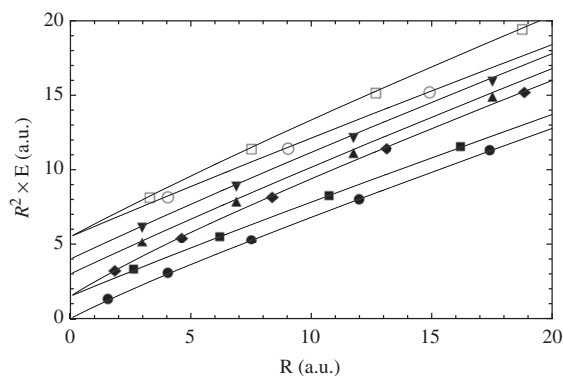


Figure 1. Energy of the S , P and D states of 3-spherium (${}^1S^e < {}^3P^o \leq {}^1P^o < {}^3P^e < {}^3D^e < {}^1D^o \leq {}^3D^o$). The quasi-exact solutions are shown by the markers.

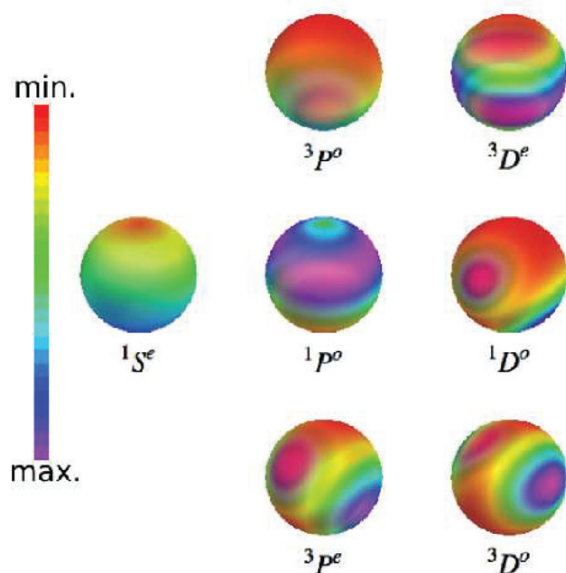


Figure 2. Density plots of the S , P and D states of 2-spherium. The squares of the wave functions when one electron is fixed at the north pole are represented. The radii are $3^{1/2}/2$, $15^{1/2}/2$, $5^{1/2}/2$, $21^{1/2}/2$, $21^{1/2}/2$, $3(5^{1/2})/2$ and $3(3^{1/2})/2$ for the ${}^1S^e$, ${}^3P^o$, ${}^1P^o$, ${}^3P^e$, ${}^3D^e$, ${}^1D^o$ and ${}^3D^o$ states, respectively.

value of $1/2$ [55,56] are known as the *natural parity singlet states*, those with a cusp value of $1/4$ [57] are the *natural and unnatural parity triplet states*, and those with a cusp value of $1/6$ [52], are the *unnatural parity singlet states*.

In previous work [29], we have observed that the ${}^1S^e$ ground state and the first excited ${}^3P^o$ state of 3-spherium possess the same singlet ($1/2$) and

triplet ($1/4$) cusp conditions as those for electrons moving in three-dimensional physical space and we have therefore argued that 3-spherium may be the most appropriate model for studying ‘real’ atomic or molecular systems. This is supported by the similarity of the correlation energy E_c of 3-spherium to that in other two-electron systems. Indeed, it can be shown [36] that, as $R \rightarrow 0$, E_c approaches -0.0476 , which is close to the corresponding values for the helium-like ions (-0.0467) [58], the Hooke’s law atom (-0.0497) [59], and two electrons in a ball (-0.0552) [46].

Most of the higher angular momentum states of 3-spherium, possess the ‘normal’ cusp values of $1/2$ and $1/4$. However, the unnatural ${}^1D^o$ and ${}^1F^e$ states have the cusp value of $1/6$.

4.2. First-order cusp condition

The wave function, radius and energy of the lowest states are given by

$$\Psi_{1,0}(u) = 1 + \gamma u, \quad R_{1,0}^2 = \frac{\delta}{4\gamma}, \quad E_{1,0} = \gamma, \quad (12)$$

which are closely related to the Kato cusp condition [56]

$$\frac{\Psi'(0)}{\Psi(0)} = \gamma. \quad (13)$$

We now generalize the Morgan–Kutzelnigg classification [53] to a D -dimensional space. Writing the interparticle wave function as

$$\Psi(u) = 1 + \frac{u}{2\kappa + D - 1} + O(u^2), \quad (14)$$

we have

$$\begin{aligned} \kappa &= 0 \text{ for natural parity singlet states,} \\ \kappa &= 1 \text{ for triplet states,} \\ \kappa &= 2 \text{ for unnatural parity singlet states.} \end{aligned} \quad (15)$$

The labels of the D -spherium states are given in Table 1.

4.3. Second-order cusp condition

The second solution is associated with

$$\Psi_{2,0}(u) = 1 + \gamma u + \frac{\gamma^2(\delta + 2)}{2\gamma(\delta + 2) + 4\delta + 6} u^2, \quad (16)$$

$$R_{2,0}^2 = \frac{(\gamma + 2)(\delta + 2) - 1}{2\gamma}, \quad (17)$$

$$E_{2,0} = \frac{\gamma(\delta + 1)}{(\gamma + 2)(\delta + 2) - 1}. \quad (18)$$

For \mathcal{D} -spherium, the second-order cusp condition is

$$\frac{\Psi''(0)}{\Psi(0)} = \frac{1}{2\mathcal{D}} \left(\frac{1}{\mathcal{D}-1} - E \right). \quad (19)$$

Following (19), the classification (15) can be extended to the second-order coalescence condition, where the wave function (correct up to second-order in u) is

$$\Psi(u) = 1 + \frac{u}{2\kappa + \mathcal{D} - 1} + \frac{u^2}{2(2\kappa + \mathcal{D})} \left(\frac{1}{2\kappa + \mathcal{D} - 1} - E \right) + O(u^3). \quad (20)$$

Thus, we have, for $\mathcal{D}=3$,

$$\frac{\Psi''(0)}{\Psi(0)} = \begin{cases} \frac{1}{6} \left(\frac{1}{2} - E \right), & \text{for } \kappa = 0, \\ \frac{1}{10} \left(\frac{1}{4} - E \right), & \text{for } \kappa = 1, \\ \frac{1}{14} \left(\frac{1}{6} - E \right), & \text{for } \kappa = 2. \end{cases} \quad (21)$$

For the natural parity singlet states ($\kappa=0$), the second-order cusp condition of 3-spherium is precisely the second-order coalescence condition derived by Tew [60], confirming that 3-spherium is an appropriate model for normal physical systems.

4.4. Third-order cusp condition

The third-order cusp condition of 3-spherium is

$$\frac{\Psi'''(0)}{\Psi(0)} = \frac{1}{18} \left(\frac{1}{8} - E + \frac{15}{16R^2} \right), \quad (22)$$

which is similar, but not strictly equivalent, to the one derived by Tew [60], due to the R -dependence of (22). The generalization to \mathcal{D} dimensions is straightforward.

4.5. Interdimensional degeneracies

As shown in Table 1, many states of \mathcal{D} -spherium have the same Hamiltonian (7) as lower angular momentum states of $(\mathcal{D}+2)$ -spherium.

Using the transformation $(\mathcal{D}, L) \rightarrow (\mathcal{D}+2, L-1)$ (see Table 1), one can see that the Hamiltonian of the ${}^3P^e$, ${}^1D^o$, ${}^3D^o$ and ${}^1F^e$ states for a given value of \mathcal{D} are respectively identical to those for ${}^1S^e$, ${}^3P^o$, ${}^1P^o$, and ${}^3D^e$ states at $\mathcal{D}+2$. The transformation $(\mathcal{D}, L) \rightarrow (\mathcal{D}+2, L-1)$, preserves the parity of the states, but ‘flips’ the spin configuration, thereby increasing by one unit the value of κ . In \mathcal{D} -spherium, we note that the Hamiltonians of the ${}^3P^e$ and ${}^3D^e$ states are identical.

Similar interdimensional degeneracies, first noticed by van Vleck [61], have been observed for various systems [44,62–65].

5. Conclusion

In this article, we have reported exact solutions of a Coulomb correlation problem, consisting of two electrons on a \mathcal{D} -dimensional sphere. The Coulomb problem can be solved exactly for an infinite set of values of the radius R for both the ground and excited states, on both the singlet and triplet manifolds. The corresponding exact solutions are polynomials in the interelectronic distance u .

The cusp conditions (up to third-order in the interelectronic distance), which are related to the behaviour of the wave function at the electron–electron coalescence point, have been analysed and classified according to the natural or unnatural parity of the state considered.

Finally, we have shown that, as in other one-, two- or three-electron systems, there exist interdimensional degeneracies between some of the states of \mathcal{D} -spherium.

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