

## Two Electrons on a Hypersphere: A Quasiexactly Solvable Model

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We show that the exact wave function for two electrons, interacting through a Coulomb potential but constrained to remain on the surface of a  $\mathcal{D}$ -sphere ( $\mathcal{D} \geq 1$ ), is a polynomial in the interelectronic distance  $u$  for a countably infinite set of values of the radius  $R$ . A selection of these radii and the associated energies are reported for ground and excited states on the singlet and triplet manifolds. We conclude that the  $\mathcal{D} = 3$  model bears the greatest similarity to normal physical systems.

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Quantum mechanical models for which it is possible to solve explicitly for a finite portion of the energy spectrum are said to be quasiexactly solvable [1]. They have ongoing value and are useful both for illuminating more complicated systems and for testing and developing theoretical approaches, such as density-functional theory (DFT) [2–4] and explicitly correlated methods [5–8]. One of the most famous two-body models is the Hooke’s law atom, which consists of a pair of electrons repelling Coulombically but trapped in a harmonic external potential with force constant  $k$ . This system was first considered nearly 50 years ago by Kestner and Sinanoglu [9], solved analytically in 1989 for one particular  $k$  value [10], and later for a countably infinite set of  $k$  values [11].

A related system consists of two electrons trapped on the surface of a sphere of radius  $R$ . This has been used by Berry and collaborators [12–15] to understand both weakly and strongly correlated systems and to suggest an “alternating” version of Hund’s rule [16]. Seidl utilized this system to develop new correlation functionals [17] within the adiabatic connection in DFT [18]. We will use the term “spherium” to describe this system.

In recent work [19], we examined various schemes and described a method for obtaining near-exact estimates of the  $^1S$  ground state energy of spherium for any given  $R$ . Because the corresponding Hartree-Fock (HF) energies are also known exactly [19], this is now one of the most complete theoretical models for understanding electron correlation effects.

In this Letter, we consider  $\mathcal{D}$ -spherium, the generalization in which the two electrons are trapped on a  $\mathcal{D}$ -sphere of radius  $R$ . We adopt the convention that a  $\mathcal{D}$ -sphere is the surface of a  $(\mathcal{D} + 1)$ -dimensional ball. (Thus, for example, the Berry system is a 2-spherium.) We show that the Schrödinger equation for the  $^1S$  and the  $^3P$  states can be solved exactly for a countably infinite set of  $R$  values and that the resulting wave functions are polynomials in the interelectronic distance  $u = |\mathbf{r}_1 - \mathbf{r}_2|$ . Other spin and angular momentum states can be addressed in the same way using the ansatz derived by Breit [20].

The electronic Hamiltonian, in atomic units, is

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

and, because each electron moves on a  $\mathcal{D}$ -sphere, it is natural to adopt hyperspherical coordinates [21,22].

For  $^1S$  states, it can be then shown [19] that the wave function  $S(u)$  satisfies the Schrödinger equation

$$\left[ \frac{u^2}{4R^2} - 1 \right] \frac{d^2S}{du^2} + \left[ \frac{(2\mathcal{D} - 1)u}{4R^2} - \frac{\mathcal{D} - 1}{u} \right] \frac{dS}{du} + \frac{S}{u} = ES. \quad (2)$$

By introducing the dimensionless variable  $x = u/2R$ , this becomes a Heun equation [23] with singular points at  $x = -1, 0, +1$ . Based on our previous work [19] and the known solutions of the Heun equation [24], we seek wave functions of the form

$$S(u) = \sum_{k=0}^{\infty} s_k u^k, \quad (3)$$

and substitution into (2) yields the recurrence relation

$$s_{k+2} = \frac{s_{k+1} + [k(k + 2\mathcal{D} - 2)\frac{1}{4R^2} - E]s_k}{(k + 2)(k + \mathcal{D})} \quad (4)$$

with the starting values

$$\{s_0, s_1\} = \begin{cases} \{0, 1\} & \mathcal{D} = 1, \\ \{1, 1/(\mathcal{D} - 1)\} & \mathcal{D} \geq 2. \end{cases} \quad (5)$$

Thus, the Kato cusp conditions [25] are

$$S(0) = 0, \quad \frac{S''(0)}{S'(0)} = 1 \quad (6)$$

for electrons on a circle ( $\mathcal{D} = 1$ ) and

$$\frac{S'(0)}{S(0)} = \frac{1}{\mathcal{D} - 1} \quad (7)$$

in higher dimensions. We note that the “normal” Kato value of  $1/2$  arises for  $\mathcal{D} = 3$ , suggesting that this may be

most appropriate model for atomic or molecular systems. We will return to this point below.

The wave function (3) reduces to the polynomial

$$S_{n,m}(u) = \sum_{k=0}^n s_k u^k \quad (8)$$

(where  $m$  is the number of roots between 0 and  $2R$ ) if, and only if,  $s_{n+1} = s_{n+2} = 0$ . Thus, the energy  $E_{n,m}$  is a root of the polynomial equation  $s_{n+1} = 0$  [where  $\text{deg}s_{n+1} = [(n+1)/2]$ ], and the corresponding radius  $R_{n,m}$  is found from (4) which yields

$$R_{n,m}^2 E_{n,m} = \frac{n}{2} \left( \frac{n}{2} + \mathcal{D} - 1 \right). \quad (9)$$

$S_{n,m}(u)$  is the exact wave function of the  $m$ th excited state of  $^1S$  symmetry for the radius  $R_{n,m}$ .

If we write the  $^3P$  state wave function as [20]

$$^3\Psi = (\cos\theta_1 - \cos\theta_2)T(u), \quad (10)$$

where  $\theta_1$  and  $\theta_2$  are the  $\mathcal{D}$ th hyperspherical angles of the two electrons [21,22], the symmetric part satisfies the Schrödinger equation

$$\left[ \frac{u^2}{4R^2} - 1 \right] \frac{d^2T}{du^2} + \left[ \frac{(2\mathcal{D}+1)u}{4R^2} - \frac{\mathcal{D}+1}{u} \right] \frac{dT}{du} + \frac{T}{u} = ET, \quad (11)$$

and the antisymmetric part provides an additional kinetic energy contribution  $\mathcal{D}/(2R^2)$ .

Substituting the power series expansion

$$T(u) = \sum_{k=0}^{\infty} t_k u^k \quad (12)$$

into (11) yields the recurrence relation

$$t_{k+2} = \frac{t_{k+1} + [k(k+2\mathcal{D})\frac{1}{4R^2} - E]t_k}{(k+2)(k+\mathcal{D}+2)} \quad (13)$$

with the starting values

$$\{t_0, t_1\} = \{1, 1/(\mathcal{D}+1)\} \quad (14)$$

yielding the cusp condition

$$\frac{T'(0)}{T(0)} = \frac{1}{\mathcal{D}+1}. \quad (15)$$

The wave function (12) reduces to the polynomial

$$T_{n,m}(u) = \sum_{k=0}^n t_k u^k \quad (16)$$

when the energy  $E_{n,m}$  is a root of  $t_{n+1} = 0$ , and the corresponding radius  $R_{n,m}$  is found from (13) which yields

$$R_{n,m}^2 E_{n,m} = \frac{n}{2} \left( \frac{n}{2} + \mathcal{D} \right). \quad (17)$$

$T_{n,m}(u)$  is the exact wave function of the  $m$ th excited state of  $^3P$  symmetry for the radius  $R_{n,m}$ .

It is illuminating to begin by examining the simplest  $^1S$  and  $^3P$  polynomial solutions. Except in the  $\mathcal{D} = 1$  case, the first  $^1S$  solution has

$$R_{1,0} = \sqrt{\frac{(2\mathcal{D}-1)(2\mathcal{D}-2)}{8}}, \quad E_{1,0} = \frac{1}{\mathcal{D}-1}, \quad (18)$$

and the first  $^3P$  solution has

$$R_{1,0} = \sqrt{\frac{(2\mathcal{D}+1)(2\mathcal{D}+2)}{8}}, \quad E_{1,0} = \frac{1}{\mathcal{D}+1}. \quad (19)$$

These are tabulated for  $\mathcal{D} = 1, 2, 3, 4$ , together with the associated wave functions, in Table I.

In the  $\mathcal{D} = 1$  case (i.e., two electrons on a circle), the first singlet and triplet solutions have  $E_{2,0} = 2/3$  and  $E_{1,0} = 1/2$ , respectively, for the same value of the radius ( $\sqrt{6}/2 \approx 1.2247$ ). The corresponding wave functions are related by  $S_{2,0} = uT_{1,0}$ . Unlike  $T_{1,0}$ , the singlet wave function  $S_{2,0}$  vanishes at  $u = 0$  and exhibits a second-order cusp condition, as shown in (6).

For the 2-spherium ( $\mathcal{D} = 2$  case), we know from our previous work [19] that the HF energy of the lowest  $^1S$  state is  $E_{\text{HF}} = 1/R$ . It follows that the exact correlation energy for  $R = \sqrt{3}/2$  is  $E_{\text{corr}} = 1 - 2/\sqrt{3} \approx -0.1547$ , which is much larger than the limiting correlation energies of the heliumlike ions ( $-0.0467$ ) [26] or Hooke's law atoms ( $-0.0497$ ) [27]. This confirms our view that electron correlation on the surface of a sphere is qualitatively different from that in three-dimensional physical space.

The 3-spherium ( $\mathcal{D} = 3$  case), in contrast, possesses the same singlet and triplet cusp conditions—Eqs. (7) and (15)—as those for electrons moving in three-dimensional physical space. Indeed, the wave functions in Table I

$$S_{1,0}(u) = 1 + u/2 \quad (R = \sqrt{5/2}), \quad (20)$$

$$T_{1,0}(u) = 1 + u/4 \quad (R = \sqrt{7}) \quad (21)$$

have precisely the form of the ansatz used in Kutzelnigg's

TABLE I. Radius  $R$ , energy  $E$ , and wave function  $S(u)$  or  $T(u)$  of the first  $^1S$  and  $^3P$  polynomial solutions for two electrons on a  $\mathcal{D}$ -sphere.

State	$\mathcal{D}$	$2R$	$E$	$S(u)$ or $T(u)$
$^1S$	1	$\sqrt{6}$	2/3	$u(1 + u/2)$
	2	$\sqrt{3}$	1	$1 + u$
	3	$\sqrt{10}$	1/2	$1 + u/2$
	4	$\sqrt{21}$	1/3	$1 + u/3$
$^3P$	1	$\sqrt{6}$	1/2	$1 + u/2$
	2	$\sqrt{15}$	1/3	$1 + u/3$
	3	$\sqrt{28}$	1/4	$1 + u/4$
	4	$\sqrt{45}$	1/5	$1 + u/5$

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

$n/m$	$\mathcal{D} = 1$				$\mathcal{D} = 2$				$\mathcal{D} = 3$				
	0	1	2	3	0	1	2	3	0	1	2	3	
	Radius												
1					0.8660					1.5811			
2	1.2247				2.6458					4.0620			
3	3.3912				5.4312	1.4150				7.5154	2.2404		
4	6.5439	1.9178			9.2211	3.7379				11.961	5.3320		
5	10.693	4.7071			14.012	7.0848	1.9256			17.404	9.3775	2.8554	
6	15.841	8.4583	2.5522		19.804	11.448	4.7683			23.846	14.410	6.5350	
7	21.989	13.199	5.9404		26.597	16.817	8.6593	2.4123		31.287	20.439	11.158	3.4415
8	29.136	18.936	10.277	3.1515	34.389	23.190	13.583	5.7566		39.728	27.466	16.768	7.6903
	Energy												
1					1.0000					0.5000			
2	0.6667				0.2857					0.1818			
3	0.1957				0.1271	1.8729				0.0930	1.0459		
4	0.0934	1.0875			0.0706	0.4294				0.0559	0.2814		
5	0.0547	0.2821			0.0446	0.1743	2.3597			0.0371	0.1279	1.3798	
6	0.0359	0.1258	1.3817		0.0306	0.0916	0.5278			0.0264	0.0722	0.3512	
7	0.0253	0.0703	0.3471		0.0223	0.0557	0.2100	2.7065		0.0197	0.0461	0.1546	1.6253
8	0.0188	0.0446	0.1515	1.6110	0.0169	0.0372	0.1084	0.6035	0.0152	0.0318	0.0854	0.4058	

increasingly popular R12 methods [5,6]. Moreover, it can be shown [28] that, as  $R \rightarrow 0$ , the correlation energy  $E_{\text{corr}}$  approaches  $-0.0476$ , which nestles between the corresponding values for the heliumlike ions ( $-0.0467$ ) [26] and the Hooke's law atom ( $-0.0497$ ) [27]. Again, this suggests that the  $\mathcal{D} = 3$  model ("electrons on a hypersphere") bears more similarity to common physical systems than the  $\mathcal{D} = 2$  model ("electrons on a sphere").

Numerical values of the energies and radii, for polynomial wave functions in  $\mathcal{D} = 1, 2, 3$ , are reported in Tables II (for  $^1S$  states) and III (for  $^3P$  states).

For fixed  $\mathcal{D}$ , the radii increase with  $n$  but decrease with  $m$ , and the energies behave in exactly the opposite way. As  $R$  (or, equivalently,  $n$ ) increases, the electrons tend to localize on opposite sides of the sphere, a phenomenon known as Wigner crystallization [29], which has also been

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

$n/m$	$\mathcal{D} = 1$				$\mathcal{D} = 2$				$\mathcal{D} = 3$				
	0	1	2	3	0	1	2	3	0	1	2	3	
	Radius												
1	1.2247				1.9365					2.6458			
2	3.3912				4.7958					6.2048			
3	6.5439	1.9178			8.6227	2.6738				10.718	3.4111		
4	10.693	4.7071			13.435	6.2041				16.205	7.6748		
5	15.841	8.4583	2.5522		19.241	10.665	3.3588			22.678	12.852	4.1285	
6	21.989	13.199	5.9404		26.043	16.094	7.5340			30.142	18.979	9.0701	
7	29.136	18.936	10.277	3.1515	33.842	22.505	12.615	4.0095		38.600	26.077	14.897	4.8130
8	37.283	25.671	15.599	7.1177	42.640	29.907	18.650	8.8083	48.054	34.155	21.654	10.411	
	Energy												
1	0.5000				0.3333					0.2500			
2	0.1739				0.1304					0.1039			
3	0.0876	1.0196			0.0706	0.7343				0.0588	0.5801		
4	0.0525	0.2708			0.0443	0.2078				0.0381	0.1698		
5	0.0349	0.1223	1.3433		0.0304	0.0989	0.9972			0.0267	0.0832	0.8067	
6	0.0248	0.0689	0.3401		0.0221	0.0579	0.2643			0.0198	0.0500	0.2188	
7	0.0186	0.0439	0.1491	1.5858	0.0168	0.0380	0.1210	1.1974		0.0153	0.0335	0.1025	0.9821
8	0.0144	0.0303	0.0822	0.3948	0.0132	0.0268	0.0690	0.3093	0.0121	0.0240	0.0597	0.2583	

observed in other systems [11,30]. As a result, for large  $R$ , the ground state energies of both the singlet and the triplet state approach  $1/(2R)$ . Analogous behavior is observed when  $\mathcal{D} \rightarrow \infty$  [31,32].

In conclusion, we have shown that the system of two electrons, interacting via a Coulomb potential but constrained to remain on a  $\mathcal{D}$ -sphere, can be solved exactly for an infinite set of values of the radius  $R$ . We find that the 3-spherium ( $\mathcal{D} = 3$  model), wherein the electrons are confined to a three-dimensional surface of a four-dimensional ball, has greater similarity to normal physical systems than the more familiar  $\mathcal{D} = 2$  case.

We believe that our results will be useful in the future development of correlation functionals within density-functional theory [33], intracule functional theory [34–39], and explicitly correlated methods [5–8]. They also shed new light on dimension-dependent correlation effects and may be used as an alternative system for studying quantum dots [40].

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