Two electrons on a hypersphere: a quasi-exactly 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 $D$-sphere ($D \geq 1$), 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 $D = 3$ 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 quasi-exactly 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 $D$-spherium, the generalization in which the two electrons are trapped on a $D$-sphere of radius $R$. We adopt the convention that a $D$-sphere is the surface of a $(D + 1)$-dimensional ball. (Thus, for example, the Berry system is $2$-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 $u = |r_1 - r_2|$. 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

$$\hat{H} = -\frac{\nabla^2}{2} - \frac{\nabla^2}{2} + \frac{1}{u}$$

and because each electron moves on a $D$-sphere, it is natural to adopt hyperspherical coordinates $\{r, \theta, \phi\}$. For $1S$ states, it can be then shown [19] that the wave function $S(u)$ satisfies the Schrödinger equation

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

By introducing the dimensionless variable $x = u/2R$, this becomes a Heun equation [22] 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

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

and substitution into (2) yields the recurrence relation

$$s_{k+2} = s_{k+1} + \frac{[k(k + 2D - 2) + 1]}{(k + 2)(k + D)} [E - s_k]$$

with the starting values

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

Thus, the Kato cusp conditions [25] are

$$S(0) = 0 \quad S''(0) = 1$$

for electrons on a circle ($D = 1$) and

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

in higher dimensions. We note that the “normal” Kato value of 1/2 arises for $D = 3$, suggesting that this may the
most appropriate model for atomic or molecular systems. We will return to this point below.

The wave function (8) reduces to the polynomial

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

(8)

(where $m$ 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 deg $s_{n+1} = [(n+1)/2]$) and the corresponding radius $R_{n,m}$ is found from (11) which yields

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

(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

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

(10)

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

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

(11)

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

Substituting the power series expansion

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

(12)

into (11) yields the recurrence relation

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

(13)

with the starting values

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

(14)

yielding the cusp condition

$$\frac{T'(0)}{T(0)} = \frac{1}{D+1}$$

(15)

The wave function (12) reduces to the polynomial

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

(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

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

(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 $D = 1$ case, the first $^1S$ solution has

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

(18)

and the first $^3P$ solution has

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

(19)

These are tabulated for $D = 1, 2, 3, 4$ together with the associated wave functions, in Table II.

In the $D = 1$ 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 $S_{2,0} = u T_{1,0}$. Unlike $T_{1,0}$, the singlet wavefunction $S_{2,0}$ vanishes at $u = 0$, and exhibits a second-order cusp condition, as shown in (19).

For the $2$-spherium ($D = 2$ case), we know from our previous work [19] that the HF energy of the lowest $^1S$ state is $E_{HF} = 1/R$. It follows that the exact correlation energy for $R = \sqrt{3}/2$ is $E_{corr} = 1 - 2/\sqrt{3} \approx -0.1547$ which is much larger than the limiting correlation energies of the helium-like ions ($-0.0467$) 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 ($D = 3$ 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 II

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

(20)

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

(21)

have precisely the form of the ansatz used in Kutzenhigg’s increasingly popular R12 methods [3, 6]. Moreover, it

| State | $D$ | $2R$ | $E$ | $S(u)$ 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    | $1 + u/3$     |
|       | 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 $D$-sphere ($D=1,2,3$)

| $n/m$ | $D=1$ | $D=2$ | $D=3$ |
|-------|--------|--------|--------|
|       | 0      | 1      | 2      | 3      | 0      | 1      | 2      | 3      | 0      | 1      | 2      | 3      |
| 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 | 17.404 | 9.3775 | 3.4415 |        |       |
| 6     | 15.841 | 8.4583 | 2.5522 | 2.6738 | 31.287 | 11.585 | 11.158 |        |       |
| 7     | 21.989 | 13.199 | 5.9404 | 2.6738 | 39.728 | 16.768 | 7.6003 |        |       |
| 8     | 29.136 | 18.936 | 10.277 | 3.1515 | 48.054 | 21.654 | 10.411 |        |       |

Radial

| Radius | $D=1$ | $D=2$ | $D=3$ |
|--------|--------|--------|--------|
| 1      | 1.0000 |        | 0.5000 |        |
| 2      | 0.2857 |        | 0.1818 |        |
| 3      | 0.1957 | 1.8729 | 0.0930 | 1.0459 |
| 4      | 0.0934 | 0.4294 | 0.0559 | 0.2814 |
| 5      | 0.0547 | 0.1279 | 0.0371 | 0.1279 | 1.3798 |
| 6      | 0.0359 | 0.3417 | 0.0197 | 0.1546 | 1.6253 |
| 7      | 0.0188 | 0.1515 | 0.0152 | 0.0854 | 0.4058 |

Energy

| Energy  | $D=1$ | $D=2$ | $D=3$ |
|---------|--------|--------|--------|
| 1       | 0.5000 |        | 0.2500 |        |
| 2       | 0.1304 |        | 0.1039 |        |
| 3       | 0.0706 | 0.7343 | 0.0588 | 0.5801 |
| 4       | 0.0443 | 0.2078 | 0.0381 | 0.1698 |
| 5       | 0.0304 | 0.9972 | 0.0267 | 0.8067 |
| 6       | 0.0221 | 0.2643 | 0.0198 | 0.2188 |
| 7       | 0.0168 | 0.1974 | 0.0153 | 0.1025 | 0.9821 |
| 8       | 0.0132 | 0.0903 | 0.0121 | 0.0597 | 0.2583 |

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

| $n/m$ | $D=1$ | $D=2$ | $D=3$ |
|-------|--------|--------|--------|
|       | 0      | 1      | 2      | 3      | 0      | 1      | 2      | 3      | 0      | 1      | 2      | 3      |
| 1     | 1.2247 |        |        |        | 2.6458 |        |        |        |       |
| 2     | 3.3912 | 4.7958 |        |        | 6.2048 |        |        |        |       |
| 3     | 6.5439 | 1.9178 | 9.2211 | 3.7379 | 10.718 | 3.4111 |        |        |       |
| 4     | 10.693 | 4.7071 | 13.435 | 6.2041 | 16.205 | 7.6748 |        |        |       |
| 5     | 15.841 | 8.4583 | 25.222 | 3.3588 | 22.678 | 12.852 | 4.1285 |        |       |
| 6     | 21.989 | 13.199 | 5.9404 | 3.3588 | 30.142 | 18.979 | 9.0701 |        |       |
| 7     | 29.136 | 18.936 | 10.277 | 3.1515 | 39.728 | 26.077 | 14.897 | 5.1303 |       |
| 8     | 37.283 | 25.671 | 15.599 | 7.1177 | 48.054 | 34.155 | 21.654 | 10.411 |       |

Radial

| Radius | $D=1$ | $D=2$ | $D=3$ |
|--------|--------|--------|--------|
| 1      | 0.5000 |        | 0.2500 |        |
| 2      | 0.1304 |        | 0.1039 |        |
| 3      | 0.0706 | 0.7343 | 0.0588 | 0.5801 |
| 4      | 0.0443 | 0.2078 | 0.0381 | 0.1698 |
| 5      | 0.0304 | 0.9972 | 0.0267 | 0.8067 |
| 6      | 0.0221 | 0.2643 | 0.0198 | 0.2188 |
| 7      | 0.0168 | 0.1974 | 0.0153 | 0.1025 | 0.9821 |
| 8      | 0.0132 | 0.0903 | 0.0121 | 0.0597 | 0.2583 |

Energy

| Energy  | $D=1$ | $D=2$ | $D=3$ |
|---------|--------|--------|--------|
| 1       | 0.5000 |        | 0.2500 |        |
| 2       | 0.1304 |        | 0.1039 |        |
| 3       | 0.0706 | 0.7343 | 0.0588 | 0.5801 |
| 4       | 0.0443 | 0.2078 | 0.0381 | 0.1698 |
| 5       | 0.0304 | 0.9972 | 0.0267 | 0.8067 |
| 6       | 0.0221 | 0.2643 | 0.0198 | 0.2188 |
| 7       | 0.0168 | 0.1974 | 0.0153 | 0.1025 | 0.9821 |
| 8       | 0.0132 | 0.0903 | 0.0121 | 0.0597 | 0.2583 |

can be shown that, as $R \to 0$, the correlation energy $E_{\text{corr}}$ approaches $-0.0476$, which nestles between the corresponding values for the helium-like ions ($-0.0467$) and the Hooke’s law atom ($-0.0497$). Again, this suggests that the $D=3$ model (“electrons on a hypersphere”) bears more similarity to common physical systems than the $D=2$ model (“electrons on a sphere”).

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

For fixed $D$, 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 which has also been observed in other systems. As a result, for large $R$, the ground state energies of both the singlet and triplet state approach $1/(2R)$. Analogous behavior
is observed when $\mathcal{D} \to \infty$ [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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