

Natural occupation numbers in two-electron quantum rings

Vincent Tognetti^{1,a)} and Pierre-François Loos²

¹Normandy Univ., COBRA UMR 6014 & FR 3038, Université de Rouen, INSA Rouen, CNRS, 1 rue Tesnière, 76821 Mont Saint Aignan, Cedex, France

²Research School of Chemistry, Australian National University, Canberra ACT 2601, Australia

(Received 24 November 2015; accepted 15 January 2016; published online 5 February 2016)

Natural orbitals (NOs) are central constituents for evaluating correlation energies through efficient approximations. Here, we report the closed-form expression of the NOs of two-electron quantum rings, which are prototypical finite-extension systems and new starting points for the development of exchange-correlation functionals in density functional theory. We also show that the natural occupation numbers for these two-electron paradigms are in general non-vanishing and follow the same power law decay as atomic and molecular two-electron systems. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4940919>]

I. INTRODUCTION

The systems consisting of two electrons on a ring, on a sphere, or on a hypersphere^{1–7} have recently attracted considerable interest due to their uniform electronic distributions. Their properties are intrinsically different^{8–10} from those of the celebrated infinite uniform electron gas (UEG), which has been the fundamental starting point for the design of exchange-correlation functionals within density functional theory (DFT).¹¹ From this perspective, these new finite UEGs are not merely toy-models but pave a tremendously promising path for the improvement of DFT.^{12,13} Therefore, it is important to better understand the properties of such prototype models.

In this paper, we will focus on the two-electrons-on-a-ring systems (also known as two-electron quantum rings) because, as shown by Loos and Gill,⁵ they exhibit exact closed-form solutions (in the nonrelativistic domain) for some “magic” radius values. This means that the electron-electron repulsion energy, a pivotal energy component in quantum chemical systems, can be exactly calculated. It is known from the seminal work by Gilbert¹⁴ that this component can be, in principle, expressed in terms of the spinless first-order (or one-particle) reduced density matrix (1-RDM),¹⁵ denoted $\rho_1(\vec{r}; \vec{r}')$. Consequently, it would be beneficial to characterize the 1-RDM for two-electron quantum rings.

This problem is equivalent to determine the full set of the so-called natural orbitals (NOs)¹⁶ since they diagonalize the 1-RDM by definition. Here, our aim is to show that they can be obtained in closed form and to discuss their main features in comparison with those for (infinite) two-electron atomic or molecular systems, which have been extensively studied by Giesbertz and van Leeuwen in a stimulating series of papers.^{17–19} Such studies are in the continuation of many works dealing with the 1-RDM and NOs for model systems, such as harmonium, the Moshinsky atom, the helium atom, the H_2^+ and H_2 molecules.^{20–31}

Furthermore, NOs are central constituents for evaluating correlation energies through approximations^{32–41} to the two-particle reduced density matrix (2-RDM). In particular, one of us is interested in the evaluation of interaction energies between atoms-in-molecules using Pendás’ interacting quantum atoms (IQAs) scheme^{42,43} and in going beyond the semi-quantitative Kohn-Sham (KS)-IQA approach⁴⁴ by incorporating correlation effects through NOs.^{45,46}

Let us also recall that, besides energetic considerations, NOs or their various avatars are also instrumental in extracting physicochemical information from quantum calculations. For example, they are linked to the popular natural bond orbital (NBO) framework⁴⁷ for studying chemical bonding, and bear some similarities with the natural transition orbital (NTO)⁴⁸ and the recent natural excitation orbital (NEO)⁴⁹ analyses employed to explore electronic excitation processes.

Atomic units are used throughout.

II. GENERAL SOLUTION

A. Natural orbitals for any polynomial solution

Let us first recall that in two-electron quantum rings (where each electron is located by an angle θ), the exact wavefunction can be factorized as the product of an intracule ($\omega = \theta_1 - \theta_2$) contribution and an extracule ($\Omega = (\theta_1 + \theta_2)/2$) contribution. The latter is associated with the total angular momentum, which we will take to be equal to zero for convenience. Therefore, only the intracule part needs to be further investigated. As described in Ref. 5, this presents degenerate pairs of solutions, one corresponding to the singlet spin state ($S = 0$) and one to the triplet ($S = 1$) spin state.

Here we will focus on the singlet state, in which the required antisymmetry of the full electronic wavefunction is brought by the spin function, while its real spatial counterpart (that we will simply call ψ) is symmetric under the exchange of the two electrons. As a consequence, throughout this paper, only spatial coordinates will be considered, the spin variables being irrelevant for our analysis.

^{a)}Author to whom correspondence should be addressed. Electronic mail: vincent.tognetti@univ-rouen.fr

Such a choice will allow a straightforward comparison with the helium atom in its singlet electronic ground state, as studied by Giesbertz and van Leeuwen. Let us recall that in the Hartree-Fock description of He, only one atomic orbital, coined “1s”, is doubly occupied, while the inclusion of electron correlation effects leads to a slight depopulation of the first NO (1.984 at the CCSD/aug-cc-pVT5Z level of theory) for the benefit of the second (0.007) and third (0.003) NOs, effects we want to study in two-electron rings.

To this aim, following Loos and Gill,⁵ we define the interelectronic distance

$$u = R\sqrt{2 - 2\cos\omega}, \quad (1)$$

where R is the radius of ring. As a solution of a Heun-like equation,⁵⁰ ψ can be cast in the general symmetric form given by

$$\psi_R^{(a,b)}(u) = u \left(1 + \frac{u}{2R}\right)^{a/2} \left(1 - \frac{u}{2R}\right)^{b/2} P^{(a,b)}(u), \quad (2)$$

where a and b are either 0 and 1, and $P^{(a,b)}$ is (in general) an infinite power series. However, for some specific values of R , this series is finite and thus reduces to a polynomial of order n . We will restrict our analysis to the family $\{a = 0, b = 0\}$, i.e., we will not consider the so-called “irrational solutions”,⁵ and examine only the following family:

$$\tilde{\psi}_R^{\{A_i\}}(u) = K_R^{\{A_i\}} \left(u + \sum_{i=2}^n A_i u^i\right) \equiv K_R^{\{A_i\}} Q_R^{\{A_i\}}(u), \quad (3)$$

where $K_R^{\{A_i\}}$ is the normalization constant. For the sake of clarity, all further dependencies on $(\{A_i\}, R)$ will not be explicitly written. Our goal is now to find the exact NOs χ_k for these particular Q functions. To do this, we recall the general NO definition for any two-electron wavefunction in any dimension (where we use Löwdin’s normalization convention⁵¹ and assume real functions),

$$\rho_1(\vec{r}_1; \vec{r}'_1) = 2 \int \psi(\vec{r}_1, \vec{r}_2) \psi(\vec{r}'_1, \vec{r}_2) d\vec{r}_2 = \sum_{k=0}^{\infty} n_k \chi_k(\vec{r}_1) \chi_k(\vec{r}'_1). \quad (4)$$

n_k being the so-called natural occupation numbers with

$$\sum_{k=0}^{\infty} n_k = 2. \quad (5)$$

The literature^{20,52,53} reports that NOs are also solutions of

$$\int \psi(\vec{r}_1, \vec{r}_2) \chi_k(\vec{r}_2) d\vec{r}_2 = c_k \chi_k(\vec{r}_1). \quad (6)$$

As demonstrated in Appendix A, these two representations are known to be linked by the following general relationship (independent of the form of the wavefunction):

$$\forall k \quad n_k = 2c_k^2. \quad (7)$$

In the particular case of (3), Eq. (6) reduces to

$$K \int_0^{2\pi} Q(u) \chi_k(\theta_2) R d\theta_2 = c_k \chi_k(\theta_1). \quad (8)$$

First, we search for even NOs. Because they are periodic functions of θ_1 , they can be expanded using the following Fourier series:

$$\chi_k(\theta_1) = \sum_{j=0}^{\infty} b_{kj} \cos(j\theta_1). \quad (9)$$

Knowing that u is a function of ω (see Eq. (1)), we expand Q as a Taylor series in $\cos\omega$,

$$Q(u) = \sum_{i=0}^{\infty} a_i \cos^i \omega. \quad (10)$$

Using Eqs. (9) and (10), Eq. (8) becomes

$$RK \int_0^{2\pi} \left[\sum_{i=0}^{\infty} a_i \cos^i(\theta_1 - \theta_2) \right] \left[\sum_{j=0}^{\infty} b_{kj} \cos(j\theta_2) \right] d\theta_2 = c_k \chi_k(\theta_1), \quad (11)$$

which is equivalent to

$$RK \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} a_i b_{kj} I_{ij}(\theta_1) = c_k \chi_k(\theta_1), \quad (12)$$

where

$$I_{ij}(\theta_1) = \int_0^{2\pi} \cos^i(\theta_1 - \theta_2) \cos(j\theta_2) d\theta_2 = \pi v_{ij} \cos(j\theta_1), \quad (13)$$

thanks to the properties of Chebyshev polynomials.⁵⁴ The expression of v_{ij} (that notably depends on the parity of integers i and j) is given by Eq. (B3). Equation (12) can thus be written as

$$\pi RK \sum_{j=0}^{\infty} d_j b_{kj} \cos(j\theta_1) = \sum_{j=0}^{\infty} c_k b_{kj} \cos(j\theta_1), \quad (14)$$

where $d_j = \sum_{i \geq j}^{\infty} a_i v_{ij}$. The uniqueness of the Fourier series expansion yields

$$\forall j \quad \pi RK d_j b_{kj} = c_k b_{kj}. \quad (15)$$

In the case of strictly decreasing d_j sequences — a condition that will be fulfilled by all of the cases studied below — Eq. (15) imposes that, for a given k value (i.e., a given NO), one and only one b_{kj} is not equal to 0. In other words, only one term in the sum of Eq. (9) does not vanish. Thus, we have demonstrated that the even NOs belong to the $\{\cos(k\theta_1)\}$ family. It can similarly be shown that the odd solutions belong to the $\{\sin(k\theta_1)\}$ one with the same $c_{k \neq 0}$ values. Such results may have been anticipated from symmetry considerations since NOs are generally adapted to the symmetry group of the system in case of non-degeneracies (see, for example, Ref. 55 for a more general discussion).

Then, combining Eqs. (7) and (15), the occupation numbers are finally given by

$$n_k = 2\pi^2 R^2 K^2 d_k^2. \quad (16)$$

B. Closed forms of natural occupations for polynomials of degree three

For the sake of brevity, we now restrict our analysis to polynomials up to degree three ($A_{i>3} = 0$). Closed-form

expressions for d_k can then be derived with Mathematica,⁵⁶ as proven in [Appendix B](#). It turns out that

$$d_k = \frac{Y_2(k)}{Y_4(k)}, \quad (17)$$

where Y_l denotes a polynomial of degree l . Hence,

$$n_k \underset{k \rightarrow \infty}{\approx} \frac{\gamma}{k^4}. \quad (18)$$

Note that we have obtained the same power law as the one reported by Giesbertz and van Leeuwen¹⁷ for two-electron systems in infinite space (like, for instance, the helium atom). The fact that two-electron quantum rings exhibit similar natural occupation decay as atoms or molecules is one more incentive to view them as powerful models for the development of new energy functionals for chemical applications. Equation (18) also calls for two additional remarks.

First, the decay law is valid whether the wavefunction corresponds to a ground or an excited state. Second, it is instructive to consider a cusplless (non-exact) polynomial wavefunction. For example,

$$\psi^{\text{cusplless}}(u) = \sum_{i=1}^M q_i u^{2i} = \sum_{i=1}^M \tilde{q}_i \cos^i \omega, \quad (19)$$

which only includes even powers of u . The Taylor series in $\cos \omega$ is now a finite sum contrarily to cases where odd powers of u (of the $[\sqrt{1 - \cos \omega}]^{2p+1}$ type) are involved. The NOs of $\psi^{\text{cusplless}}$ can be straightforwardly determined using Eqs. (11)-(15) simply by substituting a_i by \tilde{q}_i . As a consequence of the finite expansion for $\psi^{\text{cusplless}}$, the $\tilde{d}_j = \sum_{i \geq j} \tilde{q}_i v_{ij}$ values are exactly equal to zero for $j > M$. This implies, through Eq. (15), the existence of vanishing occupation numbers, a situation that cannot occur when a cusp exists at $u = 0$.

III. PARTICULAR RINGS

We now focus on specific numerical cases in order to discuss the role of the ring radius on the natural occupations.

A. The simplest (non-exact) wavefunction with a node

As a first example, let us consider the simplest $Q^{(0)}$ wavefunction featuring a node when the two electrons touch (i.e., at $u = 0$), for which $A_2^{(0)} = A_3^{(0)} = 0$ and $K^{(0)} = \frac{1}{2\sqrt{2}\pi R^2}$ (see Eq. (3)). Even if it does not correspond to an exact wavefunction, it has a clear pedagogical interest by virtue of its simplicity, which is embodied in the very compact form taken by Eq. (16),

$$n_k^{(0)} = \left(\frac{d_k^{(0)}}{2R} \right)^2. \quad (20)$$

Using the results given in [Appendix B](#), one can derive that

$$\begin{cases} n_0^{(0)} = \frac{16}{\pi^2}, n_{2m}^{(0)} = \frac{16}{\pi^2} \left(\frac{1}{-1 + 16m^2} \right)^2, \\ n_1^{(0)} = \frac{16}{9\pi^2}, n_{2m+1}^{(0)} = \frac{16}{\pi^2} \left(\frac{1}{3 + 16m + 16m^2} \right)^2. \end{cases} \quad (21)$$

Numerically, one obtains $n_0^{(0)} = 1.62$, $n_1^{(0)} = 0.18$, $n_2^{(0)} = 0.01$, $n_{k \geq 3}^{(0)} < 10^{-2}$. The correctness of this result is ensured by $n_0^{(0)} + 2 \sum_{k \geq 1} n_k^{(0)} = 2$, where the factor 2 takes into account the $\{\cos(k\theta_1), \sin(k\theta_1)\}$ degeneracy. It is remarkable that these occupation numbers are independent of the ring radius.

B. Exact ground state wavefunctions

We now consider exact ground state polynomial wavefunctions epitomized by the $R_1 = \sqrt{3/2}$ and $R_2 = \sqrt{23/2}$ radii. They are markedly characterized by the existence of a single node at $u = 0$. For the first radius value, the exact polynomial solution⁵ corresponds to $A_2^{R_1} = 1/2$, $A_{3,4,5}^{R_1} = 0$. Note that this exact value for A_2 is dictated by a Kato-like cusp condition,^{57,58} which states that, in one-dimensional systems,⁵ we have

$$\psi(u) = u(1 + u/2) + O(u^3). \quad (22)$$

The NO occupation numbers are then found to be equal to $n_0^{R_1} = 1.48$, $n_1^{R_1} = 0.26$, $n_{k \geq 2}^{R_1} < 10^{-2}$. With respect to the approximate solution discussed in [Sec. III A](#), one can see that there is a consequent depopulation of the first nodeless NO in favor of the second one (with one node), due to the now correct full description of the electron correlation.

For the second example, the exact solution is defined by $A_2^{R_2} = 1/2$, $A_3^{R_2} = 5/92$, $A_{4,5}^{R_2} = 0$,⁵ which gives $n_0^{R_2} = 1.33$, $n_1^{R_2} = 0.33$, $n_{k \geq 2}^{R_2} < 10^{-3}$. A still larger amount of electrons are now in the second NO. In view of these results, one could speculate that the higher the radius, the higher the population of the second NO.

To check the validity of this conjecture, we have considered two new ground state solutions that were not reported in [Ref. 5](#) (where only two $\{a = 0, b = 0\}$ solutions were explicitly given), which correspond to the following ring radii: $R_3 = \sqrt{\frac{93}{2} + \frac{3}{2}\sqrt{681}}$ and $R_4 = \sqrt{\frac{273}{2} + \frac{3}{2}\sqrt{3777}}$. The expressions for their solutions are gathered in [Appendix C](#). The related occupations numbers are $n_0^{R_3} = 1.17$, $n_1^{R_3} = 0.41$, and $n_0^{R_4} = 1.07$, $n_1^{R_4} = 0.45$, fully corroborating the increasing of n_1 with the ring size, even if the nodeless orbital still remains the most populated one.

Note that the population of the second NO is considerably higher (more than one order of magnitude) than the one for the helium atom. From this perspective, two-electron rings could constitute models of choice for the design of accurate correlation functionals, notably to describe strong correlation.

The observation that the electrons are mostly occupying the two first NOs is also consistent with the fact that the exact electronic distributions correspond to uniform electron densities. Indeed,

$$\begin{aligned} \rho(\vec{r}) &\equiv \rho_1(\vec{r}; \vec{r}) = \sum_{k=0}^{\infty} n_k |\chi_k(\theta_1)|^2 \\ &\approx n_0 \chi_0(\theta_1)^2 + n_1 (\chi_{1,\cos}(\theta_1)^2 + \chi_{1,\sin}(\theta_1)^2). \end{aligned} \quad (23)$$

As $\chi_0(\theta_1) \propto 1$ and $\chi_{1,\cos}(\theta_1)^2 + \chi_{1,\sin}(\theta_1)^2 \propto \cos^2\theta_1 + \sin^2\theta_1 \equiv 1$, we recover that two-electron quantum rings are UEGs.^{9,10,12}

Finally, it follows from these results and from the fact that the kinetic energy associated to the first NO is equal to zero that the KS correlation kinetic energy is mainly described by the second NO. Such a property could be of interest for the design of new correlation functionals since, for UEGs, one can in principle determine the total correlation energy from the correlation kinetic energy component, a feature notably exploited by Ragot and Cortona for the derivation of the RC correlation functional.^{59,60}

C. An example of an exact excited state wavefunction

As a final example, we now consider an exact excited state solution in the form of a fourth degree polynomial⁶¹ for $R_5 = \sqrt{\frac{93}{2} - \frac{3}{2}\sqrt{681}}$. This exact wavefunction has three nodes and its parameters are provided in [Appendix C](#).

We obtained $n_0 = 0.70$, $n_1 = 0.57$, $n_2 = 0.09$. In order to compare these results, one should first recall that $R_1 < R_5 < R_2$ and that the first NO population for the ground state of rings R_1 and R_2 was higher than 1.30, while the population of the second lower than 0.35. Accordingly, even if we do not know a closed-form expression for the ground state of ring R_5 , it is reasonable to assess that the populations of the first two NOs will obey the same inequalities. Thus, as intuitively expected, the population of the second NO considerably increases in this excited state.

However, the importance of the third NO shows that NOs may not provide a compact representation of electronic transitions (i.e., several orbitals have to be considered). Such an observation legitimizes the use of NTO⁴⁸ or NEO⁴⁹ analysis to facilitate the interpretation of such processes.

IV. CONCLUSIONS

In this paper, we have analytically determined the natural orbitals and the natural occupations for quantum systems consisting of two electrons confined on a one-dimensional sphere (i.e., a ring). They have been found to be non-vanishing and decaying following a $1/k^4$ power law for ground and excited states, similarly to two-electron atomic or molecular systems where the electrons can move in infinite space. We have observed an increase in the population of the second NO as the ring radius increases or when excited states are considered. Such results may support the use of these simple models to build energy representations, in particular for correlation, which could be subsequently applied to real chemical problems.

ACKNOWLEDGMENTS

V.T. thanks CNRS and Labex SynOrg for financial support. Professor Laurent Joubert (University of Rouen) is acknowledged for useful suggestions. P.-F.L. thanks the Australian Research Council for a Discovery Early Career

Researcher Award (No. DE130101441) and a Discovery Project Grant (No. DP140104071).

APPENDIX A: PROOF OF EQS. (6) AND (7)

Considering the full set of one-electron functions η_k satisfying

$$\int \psi(\vec{r}_1, \vec{r}_2) \eta_k(\vec{r}_2) d\vec{r}_2 = c_k \eta_k(\vec{r}_1), \quad (\text{A1})$$

the wavefunction can be expanded as

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_{i,j} \gamma_{ij} \eta_i(\vec{r}_1) \eta_j(\vec{r}_2). \quad (\text{A2})$$

Using Eq. (A1), the orthogonality of the $\{\eta_k\}$ set, and integrating over \vec{r}_2 , one can show that the $\{\eta_k\}$ diagonalize the wavefunction. Hence, the 1-RDM reads

$$\begin{aligned} 2 \int \left(\sum_i c_i \eta_i(\vec{r}_1) \eta_i(\vec{r}_2) \right) \left(\sum_j c_j \eta_j(\vec{r}'_1) \eta_j(\vec{r}_2) \right) d\vec{r}_2 \\ = 2 \sum_{i,j} c_i c_j \eta_i(\vec{r}_1) \eta_j(\vec{r}'_1) \int \eta_i(\vec{r}_2) \eta_j(\vec{r}_2) d\vec{r}_2 \\ = 2 \sum_i c_i^2 \eta_i(\vec{r}_1) \eta_i(\vec{r}'_1). \end{aligned} \quad (\text{A3})$$

APPENDIX B: EXPRESSION OF d_j

For $Q_R^{(A_2, A_3, B)}(u) = R\sqrt{2}\sqrt{1 - \cos(\theta_1 - \theta_2)} + 2A_2R^2(1 - \cos(\theta_1 - \theta_2)) + 2^{3/2}A_3R^3(1 - \cos(\theta_1 - \theta_2))^{3/2}$, one has the following Taylor expansion:

$$Q(u) = \sum_{i=0}^{\infty} a_i \cos^i(\theta_1 - \theta_2), \quad (\text{B1})$$

where $\binom{1/2}{\alpha}$ denotes a generalized binomial coefficient, and

$$\begin{cases} a_0 = \sqrt{2}R + 2A_2R^2 + 2^{3/2}A_3R^3, \\ a_1 = -\frac{1}{\sqrt{2}}R - 2A_2R^2 - 3\sqrt{2}A_3R^3, \\ a_{i \geq 2} = R\sqrt{2}(-1)^i \binom{1/2}{i} + 2^{3/2}A_3(-1)^i \binom{3/2}{i}. \end{cases} \quad (\text{B2})$$

Due to Eq. (13), the first term only involves even terms. More specifically, one can show, using the Chebyshev polynomials of the first kind,⁵⁴ that

$$\begin{cases} v_{00} = 2, \\ v_{ij} = 0 \text{ for } \begin{cases} i < j \\ \text{even } i \geq \text{odd } j, \\ \text{odd } i \geq \text{even } j \end{cases} \\ v_{ij} = \binom{i}{(i-j)/2} / 2^{i-1} \text{ for } \begin{cases} \text{even } i \geq \text{even } j \\ \text{odd } i \geq \text{odd } j \end{cases}. \end{cases} \quad (\text{B3})$$

Therefore, we have

$$\begin{aligned}
 d_0 &= a_0 v_{00} + \sum_{p=1}^{\infty} a_{2p} v_{2p,0} \\
 &= 2^{3/2} R + 4A_2 R^2 + 2^{5/2} A_3 R^3 + \sum_{p=1}^{\infty} \left[R\sqrt{2} \binom{1/2}{2p} + 2^{3/2} A_3 R^3 \binom{3/2}{2p} \right] \binom{2p}{p} / 2^{2p-1} \\
 &= \frac{8}{\pi} R + 4A_2 R^2 + \frac{64}{3\pi} A_3 R^3.
 \end{aligned} \tag{B4}$$

Similarly, using the fact that only odd terms contribute to d_1 , we obtain

$$\begin{aligned}
 d_1 &= a_1 v_{11} + \sum_{p=1}^{\infty} a_{2p+1} v_{2p+1,1} \\
 &= -\frac{1}{\sqrt{2}} R - 2A_2 R^2 - 3\sqrt{2} A_3 R^3 - \sum_{p=1}^{\infty} \left[R\sqrt{2} \binom{1/2}{2p+1} + 2^{3/2} A_3 R^3 \binom{3/2}{2p+1} \right] \binom{2p+1}{p} / 2^{2p} \\
 &= -\frac{8}{3\pi} R - 2A_2 R^2 - \frac{64}{5\pi} A_3 R^3.
 \end{aligned} \tag{B5}$$

For any even index higher or equal to 2,

$$\begin{aligned}
 d_{2m} &= \sum_{p=m}^{\infty} a_{2p} v_{2p,2m} \\
 &= \sum_{p=m}^{\infty} \left[R\sqrt{2} \binom{1/2}{2p} + 2^{3/2} A_3 R^3 \binom{3/2}{2p} \right] \binom{2p}{p-m} / 2^{2p-1} \\
 &= \frac{1}{\pi} \frac{(72 - 128m^2) R + 192A_2 R^3}{9 - 160m^2 + 256m^4}.
 \end{aligned} \tag{B6}$$

Finally, for any odd index higher or equal to 3,

$$\begin{aligned}
 d_{2m+1} &= \sum_{p=m}^{\infty} a_{2p+1} v_{2p+1,2m+1} \\
 &= -\sum_{p=m}^{\infty} \left[R\sqrt{2} \binom{1/2}{2p+1} + 2^{3/2} A_3 R^3 \binom{3/2}{2p+1} \right] \binom{2p+1}{p-m} / 2^{2p} \\
 &= \frac{1}{\pi} \frac{(40 - 128m - 128m^2) R + 192A_3 R^3}{\pi - 15 - 32m + 224m^2 + 512m^3 + 256m^4}.
 \end{aligned} \tag{B7}$$

APPENDIX C: EXACT SOLUTIONS FOR RINGS WITH RADIUS R_3 , R_4 , AND R_5

The polynomial coefficients are equal to

$$\left\{ \begin{array}{l} A_2 = \frac{1}{2}, A_3 = \frac{-3 + \sqrt{681}}{336}, A_4 = \frac{-387 + 17\sqrt{681}}{20160} \text{ for } R_3, \\ A_2 = \frac{1}{2}, A_3 = \frac{381 + 2\sqrt{3777}}{6756}, A_4 = \frac{-387 + 29\sqrt{3777}}{324288}, A_5 = \frac{-72375 + 1513\sqrt{3777}}{243432192} \text{ for } R_4, \\ A_2 = \frac{1}{2}, A_3 = -\frac{3 + \sqrt{681}}{336}, A_4 = -\frac{387 + 17\sqrt{681}}{20160} \text{ for } R_5, \end{array} \right. \tag{C1}$$

associated to the following energies:

$$\left\{ \begin{array}{l} \frac{2}{105} (31 - \sqrt{681}) \text{ for } R_3, \\ \frac{25}{13512} (91 - \sqrt{3777}) \text{ for } R_4, \\ \frac{2}{105} (31 + \sqrt{681}) \text{ for } R_5. \end{array} \right. \tag{C2}$$

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