Highly excited electronic image states of metallic nanorings

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We study electronic image states around a metallic nanoring and show that the interplay between the attractive polarization force and a repulsive centrifugal force gives rise to Rydberg-like image states trapped several nanometers away from the surface. The nanoring is modeled as a perfectly conducting isolated torus whose classical electrostatic image potential is derived analytically. The image states are computed via a two-dimensional finite-difference scheme as solutions of the effective Schrödinger equation describing the outer electron subject to this image potential. These findings demonstrate not only the existence of detached image states around nanorings but allow us also to provide general criteria on the ring geometry, i.e., the aspect ratio of the torus, that need to be fulfilled in order to support such states. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983294>]

I. INTRODUCTION

Image potential states are single-electron excitations trapped outside the crystal surface of a metal by the attractive interaction between the electron and the polarizable bulk.^{1–3} At large distances z from the surface the interaction is governed by the classical electrostatic image potential which scales in the limit of an infinitely extended flat surface as $\propto -1/(4z)$. In contrast, at short distances (a few Bohr radii), the specific microscopic material properties and many-body interactions become important.^{4–6} Although this is a well-known problem, it is worth mentioning that the reproduction of the classical image potential asymptotics for large z via density functional theory methods is possible but remains still a controversial issue.^{7,8}

On a structural as well as on a formal level, the situation for image states is reminiscent of the physics of the outer valence electron in an alkali atom. Accordingly, the experimentally observed spectra of image states above flat surfaces can be described very accurately by a Rydberg series with adapted quantum defects.² Such image states localize typically 0.5–5 nm above the surface with lifetimes that may extend to several ps.³ As the electronic decay mainly results from the interaction of the image state electron with the bulk, the study of image potential state dynamics via time-resolved two-photon photoemission spectroscopy has led to an improved understanding of scattering processes occurring at surfaces.⁹

In contrast to image states above flat surfaces, tubular image states (TIS) occur around curved surfaces like metallic nanotubes and are characterized by a high angular momentum number l satisfying typically $l \geq 6$.^{10,11} In this regime, the interplay between the repulsive centrifugal barrier and the

long-range part of the image potential forms stable radial potential wells that support detached Rydberg-like image states localized at distances of 10–50 nm from the surface. As the centrifugal barrier shields the TIS from the metallic surface, their lifetimes have been estimated to be 1 ns–1 μ s¹² which exceeds the typical lifetimes of usual image states by several orders of magnitude.

Since their prediction in 2002¹⁰ TIS have attracted much interest which led to numerous subsequent studies. This includes on the one hand explorations of novel setups like TIS at finite segmented nanowires,^{13,14} parallel nanowires,¹⁵ nanowire lattices,¹⁶ and double-walled nanotubes.¹⁷ On the other hand, this comprises also refined studies of the image force at the short-range scale for particular microscopically modeled semiconducting or conducting surfaces.^{11,18,19} Furthermore the coupling between the image states and nanomechanical oscillations of the tube has been investigated in Refs. 12 and 20.

While low- l image states have been observed experimentally via two-photon photoemission at free standing multi-walled carbon nanotubes²¹ and via scanning tunneling microscopy/spectroscopy at supported double-walled carbon nanotubes,²² an experimental observation of long-lived high- l TIS remains still an open challenge.

An experimentally more comprehensively studied system that possesses some similarities to TIS is electronic Rydberg states around C_{60} buckyballs.^{23,24} Both systems can be viewed as superatoms having instead of a charged nucleus a polarizable nanostructure which attracts the outer electron.²⁵ A major difference is, however, that image states around neutral buckyballs are not separated by a centrifugal barrier from the atomic surface and have in contrast to TIS only lifetimes on the order of 10 fs.²⁶ This has purely geometrical reasons, e.g., the image potential of a grounded sphere scales as ρ^{-2} with the radial distance ρ and does not lead to detached radial potential wells. In the context of image states around C_{60} this has been pointed out in Ref. 27.

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For the properties of highly excited image states, the object's geometry is hence of crucial importance. This motivates us to study in the present paper the image potential of a more complex but still idealized structure: a nanoring. To this aim we construct the exact expression for the classical electrostatic image potential around a metallic torus and analyze subsequently its properties for different aspect ratios. By solving the Schrödinger equation of the outer electron we demonstrate that sufficiently thin nanorings support TIS while this is not the case for thicker rings exceeding a certain critical aspect ratio. The image states can be viewed as TIS around finite nanotubes having both tube ends connected. Although the angular momentum around the tube is not conserved, we show that characteristic properties of these states can be derived from an effective radial potential. As there exist no other analytical expressions for electrostatic image potentials of finite nanostructures that are known to support TIS, we think that our results should be very relevant for a more realistic description of TIS and therefore also for their realization. Due to their long lifetimes these states could be an attractive platform for molecular electronics and nanostructure devices.

The paper is organized as follows. In Sec. II we present the underlying electrostatic problem. In Sec. II A the image potential is set up in toroidal coordinates. In Sec. II B we analyze an exemplary nanoring and point out general scaling properties of the image potential. Sec. III deals with image states trapped in the potential. In Sec. III A we describe our numerical approach which is employed in Sec. III B to compute image states. Finally, the states are analyzed and interpreted by means of an effective radial potential in Sec. III C. Our conclusions are provided in Sec. IV.

II. NANORING IMAGE POTENTIAL

A. The electrostatic problem

We consider an electron at position $\mathbf{r}_e$ in the proximity of a conducting nanoring whose surface is parametrized as a torus with major radius a and minor radius b for $a > b$, see Fig. 1. If the position of the electron is fixed, the total electrostatic potential at any point $\mathbf{r}$ outside the ring can be expressed as $\Phi_{\text{tot}}(\mathbf{r}; \mathbf{r}_e) = \Phi_{\text{coul}}(\mathbf{r}; \mathbf{r}_e) + \Phi_{\text{ind}}(\mathbf{r}; \mathbf{r}_e)$, where $\Phi_{\text{coul}}(\mathbf{r}; \mathbf{r}_e) = -1/|\mathbf{r} - \mathbf{r}_e|$ is the Coulomb potential and $\Phi_{\text{ind}}(\mathbf{r}; \mathbf{r}_e)$ is the induced potential which results from the polarization of the nanoring (for convenience we work here in atomic units).

FIG. 1. Sketch of a torus with major radius a and minor radius b . The colored arrows indicate the so-called toroidal (violet) and poloidal (green) directions.

The boundary conditions for an ideal conductor require that the total electrostatic potential is constant for all points $\mathbf{r}_s$ lying on the surface of the conductor, i.e., $\Phi_{\text{tot}}(\mathbf{r}_s; \mathbf{r}_e) = V_0$. For neutral, i.e., non-charged, conductors this constant V_0 is *a priori* not known and needs to be determined by employing the additional condition that the induced potential $\Phi_{\text{ind}}(\mathbf{r}; \mathbf{r}_e)$ is source-free, in contrast to grounded nanostructures ($V_0 = 0$) that have in general non-source-free $\Phi_{\text{ind}}(\mathbf{r}; \mathbf{r}_e)$. Here we focus exclusively on neutral nanorings. In this case, one can show that the energy needed to separate the electron and the nanostructure is given by $V_{\text{im}}(\mathbf{r}_e) = -1/2 \cdot \Phi_{\text{ind}}(\mathbf{r}_e; \mathbf{r}_e)$, which is called the image potential.²⁸

As for metallic cylinders,¹⁰ the image potential for tori can be expressed analytically, too. To this aim we introduce toroidal coordinates ξ, η , and φ which are linked to cylindrical coordinates ρ, z , and φ via

$$\rho = \frac{c \sinh \xi}{\cosh \xi - \cos \eta} \quad (1)$$

and

$$z = \frac{c \sin \eta}{\cosh \xi - \cos \eta} \quad (2)$$

with $c = \sqrt{a^2 - b^2}$. In the new toroidal coordinates, the torus surface is defined by $\xi = \xi_0$ with $\cosh \xi_0 = a/b$. Employing these relations, the image potential of the neutral torus can be constructed by combining classical electrostatic results obtained for conducting tori in different external field configurations^{29–31} and reads

$$V_{\text{im}}(\xi, \eta) = \frac{1}{2\pi c} (\cosh \xi - \sinh \eta) \left[\frac{s_1^2(\xi, \eta)}{s_1(0, 0)} - s_2(\xi) \right], \quad (3)$$

where

$$s_1(\xi, \eta) = \sum_{n=0}^{\infty} \epsilon_n \frac{Q_{n-1/2}(\cosh \xi_0)}{P_{n-1/2}(\cosh \xi_0)} P_{n-1/2}(\cosh \xi) \cos(n\eta) \quad (4)$$

and

$$s_2(\xi) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \epsilon_n \epsilon_m (-1)^m \frac{\Gamma(n-m+1/2)}{\Gamma(n+m+1/2)} \frac{Q_{n-1/2}^m(\cosh \xi_0)}{P_{n-1/2}^m(\cosh \xi_0)} \times [P_{n-1/2}^m(\cosh \xi)]^2. \quad (5)$$

Here $P_{n-1/2}$, $Q_{n-1/2}$, $P_{n-1/2}^m$, and $Q_{n-1/2}^m$ are associated Legendre functions and $\epsilon_n = 2 - \delta_{0n}$ with the Kronecker delta δ_{0n} . The detailed derivation of $V_{\text{im}}(\xi, \eta)$ is given in the Appendix. While the sum $s_1(\xi, \eta)$ converges for all $\xi \geq \xi_0$, the second sum $s_2(\xi)$ diverges for $\xi \rightarrow \xi_0$. This agrees well with the fact that the image potential of any ideal conductor will become arbitrarily large for a decreasing distance to its surface. To evaluate (3) numerically we check the convergence of the sums $s_1(\xi, \eta)$ and $s_2(\xi, \eta)$ at each coordinate $\{\xi, \eta\}$ by increasing the range of summation until a desired precision is achieved.

B. Analysis of the image potential

As an illustrative example we consider the image potential of a ring with $a = 3000$ (~ 159 nm) and $b = 30$ (~ 1.59 nm). This length b as well as the circumference $2\pi a$ are comparable to the dimensions of single- and multi-walled nanotubes with radii ranging from 0.68 nm to 7.1 nm and lengths ranging from

FIG. 2. Image potential $V_{\text{im}}(\rho, z)$ for an electron at a metallic nanoring with $a = 3000$ (~ 159 nm) and $b = 30$ (~ 1.59 nm). A logarithmically scaled contour plot of $V_{\text{im}}(\rho, z)$ is shown (lower part of the figure) to illustrate the anisotropy of the potential.

200 nm to 1600 nm which have been studied in the context of TIS.^{10,13,14,18} In Fig. 2 we depict the resulting image potential in cylindrical coordinates. The plot illustrates the attraction of the electron towards the torus surface which is a circle of radius b in the ρ - z plane. Close to the surface the potential becomes nearly isotropic with respect to the tube center $\{\rho = a, z = 0\}$ due to its divergent behavior. At larger distances from the surface, however, the anisotropy is clearly visible.

General properties of nanorings with different parameters a and b can be illustrated by defining the rescaled quantities $\tilde{\rho} = \rho/a$, $\tilde{z} = z/a$, and $\tilde{V}_{\text{im}}(\tilde{\rho}, \tilde{z}) = aV_{\text{im}}(\rho, z)$. The resulting rescaled potential $\tilde{V}_{\text{im}}(\tilde{\rho}, \tilde{z})$ depends then only on the aspect ratio b/a . Radial cuts of this rescaled potential are presented in Fig. 3 for several b/a . As can be seen, the ratio b/a , first, determines the positions of the torus surface $\tilde{\rho} = 1 \pm b/a$ where the potential curves diverge, and, second, it controls the asymmetry around $\tilde{\rho} = 1$, which becomes clearly visible for the largest $b/a = 0.5$.

What is not obvious from Fig. 3 is that also the scaling properties of the image potential depend significantly on b/a . As we will discuss in Sec. III C, the scaling is crucial for the capability of nanorings to support TIS. To analyze this property, we compare the nanoring potential to a power-law with exponent α which is typical for many image potentials, e.g., at flat surfaces ($\alpha = -1$) or at grounded metallic spheres ($\alpha = -2$).

For simplicity we restrict this analysis here only to a radial cut of the potential in the region $\rho > a$. By introducing the rescaled radial distance of the electron to the tube center $\tilde{x} = \tilde{\rho} - 1$, the potential can be rewritten as $\tilde{V}_{\text{im}}^{\text{rad}}(\tilde{x}) = \tilde{V}_{\text{im}}(\tilde{\rho}, 0)$.

FIG. 3. Radial cuts of the rescaled image potential $aV_{\text{im}}(\rho, z=0)$ as a function of the rescaled radial distance ρ/a for different ratios of the torus radii b/a as stated in the legend.

FIG. 4. Local exponent $\alpha(\tilde{x})$ as defined in (6) in dependence of the rescaled radial distance $\tilde{x}$ to the tube center ($\rho = a, z = 0$) for different ratios of the torus radii b/a .

The local exponent of the potential is then defined by

$$\alpha(\tilde{x}) = \frac{d}{d \ln \tilde{x}} \ln \left(-\tilde{V}_{\text{im}}^{\text{rad}}(\tilde{x}) \right) \quad (6)$$

which is the slope in a double logarithmic plot of $\tilde{V}_{\text{im}}^{\text{rad}}(\tilde{x})$. This exponent is depicted in Fig. 4 for different ratios b/a . All curves converge for large $\tilde{x}$ to $\alpha(\tilde{x}) = -4$, which is the expected long-range scaling for the interaction of a point charge and a polarizable neutral finite object (monopole-induced-dipole-interaction). At short distances, $\alpha(\tilde{x})$ diverges as expected for $\tilde{x} \rightarrow b/a$. In between these limits there is an intermediate regime where the exponent approaches a maximal value. The smaller the ratio b/a , the larger is this maximal value, e.g., one has $\alpha(\tilde{x}) < -2$ if $b/a \geq 0.1$. In other words, only sufficiently thin nanorings have spatial regions where the radial image potential decreases slower than $\tilde{x}^{-2}$.

III. TOROIDAL IMAGE POTENTIAL STATES

A. Computational approach

Although electronic excitations at metal surfaces are in general a complex many-body phenomenon, image potential states have been described in many situations very successfully within a simple one-electron picture.^{1,3,10} In this model, one solves the Schrödinger equation of the single outer electron subject to the image potential. As the image potential expresses only the electrostatic energy of the system, it is clear that dynamical corrections are required when retardation effects or collective excitations of the metal (e.g., plasma oscillations) become important.^{19,32}

The nanoring image potential $V_{\text{im}}(\rho, z)$ is rotationally symmetric around the z -axis and we solve the Schrödinger equation in cylindrical coordinates. The stationary solution with energy $E_{m,n}$ can be written as an eigenstate of the angular momentum operator $\hat{L}_z$,

$$\Psi_{m,n}(\rho, z, \varphi) = \frac{u_{m,n}(\rho, z)}{\sqrt{2\pi\rho}} e^{im\varphi} \quad (7)$$

with angular momentum m . The separation of the angular degree of freedom leads then to the two-dimensional stationary Schrödinger equation

$$\left[-\frac{1}{2} \left(\frac{\partial^2}{\partial \rho^2} + \frac{\partial^2}{\partial z^2} \right) + V_{\text{im}}^{\text{eff}}(\rho, z) - E_{m,n} \right] u_{m,n}(\rho, z) = 0 \quad (8)$$

for the wave function $u_{m,n}(\rho, z)$ with an effective potential

$$V_m^{\text{eff}}(\rho, z) = \frac{m^2 - 1/4}{2\rho^2} + V_{\text{im}}(\rho, z) \quad (9)$$

that includes a centrifugal barrier depending on m . The second quantum number n thus labels the different eigenstates and energies for fixed m .

Eq. (8) formally resembles a two-dimensional Schrödinger equation in Cartesian coordinates with the additional restriction that ρ needs to be positive. We compute the energetically lowest eigenstates by representing $u_{m,n}(\rho, z)$ as a vector on an equidistant rectangular grid with N gridpoints $\{\rho_i, z_i\}$ for $1 \leq i \leq N$. In this representation, V_m^{eff} becomes a diagonal matrix and the derivative operators $\partial^2/\partial\rho^2$ and $\partial^2/\partial z^2$ can be expressed as sparse matrices by employing the finite-difference approximation (for our calculations, we use a 7-point stencil for each dimension).

To compute TIS with this method, two modifications of the original physical system are necessary. First, we impose hard-wall boundary conditions at the borders of the grid which have no effect on bound states if the grid is chosen large enough (see below). Second, we introduce a cutoff energy V_{min} to regularize the divergence at the surface and replace $V_{\text{im}}(\rho, z)$ by V_{min} if $V_{\text{im}}(\rho, z) < V_{\text{min}}$. Among all computed states $u_{m,n}$ we then select states which are insensitive to the cutoff as well as to the boundary conditions. This method works well for wave functions localized in regions with $\rho \gg 1$ but it should be mentioned for completeness that hard-wall boundary conditions may in general be inappropriate for states having $m=0$ which are allowed to have finite values $\Psi_{0,n}(\rho, z)$ for $\rho \rightarrow 0$ and which are therefore not part of our analysis.

B. Numerical results

To illustratively exemplify the existence of TIS at nanorings, we employ our computational approach to determine image potential states at the nanoring with $a = 3000$ and $b = 30$. Our rectangular grid is 8000×8000 (bohr radii)² large and consists of 1100×1100 equidistant grid points. This corresponds to a spatial resolution of approximately 7 bohr radii or 0.4 nm. Furthermore we choose $m = 1$ and set $V_{\text{min}} \approx 4$ eV such that the image potential is cut off only in regions closer than 2 bohr radii to the surface. In Fig. 5 we show the ten states having the lowest integrated probability to be found in the inner torus region $((\rho - a)^2 + z^2 \leq b^2)$. This probability is on the order of 10^{-6} .

These states have a pronounced circular symmetry around the tube center $\{\rho = a, z = 0\}$ and resemble in the transversal ρ - z -plane strongly high angular momentum states around nanotubes.^{10,11} The main differences are, however, that the circular symmetry is not perfect (as can be clearly seen from the higher excited states in Fig. 5) and that the TIS are periodically extended along the toroidal φ -direction (not visible in Fig. 5).

To quantify the circular motion we define the angular momentum operator $\hat{l} = -i[(\rho - a)\partial_z - z\partial_\rho]$ which is the generator of rotations along the so-called poloidal direction, see Fig. 1. For each state, Fig. 5 contains the expectation value of the squared angular momentum in terms of an effective angular momentum quantum number $l_{\text{eff}}^2 = \langle \hat{l}^2 \rangle$. The numerical accuracy of l_{eff} depends on our spatial resolution (here $\Delta\rho = \Delta z \approx 7$) and can for this example be estimated to $\Delta l_{\text{eff}} \approx 0.02$.

For the presented states, the number l_{eff} lies always close to an integer value counting the number of maxima of the electronic wave function in the ρ - z -plane, i.e., half of the maxima in the density plots. States having the same number of radial and angular nodes appear as energetically nearly degenerate pairs (differences below 1 μeV) and have a different parity along the z -axis. In the limit of an exact circular symmetry, the degeneracy would become exact and l_{eff} would become an integer.

The above analyzed states correspond hence to a regime where the image potential experienced by the electron is nearly circularly symmetric. This situation is comparable to the case of two parallel (infinitely extended) nanotubes sharing an electronic image state which has been analyzed in Ref. 16. For sufficiently large tube separations, all image states are gerade or ungerade superpositions of single-tube states and can be labeled by a good angular momentum quantum number. The situation changes, however, for smaller tube separations where an increasing asymmetric distortion leads to a collapse of the electronic states onto the tubes. A similar effect can be observed in the nanoring system for an increasing toroidal angular momentum m . This is illustrated in Fig. 6 where we follow the energies and densities of the six energetically highest TIS presented in Fig. 5. The densities can be compared to Fig. 5 and illustrate the impact of the additional centrifugal potential. As can be seen, an increasing m distorts the circular symmetry of the TIS. For high m this distortion destabilizes the system such that the wave functions are less well-separated from the

FIG. 5. Probability density $|u_{1,n}(\rho, z)|^2$ of the first ten TIS having the lowest probability in the inner region of the nanoring with $a = 3000$ (~ 159 nm) and $b = 30$ (~ 1.59 nm). Additionally, their energy E and poloidal angular momentum l_{eff} are displayed.

FIG. 6. Energies E and densities $|u_{m,n}(\rho, z)|^2$ of selected TIS in dependence of the angular momentum number m for the nanoring with $a = 3000$ (~ 159 nm) and $b = 30$ (~ 1.59 nm). The blue dots in (a) represent the numerically obtained energies (on this scale all energies are two-fold degenerate) which are compared to the approximation based on Eq. (10). The insets (b)-(e) depict the density $|u_{m,n}(\rho, z)|^2$ of the TIS and contain further information on their energy E and their angular momentum l_{eff} .

surface but also less well bound to the nanoring, see Fig. 6(e). To a good approximation, the energy shift with respect to m of the TIS $u_{m,n}(\rho, z)$ can be described by the parabola

$$E_{m,n} \approx E_{1,n} + \frac{m^2 - 1/4}{2a^2} \quad (10)$$

which is shown in Fig. 6(a). This is the expected behavior based on Eq. (9) in the limit that the TIS localize sufficiently well at a mean distance a from the coordinate center and that the state dependent offset $E_{0,n}$ can be approximately replaced by $E_{1,n}$.

C. Effective radial potential

In a regime where the image potential is almost circularly symmetric around the tube center $\{\rho, z\} = \{a, 0\}$, it is beneficial to analyze instead of the full image potential the effective radial potential

$$V_{l,m}^{\text{eff}}(\rho) = \frac{l^2 - \frac{1}{4}}{2|\rho - a|^2} + V_m^{\text{eff}}(\rho, 0). \quad (11)$$

$V_{l,m}^{\text{eff}}(\rho)$ includes an additional centrifugal barrier associated with the angular momentum l . It can be viewed as an approximation for the potential energy associated with the degree of freedom describing radial motion with respect to the tube center. This approximation becomes accurate for states localized sufficiently close to the tube surface where the potential $V_m^{\text{eff}}(\rho, z)$ is circularly symmetric. In a more sophisticated treatment, small anisotropies could be taken into account by separating the circular and radial motions adiabatically and analyzing instead of (11) a resulting set of appropriately circularly averaged adiabatic potential curves.

In Fig. 7 the radial potential from (11) is depicted for the exemplary nanoring ($a = 3000$, $b = 30$) for an angular momentum $m = 1$ and effective angular momenta l ranging from 5 to 12. In the figure, all curves with $7 \leq l \leq 10$ possess potential wells that are separated by centrifugal barriers from the nanoring surface. As expected from the ring geometry, these wells are non-symmetric with respect to reflections at the axis $\rho = a$. Further asymmetry stems from the centrifugal potential associated with m which leads to the divergent behavior for $\rho \rightarrow 0$. The properties of the wells can be compared to the exact solutions from Fig. 5. For example, the curve with $l = 9$ possesses potential wells at $\rho \approx 130$ nm and $\rho \approx 190$ nm with depths of approximately 1 meV. These values agree well with the energies and the radial extent of the four TIS possessing $l_{\text{eff}} \approx 9$ in Fig. 5. Their radial wave functions can be

interpreted as the lowest and first excited radial states in these wells. Similar agreement can be found for the other states in Fig. 5. Furthermore, the radial potential predicts that image potential states with $l_{\text{eff}} > 10$ and $l_{\text{eff}} < 7$ are either not bound to the ring or are not detached from its surface which agrees with our numerical results.

In a regime where the circular and the radial motions are approximately separable, the effective potential $V_{l,m}^{\text{eff}}(\rho)$ is consequently a useful tool to identify angular momenta l_{eff} leading to TIS and to specify their properties. In the following we will employ $V_{l,m}^{\text{eff}}(\rho)$ to estimate general criteria for the existence of TIS at nanorings in a regime where the impact of m is small. A general framework to study the conditions under which infinite metal cylinders support TIS has been provided in Ref. 11. The authors characterized the effective radial image potentials by the dimensionless parameter $\lambda_l = (l^2 - 1/4)a_0/(2b)$, where b is the cylinder radius, a_0 is the Bohr radius ($a_0 = 1$ in the present work), and l is the angular momentum. By analyzing the scaling properties of the image potential, the authors concluded that TIS exist only for $\lambda_l \geq 0.9$. If this condition is not satisfied, the angular momentum is too small for the formation of detached potential wells. Although this is not a strict criterion for the existence of TIS, e.g., for particular cases one has to look carefully at the height of the centrifugal barriers and the depths of the potential wells, it is a very useful criterion to estimate properties of TIS for infinite cylinders having different radii.

FIG. 7. The effective radial potential $V_{l,m}^{\text{eff}}(\rho)$ from Eq. (11) for the nanoring with major radius $a = 3000$ (~ 159 nm) and minor radius $b = 30$ (~ 1.59 nm). The angular momenta are $m = 1$ and $5 \leq l \leq 12$. The inset depicts these curves close to the nanoring surface. In both plots the inner region of the nanoring is marked in gray color.

In the following we adapt this procedure to derive analogous criteria for the nanoring in the regime where the potential (11) describes the system adequately and where the impact of m is small. By employing (9) and (11) we define the rescaled effective radial potential

$$\tilde{V}_{\lambda_l, \lambda_m}^{\text{eff}}(\tilde{\rho}) = aV_{l,m}^{\text{eff}}(\rho) = \frac{b}{a} \left(\frac{\lambda_l}{|\tilde{\rho} - 1|^2} + \frac{\lambda_m}{\tilde{\rho}^2} \right) + \tilde{V}_{\text{im}}(\tilde{\rho}, 0), \quad (12)$$

where λ_l and λ_m are linked to l and m via $\lambda_l = (l^2 - 1/4)/(2b)$ and $\lambda_m = (m^2 - 1/4)/(2b)$. The quantities $\tilde{\rho} = \rho/a$ and $\tilde{V}_{\text{im}}(\tilde{\rho}, 0) = aV_{\text{im}}(\rho, 0)$ are the rescaled radius and the rescaled image potential as defined in Section II B. The potential $\tilde{V}_{\lambda_l, \lambda_m}^{\text{eff}}(\tilde{\rho})$ depends explicitly, and through $\tilde{V}_{\text{im}}(\tilde{\rho}, 0)$ also implicitly, on the ratio b/a but not on a or b individually. If $\tilde{V}_{\lambda_l, \lambda_m}^{\text{eff}}(\tilde{\rho})$ possesses for certain parameters b/a , λ_l , and λ_m detached potential wells, one can therefore conclude that all $V_{l,m}^{\text{eff}}(\rho)$ for the same b/a will also possess detached potential wells if $l^2 - 1/4 = 2b\lambda_l$ and $m^2 - 1/4 = 2b\lambda_m$. For the systems analyzed here, the parameter λ_m is, however, only of minor importance, cf. Fig. 7.

For the potential curves in Fig. 7, where $b/a = 0.01$, one finds, e.g., that detached potential wells exist for $0.8 \leq \lambda_l \leq 1.8$. In Fig. 8 we illustrate how this interval changes if one goes to a different aspect ratio b/a . For small b/a the upper bound becomes very high, e.g., one finds for $b/a = 0.001$ that $0.9 \leq \lambda_l \leq 12$ (not visible in Fig. 7). In contrast for larger b/a the interval becomes very narrow and shrinks ultimately for $b/a = 0.04$ to approximately zero. Fig. 8 traces therefore the transition from infinite nanotubes (no upper bound on λ_l), to thin nanorings (upper and lower bound on λ_l), to “thick” nanorings (no TIS). It is to be expected that a scaling analysis of TIS around finite nanotubes with varying aspect ratios, which have been investigated in Refs. 13 and 14, should yield very similar results.

An improved understanding of why too thick nanorings do not support TIS can be obtained from the analysis of the local power-law scaling of the nanoring image potential carried out in Sec. II B. A basic calculation shows that an effective radial potential of the form $V^{\text{eff}}(\rho) = c_1\rho^\alpha + c_2\rho^{-2}$, where c_1 , c_2 , and α are constants, possesses minimal extremal values only if $\alpha > -2$. This is, for example, the reason why there exist no TIS around metallic nanospheres, cf. Ref. 27. This criterion can also be applied locally to the nanoring system: As illustrated in Fig. 4, nanorings with $b/a \geq 0.1$ have always local exponents

FIG. 8. The lower bound λ_l^{min} and the upper bound λ_l^{max} on the parameter $\lambda_l = (l^2 - 1/4)/(2b)$ for which the rescaled nanoring potential $\tilde{V}_{\lambda_l, \lambda_m}^{\text{eff}}(\tilde{\rho})$ in Eq. (12) possesses detached potential wells. These bounds depend on the nanoring aspect ratio b/a . The influence of λ_m is neglected, i.e., $\lambda_m = 0$.

$\alpha < -2$ and one can therefore conclude that TIS exist only around thin nanorings with $b/a < 0.1$ which agrees with our discussion of Fig. 8.

Finally, we employ the potential $V_{l,m}^{\text{eff}}(\rho)$ given in (11) to estimate the lifetimes of the TIS presented in Fig. 5 and focus on the collapse of the external electron into the bulk. Other decay mechanisms are spontaneous radiative emission or phonon-assisted collapse which have been addressed for TIS in Refs. 10 and 12. As the states are very similar to the original TIS around infinite nanotubes, we adapt the procedure proposed in Ref. 10. Once an electron is inside the bulk, the decay happens typically relatively fast and the to this decay channel associated lifetimes can therefore be estimated from the rate by which electron density tunnels through the centrifugal barrier. For a state with angular momenta l and m and an energy E , this lifetime is semi-classically given by $\tau \approx \Delta_t \exp(-2\gamma)$ with $\gamma = \int_{\rho_1}^{\rho_2} d\rho |v(\rho)|$, $\Delta_t = 2 \int_{\rho_1}^{\rho_2} d\rho / |v(\rho)|$, and $v(\rho) = \sqrt{2(E - V_{l,m}^{\text{eff}}(\rho))}$. The integrals are evaluated between the two turning points $\rho_2 > \rho_1 > (a + b)$ enclosing the centrifugal barrier. Illustratively Δ_t can be interpreted as the average time spent in the barrier and $\exp(-2\gamma)$ is the transmission coefficient. By evaluating these integrals numerically we obtain for the states with $l \approx 8$ and $E = -1.71$ meV a lifetime of $\tau \approx 2 \mu\text{s}$. The radially excited states with $l \approx 8$ and $E = -0.854$ meV have a slightly reduced lifetime of $\tau \approx 0.7 \mu\text{s}$. The lifetimes of higher angular momentum states increase exponentially with l . Therefore the radially excited states with $l \approx 9$ and $E = -0.223$ meV have already a lifetime of $\tau \approx 300$ ms. This estimation sets of course only an upper limit but indicates that the lifetimes of the here discussed TIS are comparable to the lifetimes of TIS around infinite nanotubes and, consequently, substantially higher than the lifetimes of image states above flat metals.

IV. CONCLUSIONS

In the present work, we constructed an analytical expression for the electrostatic image potential between a point charge and a neutral metallic ring. We analyzed this potential and demonstrated that it supports image states “circulating” the torus which can be viewed as a curvilinear generalization of tubular image states around nanocylinders.¹⁰ In contrast to the latter, the angular momentum l shielding the states from the torus surface is not conserved and the states are not circularly symmetric. The second angular momentum m (associated with the motion along the nanoring) is conserved and can be used to tune the energy and also to some extent the shape of the image states. Too high m will, however, couple the different l states too strongly and destabilize the system. The main features of TIS can be explained by means of an effective radial potential including a centrifugal barrier associated with l . By analyzing the scaling properties of this potential, we argued that centrifugally detached high angular momentum image states exist only around sufficiently thin nanorings where the major radius is roughly 25 times larger than the minor radius. However, it has to be expected that nanorings (like nanotubes) also support low angular momentum image states probing the surface, whose investigation might be an interesting subject for future studies.

In the last decades there has been a tremendous progress in the development of nanofabrication techniques³³ and the production of almost perfectly ring-shaped silver nanowires with dimensions $a \approx 5 \mu\text{m}$ and $b \approx 50 \text{ nm}$ is already possible.³⁴ Furthermore image states around C_6F_6 ³⁵ or even larger planar molecules with hollow cores could exhibit properties similar to the here discussed states.

Compared to TIS around straight cylindrical structures, the additional curvature of nanorings offers interesting new applications. For example, the repulsive mutual Coulomb interaction of two or more simultaneously excited electrons at a nanoring could lead to special equilibrium configurations where each electron resides at a particular angle along the ring. Another interesting geometry-related subject would be the investigation of topological effects such as Aharonov-Bohm phases along different paths that could be controlled via external magnetic fields.

The here presented results are only a first exploration of TIS at curved nanowires but should be of relevance for all future studies and applications of TIS at even more complex-shaped nanostructures.

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APPENDIX: DERIVATION OF THE IMAGE POTENTIAL FOR THE TORUS

In order to derive an exact expression of the classical electrostatic image potential of a neutral metallic torus, we construct first the electrostatic potential $\Phi_{\text{tot}}(\mathbf{r}; \mathbf{r}_e)$ outside the torus in the presence of an electron at position $\mathbf{r}_e$. This setup is very similar to the problem of a point charge in the proximity of an isolated, neutral, and conducting sphere³⁶ and can be solved by a related approach. To this aim we write Φ_{tot} as a linear superposition of the form

$$\Phi_{\text{tot}}(\mathbf{r}; \mathbf{r}_e) = \Phi_{\text{tot}}^g(\mathbf{r}; \mathbf{r}_e) + \alpha(\mathbf{r}_e)\Phi^1(\mathbf{r}), \quad (\text{A1})$$

where Φ_{tot}^g is the potential around a grounded metallic torus in the presence of the electron and Φ^1 is the particular potential of a charged metallic torus with the constant surface potential $\Phi^1|_A = 1$. The factor $\alpha(\mathbf{r}_e)$ needs to be determined from the condition that the total charge in the inner torus region vanishes, i.e., that the induced potential is source free.

The solution Φ_{tot}^g has been presented in Ref. 29. It can be written as $\Phi_{\text{tot}}^g(\mathbf{r}; \mathbf{r}_e) = \Phi_{\text{ind}}^g(\mathbf{r}; \mathbf{r}_e) - 1/|\mathbf{r} - \mathbf{r}_e|$, where the induced potential reads in toroidal coordinates

$$\begin{aligned} \Phi_{\text{ind}}^g(\mathbf{r}; \mathbf{r}_e) = & \frac{1}{\pi c} (\cosh \xi - \cos \eta)^{1/2} (\cosh \xi_e - \cos \eta_e)^{1/2} \\ & \cdot \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \epsilon_n \epsilon_m (-1)^m \frac{\Gamma(n-m+1/2)}{\Gamma(n+m+1/2)} \\ & \times \frac{\cos[m(\varphi - \varphi_e)] \cos[n(\eta - \eta_e)]}{P_{n-1/2}^m(\cosh \xi_0)} \\ & \cdot Q_{n-1/2}^m(\cosh \xi_0) P_{n-1/2}^m(\cosh \xi_e) P_{n-1/2}^m(\cosh \xi). \end{aligned} \quad (\text{A2})$$

Here ξ_e , η_e , and φ_e are the toroidal coordinates of the electron. For large $r \rightarrow \infty$, i.e., $\{\xi, \eta\} \rightarrow \{0, 0\}$, one finds

$$\begin{aligned} \Phi_{\text{ind}}^g & \rightarrow \frac{\sqrt{2}}{\pi r} (\cosh \xi_e - \cos \eta_e)^{1/2} \sum_{n=0}^{\infty} \epsilon_n \frac{Q_{n-1/2}(\cosh \xi_0)}{P_{n-1/2}(\cosh \xi_0)} \\ & \times P_{n-1/2}^m(\cosh \xi_e) \cos(n\eta_e). \end{aligned} \quad (\text{A3})$$

By comparing this expression to the multipole expansion $\Phi_{\text{ind}}(\mathbf{r}) = q_{\text{ind}}/r + \mathcal{O}(1/r^2)$ and by substituting (4), one can identify the induced positive monopole

$$q_{\text{ind}}(\mathbf{r}_e) = \frac{\sqrt{2}}{\pi} (\cosh \xi_e - \cos \eta_e)^{1/2} s_1(\xi_e, \eta_e). \quad (\text{A4})$$

This monopole needs now to be compensated by the potential $\alpha(\mathbf{r}_e)\Phi^1(\mathbf{r})$. The therefore required solution $\Phi^1(\mathbf{r})$ is stated in Ref. 30 [p. 239] and Ref. 31 [p. 73]. By employing Whipple's transformation for Legendre functions and (4), it can be expressed in toroidal coordinates as

$$\begin{aligned} \Phi^1(\mathbf{r}) & = \frac{\sqrt{2}}{\pi} \sqrt{\cosh \xi - \cos \eta} \sum_{n=0}^{\infty} \epsilon_n \frac{Q_{n-1/2}(\cosh \xi_0)}{P_{n-1/2}(\cosh \xi_0)} \\ & \times P_{n-1/2}(\cosh \xi) \cos(n\eta) \\ & = \frac{\sqrt{2}}{\pi} \sqrt{\cosh \xi - \cos \eta} s_1(\xi, \eta). \end{aligned} \quad (\text{A5})$$

From the long-range behavior of (A5), one can derive the capacitance of the torus $C = 2c/\pi \cdot s_1(0, 0)$ which depends only on the geometry of the torus and links the induced charge to the surface potential.^{30,31} Due to the linearity of the Laplace equation, the solution $\alpha(\mathbf{r}_e)\Phi^1(\mathbf{r})$ corresponds to a torus with surface potential $\alpha(\mathbf{r}_e)$ carrying a charge $C\alpha(\mathbf{r}_e)$. Consequently, by setting $\alpha(\mathbf{r}_e) = -q_{\text{ind}}(\mathbf{r}_e)/C$, one obtains with (A1), (A4), and (A5) the total potential

$$\begin{aligned} \Phi_{\text{tot}}(\mathbf{r}; \mathbf{r}_e) & = \Phi_{\text{tot}}^g(\mathbf{r}; \mathbf{r}_e) - \frac{q_{\text{ind}}(\mathbf{r}_e)}{C} \Phi^1(\mathbf{r}) \\ & = \Phi_{\text{tot}}^g(\mathbf{r}; \mathbf{r}_e) - \frac{1}{\pi c} (\cosh \xi_e - \cos \eta_e)^{1/2} \\ & \times (\cosh \xi - \cos \eta)^{1/2} \frac{s_1(\xi_e, \eta_e) s_1(\xi, \eta)}{s_1(0, 0)}. \end{aligned} \quad (\text{A6})$$

With (A2) and (5) the image potential is consequently given by

$$\begin{aligned} V_{\text{im}}(\mathbf{r}) & = -\frac{1}{2} \left(\Phi_{\text{ind}}^g(\mathbf{r}; \mathbf{r}) - \frac{q_{\text{ind}}(\mathbf{r})}{C} \Phi^1(\mathbf{r}) \right) \\ & = \frac{1}{2\pi c} (\cosh \xi - \cos \eta) \left[\frac{s_1^2(\xi, \eta)}{s_1(0, 0)} - s_2(\xi) \right]. \end{aligned} \quad (\text{A7})$$

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