Comparative Analysis of Absorption Resonances between Carbynes and Cyclo[n]carbons

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Supporting Information Available

SI.1 Electronic properties of finite atomic structures

The optical properties of finite atomic systems depend on the boundary conditions set on the electron wavefunctions. The optical dependence on the imposed boundary conditions is

demonstrated by considering the two types of boundaries, namely the periodic and *fixed ends* (wherein we will refer here as the *hard wall* boundary case). Exploration of the difference between these two types of boundary conditions can be tracked back to 1950s and the theory of atomic vibrations in 1D crystal lattices with impurities[1,2] and disordered arrays.[3] The use of the transfer matrix method to these atomic structures can provide a general way of solving the eigenvalues and eigenvectors. Also, the transfer matrix method provides insight into the progression from a set of simultaneous equations from a Hamitonian to its reduced form of the secular equation. This technique has been implemented to calculate the electronic properties of solid surfaces,[4,5] layered compounds,[6] 1D carbon nanostructures such as graphene nanoribbons and carbon nanotubes,[7] coupled quantum rings[8] and PT-symmetric oligomer chains.[9] Here, we implement the transfer matrix method to simple carbon nanostructures such as carbynes (polyynes or cumulenes) and cyclo[n]carbons (polyynic or cumulenic carbon rings). A detailed investigation of their electronic properties is provided within the tight-binding model approach.

SI.1.1 Atomic ring

An atomic ring can be a representative model for cumulenic cyclo[n]carbon with a simple structure shown in Fig. SI1. The Hamiltonian elements can be written as m_{ij}, where i is the row number for the initial atomic location of the electron and j is the column number of the atomic location where the electron jumps next. Considering the nearest-neighbor interactions within the single-orbital (p_z) tight-binding model framework, the matrix elements follow a pattern given by

$$m_{ij} = \begin{cases} \gamma, & \text{if } j = i \pm 1, \\ 0, & \text{if otherwise or } j = i. \end{cases} \tag{SI1}$$

where γ is the hopping parameter between the nearest neighbor atoms. The resulting Hamiltonian has non-zero elements at the topmost right, bottom left and off-diagonal locations in which the cyclic nature of the periodic boundary conditions for the atomic ring is considered

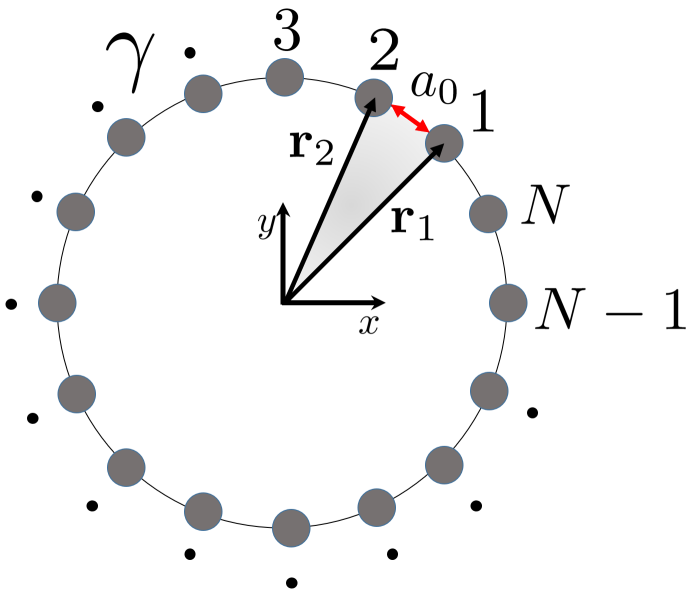


Figure SI1: An atomic ring structure with nearest-neighbor distance a_0, the radial vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ as the atomic locations, and the hopping parameter γ of the tight-binding method calculations.

for the last and first atoms. The Hamiltonian for the atomic ring system can be expressed as

$$H = \begin{pmatrix} 0 & \gamma & 0 & 0 & \dots & 0 & \gamma \\ \gamma & 0 & \gamma & 0 & \dots & 0 & 0 \\ 0 & \gamma & 0 & \gamma & \dots & 0 & 0 \\ 0 & 0 & \gamma & 0 & \dots & 0 & 0 \\ \vdots & & & & \ddots & & \vdots \\ \gamma & 0 & 0 & 0 & \dots & \gamma & 0 \end{pmatrix} \tag{SI2}$$

Then, the eigenvalue problem can be written by

$$H\widetilde{C} = E\widetilde{C} \tag{SI3}$$

$$\begin{pmatrix} 0 & \gamma & 0 & 0 & \dots & 0 & \gamma \\ \gamma & 0 & \gamma & 0 & \dots & 0 & 0 \\ 0 & \gamma & 0 & \gamma & \dots & 0 & 0 \\ 0 & 0 & \gamma & 0 & \dots & 0 & 0 \\ \vdots & & & \ddots & & & 0 \\ \gamma & 0 & 0 & 0 & \dots & \gamma & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_{N-1} \\ c_N \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_{N-1} \\ c_N \end{pmatrix} \tag{SI4}$$

where N is the number of atoms in the atomic ring. The matrix in Eq. (SI4) can be explicitly written as a set of simultaneous equations:

$$\begin{aligned} -c_1E + c_2\gamma + c_N\gamma &= 0; \\ c_1\gamma - c_2E + c_3\gamma &= 0; \\ c_2\gamma - c_3E + c_4\gamma &= 0; \\ &\vdots \\ c_1\gamma + c_{N-1}\gamma - c_NE &= 0 \end{aligned} \tag{SI5}$$

The first and last row from the set of equations in Eq. (SI5) are similar to the rest of the equations if the periodic boundary condition is imposed to the coefficients c_1 and c_N, i.e. $c_1 = c_{N+1}$ and $c_0 = c_N$. This restriction represents the cyclic nature of an atomic ring. The set of equations of Eq. (SI5) can be rewritten into a condensed form as follows:

$$c_{j-1}\gamma - c_jE + c_{j+1}\gamma = 0; \quad \text{for } j = 1, \dots, N \tag{SI6}$$

$$\begin{aligned} \tfrac{1}{\gamma}\left(c_{j-1}\gamma - c_jE + c_{j+1}\gamma\right) &= 0 \\ c_{j-1} - c_j\tfrac{E}{\gamma} + c_{j+1} &= 0 \\ c_{j+1} + c_{j-1} - c_j\left(2\alpha\right) &= 0 \end{aligned} \tag{SI7}$$

$$c_{j+1} = -c_{j-1} + 2\alpha c_j; \quad \text{for } j = 1, \dots, N \tag{SI8}$$

where a dimensionless energy α is introduced with a factor of 2 for a simplified expression of the final solution, i.e. $2\alpha = \frac{E}{\gamma}$. The set of equations from Eq. (SI8) can be solved using the transfer matrix method [1–3] by expressing it into a matrix form

$$\begin{pmatrix} c_j \\ c_{j+1} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 2\alpha \end{pmatrix} \begin{pmatrix} c_{j-1} \\ c_j \end{pmatrix} \tag{SI9}$$

We define the following vector and matrix expressions from Eq. (SI9) by

$$C_{j+1} \equiv \begin{pmatrix} c_j \\ c_{j+1} \end{pmatrix};$$

$$C_j \equiv \begin{pmatrix} c_{j-1} \\ c_j \end{pmatrix}; \tag{SI10}$$

$$T \equiv \begin{pmatrix} 0 & 1 \\ -1 & 2\alpha \end{pmatrix}$$

which gives a compact form of the expression of Eq. (SI10)

$$C_{j+1} = TC_j; \quad \text{for } j = 1, \ldots, N \tag{SI11}$$

It can be shown from the first three terms of Eq. (SI11) that the recursive relation of the expression is:

$$\begin{aligned} &C_2 = TC_1; \\ &C_3 = TC_2 = TTC_1 = T^2C_1; \\ &C_4 = TC_3 = TT^2C_1 = T^3C_1 \\ &\vdots \\ &C_{N+1} = TC_N = TT^{N-1}C_1 = T^NC_1. \end{aligned} \tag{SI12}$$

Thus, the recursive relation yields

$$C_{N+1} = T^N C_1 \,. \tag{SI13}$$

From the periodic boundary conditions imposed in Eq. (SI6), the vector C_{N+1} is equivalent to C_1:

$$C_{N+1} = \begin{pmatrix} c_N \\ \\ c_{N+1} \end{pmatrix} = \begin{pmatrix} c_0 \\ \\ c_1 \end{pmatrix} = C_1 \tag{SI14}$$

The matrix equation in Eq. (SI13) becomes

$$C_1 = T^N C_1 \tag{SI15}$$

$$\left(T^N - I\right) C_1 = 0 \tag{SI16}$$

which has non-zero solutions only when

$$\det\left(T^N - I\right) = 0 \tag{SI17}$$

The equation shown in Eq. (SI17) can be solved to obtain the eigenvalues of the Hamiltonian given in Eq. (SI2). The calculation of T^N can be done by utilizing the transformation properties of matrices, i.e.

$$T^N = U \Lambda^N U^{-1} \tag{SI18}$$

where Λ is the diagonal form of T or the eigenvalue matrix of T, and U is the transformation matrix of T which gives a new diagonal basis for T from its old non-diagonal basis. The transformation matrix U can be generated by starting on a zero matrix of correct dimensions and replacing its columns with the eigenvectors of T. The matrix U can be used for the *similarity transformation* of Λ:[10]

$$\Lambda = U^{-1} T U \tag{SI19}$$

From this definition of Λ, the matrix T^Ncan be written in the following manner:

$$\begin{aligned} T^N &= \underbrace{\left(U\Lambda U^{-1}\right)}_{N}\ \underbrace{\left(U\Lambda U^{-1}\right)}_{N-1}\ \underbrace{\left(U\Lambda U^{-1}\right)}_{N-2}\ \ldots\ \underbrace{\left(U\Lambda U^{-1}\right)}_{2}\ \underbrace{\left(U\Lambda U^{-1}\right)}_{1} \\ &= U\Lambda^N U^{-1} \end{aligned} \tag{SI20}$$

where the property of an inversion transformation matrix is utilized, i.e.

$$UU^{-1} = U^{-1}U = I \tag{SI21}$$

The matrices Λ and U from Eq. (SI18) can be specified by solving the eigenvalue problem of the transfer matrix T:

$$TV = \lambda V \tag{SI22}$$

$$\left(T - \lambda I\right) V = 0 \tag{SI23}$$

The eigenvalues of T can then be calculated by equating the determinant of Eq. (SI23) to zero:

$$\begin{aligned} \det\left(T - \lambda I\right) &= \det\left(\left(\begin{array}{cc} 0 & 1 \\ -1 & 2\alpha \end{array}\right) - \lambda \left(\begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array}\right)\right) \\ &= \det\left(\begin{array}{cc} -\lambda & 1 \\ -1 & 2\alpha - \lambda \end{array}\right) \end{aligned} \tag{SI24}$$

$$\det\left(T - \lambda I\right) = \lambda^2 - 2\alpha\lambda + 1 = 0 \tag{SI25}$$

Since the determinant in Eq. (SI25) is a simple quadratic equation, we can get the solutions of λ using the special quadratic formula:

$$\lambda_{1,2} = \frac{-\left(-2\alpha\right) \pm \sqrt{\left(-2\alpha\right)^2 - 4}}{2} \tag{SI26}$$

$$\lambda_{1,2} = \alpha \pm \sqrt{\alpha^2 - 1} \tag{SI27}$$

The λ solutions are substituted back to the eigenvalue problem of Eq. (SI22) to obtain the relations of the eigenvector components. For the first solution λ_1, we take the "$+$" operator of Eq. (SI27) and get the following vector elements of V_1:

$$\begin{pmatrix} -\lambda_1 & 1 \\ -1 & 2\alpha - \lambda_1 \end{pmatrix} \begin{pmatrix} V_{11} \\ V_{12} \end{pmatrix} = 0 \tag{SI28}$$

with the first row of the equation explicitly written as

$$-\lambda_1 V_{11} + V_{12} = 0 \tag{SI29}$$

$$V_{12} = \lambda_1 V_{11} \tag{SI30}$$

Similarly, the "$-$" operator is selected for the second solution λ_2 and substituted in Eq. (SI22) to get the vector components of V_2:

$$\begin{pmatrix} -\lambda_2 & 1 \\ -1 & 2\alpha - \lambda_2 \end{pmatrix} \begin{pmatrix} V_{21} \\ V_{22} \end{pmatrix} = 0 \tag{SI31}$$

$$-\lambda_2 V_{21} + V_{22} = 0 \tag{SI32}$$

$$V_{22} = \lambda_2 V_{21} \tag{SI33}$$

The first and second transfer matrix eigenvectors can be explicitly written as

$$V_1 = \begin{pmatrix} V_{11} \\ \lambda_1 V_{11} \end{pmatrix}; \quad V_2 = \begin{pmatrix} V_{21} \\ \lambda_2 V_{22} \end{pmatrix} . \tag{SI34}$$

Since the determinants of the matrices in Eqs. (SI28) and (SI31) are equal to zeroes, these systems of equations do not have unique solutions so that their vector components may take any arbitrary value. We can then set the vector components V_{11} and V_{22} equal to one for

simplification. Then, the eigenvectors can be expressed explicitly as

$$V_1 = \begin{pmatrix} 1 \\ \lambda_1 \end{pmatrix}; \qquad V_2 = \begin{pmatrix} 1 \\ \lambda_2 \end{pmatrix} \tag{SI35}$$

where these two eigenvectors form the columns of the transformation matrix U:

$$U = \begin{pmatrix} V_1 & V_2 \end{pmatrix} \tag{SI36}$$

$$U = \begin{pmatrix} 1 & 1 \\ \lambda_1 & \lambda_2 \end{pmatrix} \tag{SI37}$$

The inverse matrix U^{-1} is needed for the calculation of T^Nas specified in Eq. (SI18). Since the inverse of a 2 x 2 matrix is given by

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \frac{1}{ad - bc} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix}, \tag{SI38}$$

then the inverse matrix U^{-1} can be written explicitly as

$$U^{-1} = \begin{pmatrix} 1 & 1 \\ \lambda_1 & \lambda_2 \end{pmatrix}^{-1} = \frac{1}{\lambda_2 - \lambda_1} \begin{pmatrix} \lambda_2 & -1 \\ -\lambda_1 & 1 \end{pmatrix}. \tag{SI39}$$

We let the expression for the diagonal matrix Λ^N to be

$$\Lambda^N = \begin{pmatrix} \lambda_1^N & 0 \\ 0 & \lambda_2^N \end{pmatrix} \frac{1}{\lambda_2 - \lambda_1} \begin{pmatrix} \lambda_2 & -1 \\ -\lambda_1 & 1 \end{pmatrix} \tag{SI40}$$

Substituting these matrices in Eq. (SI39) and Eq. (SI40) into Eq. (SI18), we get the expression of T^N:

$$T^N = U\Lambda^N U^{-1}\,,$$

$$T^N = \begin{pmatrix} 1 & 1 \\ \lambda_1 & \lambda_2 \end{pmatrix} \begin{pmatrix} \lambda_1^N & 0 \\ 0 & \lambda_2^N \end{pmatrix} \frac{1}{\lambda_2 - \lambda_1} \begin{pmatrix} \lambda_2 & -1 \\ -\lambda_1 & 1 \end{pmatrix}. \tag{SI41}$$

The solutions λ_1 and λ_2 can be written in terms of a complex exponential function:

$$\lambda_1 = \mathrm{e}^{i\theta} = \cos\theta + i\sin\theta = \cos\theta + \sqrt{\cos^2\theta - 1} \tag{SI42}$$

$$\lambda_2 = \mathrm{e}^{-i\theta} = \cos\theta - i\sin\theta = \cos\theta - \sqrt{\cos^2\theta - 1} \tag{SI43}$$

with θ as a new variable. Then, the N^{th} power expressions of the λ_1 and λ_2 are equal to

$$\lambda_1^N = \mathrm{e}^{i\theta N} = \left(\cos\theta + \sqrt{\cos^2\theta - 1}\right)^N \tag{SI44}$$

$$\lambda_2^N = \mathrm{e}^{-i\theta N} = \left(\cos\theta - \sqrt{\cos^2\theta - 1}\right)^N \tag{SI45}$$

By observation, the quadratic equation solutions of λ_1 and λ_2 are equivalent to the expressions in Eq. (SI42) and Eq. (SI43) so that α can be expressed as

$$\alpha = \cos\theta \tag{SI46}$$

This change of variable is possible when α satisfies the condition that $|\alpha| \leq 1$. Substituting the complex exponential values from Eq. (SI42) to Eq. (SI43) and simplifying the expression results to

$$T^N = \frac{1}{\lambda_2 - \lambda_1} \begin{pmatrix} \lambda_1^N\lambda_2 - \lambda_1\lambda_2^N & \lambda_1 - \lambda_2^N \\ \lambda_1^{N+1}\lambda_2 - \lambda_1\lambda_2^{N+1} & \lambda_2^{N+1} - \lambda_1^{N+1} \end{pmatrix}$$

$$T^N = \frac{1}{\mathrm{e}^{-i\theta} - \mathrm{e}^{i\theta}} \begin{pmatrix} \mathrm{e}^{i\theta N}\mathrm{e}^{-i\theta} - \mathrm{e}^{i\theta}\mathrm{e}^{i\theta N} & \mathrm{e}^{-i\theta N} - \mathrm{e}^{i\theta N} \\ \mathrm{e}^{i\theta(N+1)}\mathrm{e}^{-i\theta} - \mathrm{e}^{i\theta}\mathrm{e}^{-i\theta(N+1)} & \mathrm{e}^{-i\theta(N+1)} - \mathrm{e}^{i\theta(N+1)} \end{pmatrix} \tag{SI47}$$

$$T^N = \frac{1}{\mathrm{e}^{-i\theta} - \mathrm{e}^{i\theta}} \begin{pmatrix} \mathrm{e}^{i\theta(N-1)} - \mathrm{e}^{-i\theta(N-1)} & \mathrm{e}^{-i\theta N} - \mathrm{e}^{i\theta N} \\ \mathrm{e}^{i\theta N} - \mathrm{e}^{-i\theta N} & \mathrm{e}^{-i\theta(N+1)} - \mathrm{e}^{i\theta(N+1)} \end{pmatrix} \tag{SI48}$$

$$T^N = \frac{1}{-2i\sin\theta} \begin{pmatrix} 2i\sin\left(\theta\left(N-1\right)\right) & -2i\sin\left(\theta N\right) \\ 2i\sin\left(\theta N\right) & -2i\sin\left(\theta\left(N+1\right)\right) \end{pmatrix}$$

$$T^N = \frac{1}{\sin\theta} \begin{pmatrix} -\sin\left(\theta\left(N-1\right)\right) & \sin\left(\theta N\right) \\ -\sin\left(\theta N\right) & \sin\left(\theta\left(N+1\right)\right) \end{pmatrix} \tag{SI49}$$

Placing the T^N expression in the argument of the secular equation from Eq. (SI16) shows that

$$T^N - I = \frac{1}{\sin\theta} \begin{pmatrix} -\sin\left(\theta\left(N-1\right)\right) & \sin\left(\theta N\right) \\ -\sin\left(\theta N\right) & \sin\left(\theta\left(N+1\right)\right) \end{pmatrix} - \frac{1}{\sin\theta} \begin{pmatrix} \sin\theta & 0 \\ 0 & \sin\theta \end{pmatrix} \tag{SI50}$$

$$T^N - I = \frac{1}{\sin\theta} \begin{pmatrix} -\sin\left(\theta\left(N-1\right)\right) - \sin\theta & \sin\left(\theta N\right) \\ -\sin\left(\theta N\right) & \sin\left(\theta\left(N+1\right)\right) - \sin\theta \end{pmatrix} \tag{SI51}$$

and consequently results in the explicit expression for the determinant of the argument of the secular equation:

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta} \begin{vmatrix} -\sin\left(\theta\left(N-1\right)\right) - \sin\theta & \sin\left(\theta N\right) \\ -\sin\left(\theta N\right) & \sin\left(\theta\left(N+1\right)\right) - \sin\theta \end{vmatrix} \tag{SI52}$$

$$\begin{aligned} \det\left(T^N - I\right) = \ & \tfrac{1}{\sin^2\theta}\left\{\left(-\sin\left(\theta\left(N-1\right)\right) - \sin\theta\right)\left(\sin\left(\theta\left(N+1\right)\right) - \sin\theta\right)\right. \\ & \left. + \sin^2\left(\theta N\right)\right\} \end{aligned} \tag{SI53}$$

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta}\{-\sin\left(\theta\left(N-1\right)\right)\sin\left(\theta\left(N+1\right)\right) - \sin\theta\sin\left(\theta\left(N+1\right)\right) + \sin\theta\sin\left(\theta\left(N-1\right)\right) + \sin^2\theta + \sin^2\left(\theta N\right)\} \tag{SI54}$$

Using the trigonometric product-sum identity:

$$\sin\left(\frac{\alpha+\beta}{2}\right)\sin\left(\frac{\alpha-\beta}{2}\right) = -\frac{1}{2}\left(\cos\alpha - \cos\beta\right), \tag{SI55}$$

we get the following relations for the expressions inside the curly brackets of Eq. (SI54)

$$-\sin\left(\theta N+\theta\right)\sin\left(\theta N+\theta\right) = \frac{1}{2}\cos\left(2\theta N\right) - \frac{1}{2}\cos\left(2\theta\right) \tag{SI56}$$

$$\begin{aligned} -\sin\theta\sin\left(\theta N+\theta\right) &= \tfrac{1}{2}\cos\left(\theta N+2\theta\right) - \tfrac{1}{2}\cos\left(\theta N\right) \\ &= \tfrac{1}{2}\cos\left(\theta\left(N+2\right)\right) - \tfrac{1}{2}\cos\left(\theta N\right) \end{aligned} \tag{SI57}$$

$$\begin{aligned} \sin\theta\sin\left(\theta N-\theta\right) &= -\tfrac{1}{2}\cos\left(\theta N\right) + \tfrac{1}{2}\cos\left(\theta N-2\theta\right) \\ &= -\tfrac{1}{2}\cos\left(\theta N\right) + \tfrac{1}{2}\cos\left(\theta\left(N-2\right)\right) \end{aligned} \tag{SI58}$$

By substituting these three trigonometric relations Eq. (SI56), Eq. (SI57) and Eq. (SI58), the secular equation in Eq. (SI54) results to

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta}\left\{\tfrac{1}{2}\cos\left(2\theta N\right) - \tfrac{1}{2}\cos\left(2\theta\right) + \tfrac{1}{2}\cos\left(\theta\left(N+2\right)\right) - \tfrac{1}{2}\cos\left(\theta N\right) - \tfrac{1}{2}\cos\left(\theta N\right) + \tfrac{1}{2}\cos\left(\theta\left(N-2\right)\right) + \sin^2\theta + \sin^2\left(\theta N\right)\right\} \tag{SI59}$$

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta}\left\{\tfrac{1}{2}\cos\left(2\theta N\right) - \tfrac{1}{2}\cos\left(2\theta\right) + \tfrac{1}{2}\cos\left(\theta\left(N+2\right)\right) - \tfrac{1}{2}\cos\left(\theta N\right) - \tfrac{1}{2}\cos\left(\theta N\right) + \tfrac{1}{2}\cos\left(\theta\left(N-2\right)\right) + \frac{1-\cos(2\theta)}{2} + \frac{1-\cos(2\theta N)}{2}\right\} \tag{SI60}$$

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta}\left\{\frac{1}{2}\cos\left(2\theta N\right) - \frac{1}{2}\cos\left(2\theta\right) + \frac{1}{2}\cos\left(\theta\left(N+2\right)\right) - \frac{1}{2}\cos\left(\theta N\right)\right. \tag{SI61}$$
$$\left. -\frac{1}{2}\cos\left(\theta N\right) + \frac{1}{2}\cos\left(\theta\left(N-2\right)\right) - \frac{1}{2}\cos\left(2\theta\right) - \frac{1}{2}\cos\left(2\theta N\right) + 1\right\}$$

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta}\left\{-\cos\left(2\theta\right) + \frac{1}{2}\left(\cos\left(\theta\left(N+2\right)\right) + \cos\left(\theta\left(N-2\right)\right)\right)\right. \tag{SI62}$$
$$\left. -\cos\left(\theta N\right) + 1\right\}$$

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta}\left\{-\cos\left(2\theta\right) + \cos\left(\theta N\right)\cos\left(2\theta\right) - \cos\left(\theta N\right) + 1\right\} \tag{SI63}$$

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta}\left\{1 - \cos\left(2\theta\right) + -\cos\left(\theta N\right)\left(1 - \cos\left(2\theta\right)\right)\right\} \tag{SI64}$$

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta}\left(1 - \cos\left(2\theta\right)\right)\left(1 - \cos\left(\theta N\right)\right) \tag{SI65}$$

$$\det\left(T^N - I\right) = \frac{1}{\sin^2\theta}\left(2\sin^2\theta\right)\left(1 - \cos\left(\theta N\right)\right) \tag{SI66}$$

$$\det\left(T^N - I\right) = 2\left(1 - \cos\left(\theta N\right)\right) \tag{SI67}$$

Since $\det\left(T^N - I\right) = 0$, then we get an explicit expression for the previously defined variable θ

$$2\left(1 - \cos\left(\theta N\right)\right) = 0 \tag{SI68}$$

$$\cos\left(\theta N\right) = 1 \tag{SI69}$$

$$\theta_l N = 2\pi l, \text{ for } l = 1, 2, 3, ... \tag{SI70}$$

$$\theta_l = \frac{2\pi l}{N} \tag{SI71}$$

From the previously defined variables $2\alpha = \dfrac{E}{\gamma}$ and $\alpha = \cos\theta$ from Eq. (SI46), the energies E of the atomic ring can be expressed as

$$E = 2\alpha\gamma = 2\gamma\cos\theta \tag{SI72}$$

which results to

$$E = 2\gamma \cos\left(\frac{2\pi l}{N}\right), \text{ for } l = 1, 2, 3, ..., N \tag{SI73}$$

$$\theta_l = \frac{2\pi l}{N}\,. \tag{SI74}$$

To check the eigenvalue results, another method of deriving the secular equation is to use the relation between the matrix trace Tr and the determinant in question:[11]

$$\det\left(T^N - I\right) = \det\left(T^N\right) + \det\left(I\right) - \mathrm{Tr}\left(T^N I\right) \tag{SI75}$$

The trace of a N x N matrix M is given by

$$\mathrm{Tr}\left(M\right) = \sum_{i=1}^{N} M_{ii} \tag{SI76}$$

Since the matrix T is expressed by a 2 x 2 matrix in Eq. (SI10) and has the following property of determinant

$$\det\left(T^N\right) = \left(\det\left(T\right)\right)^N, \tag{SI77}$$

then the determinant can be written as

$$\det\left(T\right) = \begin{vmatrix} 0 & 1 \\ -1 & 2\alpha \end{vmatrix} = 1 \tag{SI78}$$

$$\det\left(T^N\right) = 1^N = 1 \tag{SI79}$$

$$\det\left(I\right) = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = 1 \tag{SI80}$$

Substituting these unitary values to Eq. (SI75) results to the value of $\mathrm{Tr}\left(T^N\right)$:

$$\det\left(T^N - I\right) = 1 + 1 - \mathrm{Tr}\left(T^N I\right) = 0 \tag{SI81}$$

$$\mathrm{Tr}\left(T^N\right) = 2 \tag{SI82}$$

Applying the cyclic property of the trace operation:

$$\mathrm{Tr}\left(ABC\right) = \mathrm{Tr}\left(BCA\right) = \mathrm{Tr}\left(CAB\right) \tag{SI83}$$

to T^N expressed in terms of the *similarity transform* of its the diagonal matrix in Eq. (SI20) results to

$$\mathrm{Tr}\left(T^N\right) = \mathrm{Tr}\left(U\Lambda^N U^{-1}\right) = \mathrm{Tr}\left(\Lambda^N U^{-1}U\right) = \mathrm{Tr}\left(\Lambda^N I\right) = \mathrm{Tr}\left(\Lambda^N\right) \tag{SI84}$$

$$\mathrm{Tr}\left(T^N\right) = \mathrm{Tr}\left(\Lambda^N\right) = \mathrm{Tr}\begin{pmatrix} \lambda_1^N & 0 \\ 0 & \lambda_2^N \end{pmatrix} = \lambda_1^N + \lambda_2^N \tag{SI85}$$

With the complex exponential functions Eq. (SI44)) and Eq. (SI45) and the trace value of T^N in Eq. (SI82), the right hand side of Eq. (SI85) reduces to

$$\mathrm{Tr}\left(T^N\right) = \mathrm{e}^{i\theta N} + \mathrm{e}^{-i\theta N} = 2\cos\left(\theta N\right) \tag{SI86}$$

$$2\cos\left(\theta N\right) = 2 \tag{SI87}$$

$$\cos\left(\theta N\right) = 1 \tag{SI88}$$

which gives similar results of θ found in Eq. (SI74) and the eigenenergies in Eq. (SI73).

We proceed to the calculations of the eigenvectors $\widetilde{C} = (c_1, c_2, c_3, \ldots, c_{N-1}, c_N)$ from the eigenenergies E_1. The information given by the eigenvectors defines the optical properties of the system and specifies the optical selection rules of the transitions between energy levels. The two eigenvector components c_j can be arbitrarily chosen within the transfer matrix method since the solution $\theta_l = \frac{2\pi l}{N}$ gives a zero matrix to the expression $\left(T^N - 1\right)$. Once the vector $C_1 = (c_0, c_1)^{\mathrm{T}}$ is defined, the rest of the vectors $C_j = (c_{j-1}, c_j)^{\mathrm{T}}$ can be obtained by applying the recursive relation $C_{j+1} = TC_j$, for $j = 2, 3, \ldots, N-1, N$. It is important

to emphasize the difference between the notations of the letters T and T. The T used in the recursive relation $C_{j+1} = TC_j$ is a transfer matrix while the T in $C_j = (c_{j-1}, c_j)^{\mathrm{T}}$ is the transpose operator for a row vector to change to a column vector.

Initially, we can reasonably set the arbitrary values of the initial eigenvector of the Hamiltonian C_1 equal to the initial eigenvector of the transfer matrix V_1. There are two main reasons for this practical choice of eigenvectors, namely (1) the eigenproblem of the transfer matrix T has been previously solved for the eigenvectors V_1 and (2) the simplicity of the solution provides a neat form for all the c_j components of the eigenvectors C_j. Specifically, the initial vector C_1 is presented as follows

$$TC_1 = TV_1 = \lambda_1 V_1 \tag{SI89}$$

$$C_j = T^{j-1}C_1 = T^{j-1}V_1 = \lambda_1^{j-1}V_1 = \lambda_1^{j-1}\begin{pmatrix} 1 \\ \lambda_1 \end{pmatrix} \tag{SI90}$$

so that the components c_j can be obtained as

$$\begin{pmatrix} c_{j-1} \\ c_j \end{pmatrix} = \lambda_1^{j-1}\begin{pmatrix} 1 \\ \lambda_1 \end{pmatrix} = \begin{pmatrix} \lambda_1^{j-1} \\ \lambda_1^{j} \end{pmatrix} \tag{SI91}$$

$$c_j = \lambda_1^j = \mathrm{e}^{i\theta_l j}, \text{ for } j = 1, 2, 3, \ldots, N-1, N \tag{SI92}$$

and where $\theta_l = \frac{2\pi l}{N}$ with $l = 1, 2, 3, \ldots, N-1, N$ from the previous derivations of Eq. (SI74).

Then, the eigenvectors of the Hamiltonian matrix in Eq. (SI2) are presented by

$$\left.\begin{array}{l} c_1 = \mathrm{e}^{i\theta_l} \\ c_2 = \mathrm{e}^{i\theta_l 2} \\ c_3 = \mathrm{e}^{i\theta_l 3} \\ c_4 = \mathrm{e}^{i\theta_l 4} \\ \vdots \\ c_{N-1} = \mathrm{e}^{i\theta_l (N-1)} \\ c_N = \mathrm{e}^{i\theta_l (N)} \end{array}\right\} \widetilde{C}_l = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_{N-1} \\ c_N \end{pmatrix} = \begin{pmatrix} \mathrm{e}^{i\theta_l} \\ \mathrm{e}^{i\theta_l 2} \\ \mathrm{e}^{i\theta_l 3} \\ \mathrm{e}^{i\theta_l 4} \\ \vdots \\ \mathrm{e}^{i\theta_l (N-1)} \\ \mathrm{e}^{i\theta_l N} \end{pmatrix} \tag{SI93}$$

The eigenvector components c_j with specified θ_l can quickly be checked that they satisfy the periodic boundary conditions in Eq. (SI14), i.e. $c_0 = c_N$ and $c_1 = c_{N+1}$.

Alternatively, the eigenvectors shown in Eq. (SI93) can be used to obtain the eigenenergies in a much simpler approach. The other approach we call here as the "judicious guess" method is a reverse process from the one discussed above since the previous one calculated the eigenvectors from the eigenvalues. We begin with the Hamiltonian in Eq. (SI2) again but assume that we do not know about the eigenvalue solution above. We take an initial guess that the eigenvectors are expressed as

$$\widetilde{C} = \begin{pmatrix} \mathrm{e}^{ik} \\ \mathrm{e}^{ik2} \\ \mathrm{e}^{ik3} \\ \mathrm{e}^{ik4} \\ \vdots \\ \mathrm{e}^{ik(N-1)} \\ \mathrm{e}^{ikN} \end{pmatrix} \tag{SI94}$$

where k is the angular momentum of the electron in the atomic ring. The boundary condi-

tions are defined by

$$\widetilde{c}_0 = \mathrm{e}^{ik(0)} = 1 = \widetilde{c}_N = \mathrm{e}^{ikN} \tag{SI95}$$

where $\widetilde{c}_0$ and $\widetilde{c}_N$ are the components of the eigenvector in Eq.(SI94). In considering the two approaches, whether the transfer matrix or "judicious guess" method, we have to look beyond the frame of the problem and consider the auxiliary components of the eigenvectors such as c_0 and c_{N+1} for the cyclic nature of rings. Then, the Hamiltonian eigenvalue problem can be explicitly written as

$$H\widetilde{C} = E\widetilde{C} \tag{SI96}$$

$$\begin{pmatrix} 0 & \gamma & 0 & 0 & \dots & 0 & \gamma \\ \gamma & 0 & \gamma & 0 & \dots & 0 & 0 \\ 0 & \gamma & 0 & \gamma & \dots & 0 & 0 \\ 0 & 0 & \gamma & 0 & \dots & 0 & 0 \\ \vdots & & & & \ddots & & \\ 0 & 0 & 0 & 0 & \dots & 0 & \gamma \\ \gamma & 0 & 0 & 0 & \dots & \gamma & 0 \end{pmatrix} \begin{pmatrix} \mathrm{e}^{ik} \\ \mathrm{e}^{ik2} \\ \mathrm{e}^{ik3} \\ \mathrm{e}^{ik4} \\ \vdots \\ \mathrm{e}^{ik(N-1)} \\ \mathrm{e}^{ikN} \end{pmatrix} = E \begin{pmatrix} \mathrm{e}^{ik} \\ \mathrm{e}^{ik2} \\ \mathrm{e}^{ik3} \\ \mathrm{e}^{ik4} \\ \vdots \\ \mathrm{e}^{ik(N-1)} \\ \mathrm{e}^{ikN} \end{pmatrix} \tag{SI97}$$

that can be presented as a set of simultaneous equations

$$\begin{aligned} \gamma\mathrm{e}^{ik2} - E\mathrm{e}^{ik} + \gamma\mathrm{e}^{ikN} &= 0 \\ \gamma\mathrm{e}^{ik} - E\mathrm{e}^{ik2} + \gamma\mathrm{e}^{ik3} &= 0 \\ \gamma\mathrm{e}^{ik2} - E\mathrm{e}^{ik3} + \gamma\mathrm{e}^{ik4} &= 0 \\ &\vdots \\ \gamma\mathrm{e}^{ik(N-2)} - E\mathrm{e}^{ik(N-1)} + \gamma\mathrm{e}^{ikN} &= 0 \\ \gamma\mathrm{e}^{ik} - E\mathrm{e}^{ikN} + \gamma\mathrm{e}^{ik(N-1)} &= 0 \end{aligned} \tag{SI98}$$

or equivalently reduced to a condensed form accounting the periodic boundary conditions

given in Eq. (SI95)

$$\gamma \mathrm{e}^{ik(j-1)} - E\mathrm{e}^{ikj} + \gamma \mathrm{e}^{ik(j+1)} = 0, \text{ for } j = 1, 2, 3, ..., N \tag{SI99}$$

$$e^{ik(j-1)} + \mathrm{e}^{ik(j+1)} = \frac{E}{\gamma}\mathrm{e}^{ikj} \tag{SI100}$$

$$e^{-ik} + \mathrm{e}^{ik} = \frac{E}{\gamma} \tag{SI101}$$

$$E = 2\gamma \cos(k) \tag{SI102}$$

The value of angular momentum k can be obtained from the boundary conditions in Eq. (SI95)

$$e^{ikN} = \cos(kN) + i \sin(kN) = 1 \tag{SI103}$$

$$\cos(kN) = 1 \tag{SI104}$$

$$k_l N = 2\pi l, \text{ for } l = 1, 2, 3, ..., N \tag{SI105}$$

$$k_l = \frac{2\pi l}{N} \tag{SI106}$$

Thus, the eigenenergies for the atomic ring reduce to

$$E = 2\gamma \cos\left(\frac{2\pi l}{N}\right), \text{ for } l = 1, 2, 3, ..., N \tag{SI107}$$

that is equal to the expression we have previously calculated in Eq. (SI73).

The two approaches above give the same expression of the eigenenergies in the atomic ring system. However, the transfer matrix method and the "judicious guess" are not equivalent. Each method has its advantages and disadvantages. Consequently, we cannot specify which one is better. Both methods differ in their mathematical insight, which may or may not be intuitive in some cases.

For the transfer matrix method, the insight into this technique is emphasized on the

transitions of a simultaneous set of equations in Eq. (SI6) that can be presented into a reduced form as Eq. (SI8). On the other hand, the "judicious guess" method is based on the insight of the eigenvector form or expression of the eigenvector components. Based on our previous calculations, the "judicious guess" method is simpler but the transfer matrix method applies to broader and more general types of atomic systems (see the study done by Downing et. al. in Ref. 9). Oftentimes, the transfer matrix method provides the grounds of the eigenvector expressions to the "judicious guess" method. But the transfer matrix method drastically increases the sophistication to its set of equations as the system becomes more complex, such as the eigenvalue calculations of tridiagonal block Hamiltonians.[12,13]

SI.1.2 Finite atomic chain

The second type of boundary condition is found in finite atomic chain and is known as the *fixed ends* or *hard wall* boundary condition. This type of boundary condition was investigated in detail during the 1950s in the study of one-dimensional systems such as the atomic chain shown in Fig. SI2.[1–3]

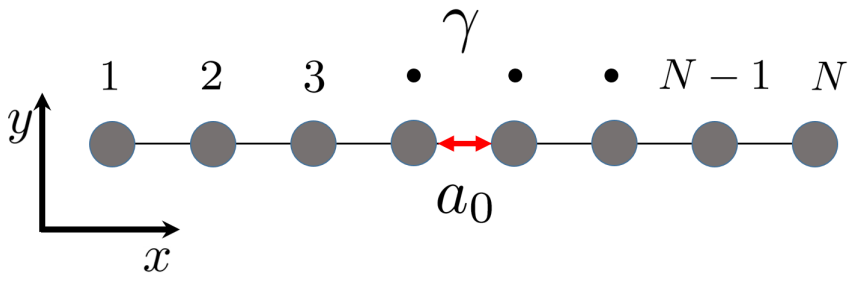


Figure SI2: A finite atomic chain with a nearest-neighbor distance a_0 and a hopping parameter γ for the tight-binding method calculations.

Since the two methods are described in full detail in the previous section, the following discussion places importance on the differences in the calculations between the atomic chain and the atomic ring. We begin by setting up the tight-binding Hamiltonian matrix again for the atomic chain. The Hamiltonian matrix elements can be defined as m_{ij}, where i is the row number for the initial atomic location of the electron and j is the column number

to the final atomic location of the electron. For the atomic chain with the nearest-neighbor interaction in the tight-binding model framework, the Hamiltonian matrix elements obey the following rules:

$$m_{ij} = \begin{cases} \gamma, & \text{if } j = i \pm 1, \\ 0, & \text{if otherwise or} j = i, j = N+1, j = 0. \end{cases} \tag{SI108}$$

where N is the number of atoms in the chain and which results to Hamiltonian H of the form

$$H = \begin{pmatrix} 0 & \gamma & 0 & 0 & \dots & 0 & 0 \\ \gamma & 0 & \gamma & 0 & \dots & 0 & 0 \\ 0 & \gamma & 0 & \gamma & \dots & 0 & 0 \\ 0 & 0 & \gamma & 0 & \dots & 0 & 0 \\ \vdots & & & & \ddots & & \\ 0 & 0 & 0 & 0 & \dots & 0 & \gamma \\ 0 & 0 & 0 & 0 & \dots & \gamma & 0 \end{pmatrix} \tag{SI109}$$

Then, the eigenvalue problem for the Hamiltonian is given by

$$H\widetilde{C} = E\widetilde{C}$$

$$\begin{pmatrix} 0 & \gamma & 0 & 0 & \dots & 0 & 0 \\ \gamma & 0 & \gamma & 0 & \dots & 0 & 0 \\ 0 & \gamma & 0 & \gamma & \dots & 0 & 0 \\ 0 & 0 & \gamma & 0 & \dots & 0 & 0 \\ \vdots & & & & \ddots & & \\ 0 & 0 & 0 & 0 & \dots & 0 & \gamma \\ 0 & 0 & 0 & 0 & \dots & \gamma & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_{N-1} \\ c_N \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_{N-1} \\ c_N \end{pmatrix} \tag{SI110}$$

with the corresponding set of simultaneous equations

$$\begin{aligned} -c_1 E + c_2\gamma &= 0; \\ c_1\gamma - c_2 E + c_3\gamma &= 0; \\ c_2\gamma - c_3 E + c_4\gamma &= 0; \\ &\vdots \\ c_{N-2}\gamma - c_{N-1}E + c_N\gamma &= 0; \\ c_{N-1}\gamma - c_N E &= 0; \end{aligned} \quad . \tag{SI111}$$

By observation, the first and last expressions differ from the rest of the equations which lose the cyclic pattern of Eq. (SI111). We can do a trick to implement a correction to produce the same cyclic form as the atomic ring structure by adding zero-valued variables c_0 and c_{N+1} into the first and last equations, respectively. Then, the set of equations in Eq. (SI111) can be rewritten into

$$\begin{aligned} c_0\gamma - c_1 E + c_2\gamma &= 0; \\ c_1\gamma - c_2 E + c_3\gamma &= 0; \\ c_2\gamma - c_3 E + c_4\gamma &= 0; \\ &\vdots \\ c_{N-2}\gamma - c_{N-1}E + c_N\gamma &= 0; \\ c_{N-1}\gamma - c_N E + c_{N+1}\gamma &= 0; \end{aligned} \tag{SI112}$$

where the additional terms are equal to zero, i.e.

$$c_0 = c_{N+1} = 0 \tag{SI113}$$

and the equations can be reduced into a condensed form

$$c_{j-1}\gamma - c_j E + c_{j+1}\gamma = 0, \text{ for } l = 1, 2, 3, ..., N. \tag{SI114}$$

Rearranging the terms in Eq. (SI114) and introducing again a dimensionless energy α defined by

$$2\alpha = \frac{E}{\gamma} \tag{SI115}$$

results to

$$c_{j+1} = -c_{j-1} + c_j \frac{E}{\gamma} \tag{SI116}$$

$$c_{j+1} = -c_{j-1} + 2\alpha c_j, \text{ for } l = 1, 2, 3, ..., N. \tag{SI117}$$

The transfer matrix method is again carried out to solve Eq. (SI117) in the same way as the atomic ring

$$\begin{pmatrix} c_j \\ c_{j+1} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 2\alpha \end{pmatrix} \begin{pmatrix} c_{j-1} \\ c_j \end{pmatrix} \tag{SI118}$$

$$C_{j+1} = TC_j \tag{SI119}$$

where we introduce the same notations from Eq. (SI10). This recursive relation of Eq. (SI119) is equivalent to Eq. (SI11) which can be reduced to Eq. (SI13) when applied N times, i.e.

$$C_{N+1} = T^N C_1$$

$$\begin{pmatrix} c_N \\ c_{N+1} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 2\alpha \end{pmatrix}^N \begin{pmatrix} c_0 \\ c_1 \end{pmatrix}. \tag{SI120}$$

This equation and its corresponding derivations may be the same, but it is important to note that there are restrictions imposed on the coefficients c_0 and c_{N+1} for the atomic chain, specifically

$$c_{N+1} = \left(T^N\right)_{21} c_0 + \left(T^N\right)_{22} c_1 = 0\,. \tag{SI121}$$

Since c_1 is a non-zero valued variable while $c_0 = 0$, we have

$$\left(T^N\right)_{22} = 0\,. \tag{SI122}$$

Equating this matrix element in Eq.(SI122) to the solution of T^N of Eq. (SI49) shows that

$$\left(T^N\right)_{22} = \sin\left[\theta\left(N+1\right)\right] \tag{SI123}$$

$$\sin\left[\theta\left(N+1\right)\right] = 0 \tag{SI124}$$

and leads to the solutions of θ:

$$\theta_l = \frac{\pi l}{N+1}, \text{ for } l = 1, 2, 3, ..., N. \tag{SI125}$$

Substituting this solution in Eq. (SI115) gives the explicit values of the eigenenergies for the atomic chain

$$E = 2\gamma\cos\theta \tag{SI126}$$

$$E_l = 2\gamma\cos\left(\frac{\pi l}{N+1}\right), \text{ for } l = 1, 2, 3, ..., N. \tag{SI127}$$

Now that we have the eigenenergies Eq. (SI127) from the secular equation, the next step is to solve for the eigenvectors $\widetilde{C}$ for the Hamiltonian in Eq. (SI109). The components of the eigenvectors $\widetilde{C}$ can be generated from the initial vector C_1 like the atomic ring problem but taking into account the boundary condition $c_0 = 0$. The vector C_1 cannot be chosen as the eigenvector for the transfer matrix T since the components of C_1 are not arbitrary. We can go around the problem by generalizing the two eigenvectors of T, namely V_1 and V_2, and taking their linear combinations for the vector components of C_1. With the correct choice of the linear combination of the coefficients, the boundary condition for the atomic chain can also be satisfied. A practical solution to the initial vector is

$$C_1 = \frac{1}{2i}\left(V_1 - V_2\right) \tag{SI128}$$

where V_1 and V_2 are the eigenvectors of the transfer matrix T defined in Eq. (SI35). Utilizing the matrix operation in Eq. (SI15) and the definition of C_1 in Eq. (SI128), the eigenvector

C_j can then be explicitly written as

$$C_j = T^{j-1} C_1 \tag{SI129}$$

$$C_j = T^{j-1} \frac{1}{2i} (V_1 - V_2) = \frac{1}{2i} \left(T^{j-1} V_1 - T^{j-1} V_2 \right) \tag{SI130}$$

We recall that the eigenvalue problem for the transfer matrix T is given by $TV = \lambda V$ so that

$$T^{j-1} V_1 = \lambda^{j-1} V_1; \; T^{j-1} V_2 = \lambda^{j-1} V_2. \tag{SI131}$$

Substituting these values into Eq. (SI130) results to

$$C_j = \frac{1}{2i} \left(\lambda_1^{j-1} V_1 - \lambda_2^{j-1} V_2 \right) \tag{SI132}$$

$$\begin{aligned} C_j &= \tfrac{1}{2i} \left(\lambda_1^{j-1} \begin{pmatrix} 1 \\ \lambda_1 \end{pmatrix} - \lambda_2^{j-1} \begin{pmatrix} 1 \\ \lambda_2 \end{pmatrix} \right) \\ &= \tfrac{1}{2i} \left(\begin{pmatrix} \lambda_1^{j-1} \\ \lambda_1^{j} \end{pmatrix} - \begin{pmatrix} \lambda_2^{j-1} \\ \lambda_2^{j} \end{pmatrix} \right) \end{aligned} \tag{SI133}$$

$$C_j = \frac{1}{2i} \begin{pmatrix} \lambda_1^{j-1} - \lambda_2^{j-1} \\ \lambda_1^{j} - \lambda_2^{j} \end{pmatrix} \tag{SI134}$$

From the exponential form of the eigenvalues in Eq. (SI42) and Eq. (SI43), the c_j matrix components for the finite chain can also be expressed as

$$\lambda_1^{j-1} - \lambda_2^{j-1} = \mathrm{e}^{i\theta_l (j-1)} - \mathrm{e}^{-i\theta_l (j-1)} = 2i \sin\left(\theta_l \left(j-1\right)\right) \tag{SI135}$$

$$\lambda_1^{j} - \lambda_2^{j} = \mathrm{e}^{i\theta_l j} - \mathrm{e}^{-i\theta_l j} = 2i \sin\left(\theta_l j\right) \tag{SI136}$$

so that eigenvector C_j can be written in terms of the sin function

$$C_j = \begin{pmatrix} c_{j-1} \\ c_j \end{pmatrix} = \begin{pmatrix} \sin\left(\theta_l\left(j-1\right)\right) \\ \sin\left(\theta_l j\right) \end{pmatrix} \tag{SI137}$$

Thus, the eigenvectors $\widetilde{C}_l$ for the Hamiltonian of the atomic ring from Eq. (SI109) are now written as

$$\widetilde{C}_l = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_{N-1} \\ c_N \end{pmatrix} = \begin{pmatrix} \sin\left(\theta_l\right) \\ \sin\left(\theta_l 2\right) \\ \sin\left(\theta_l 3\right) \\ \sin\left(\theta_l 4\right) \\ \vdots \\ \sin\left(\theta_l\left(N-1\right)\right) \\ \sin\left(\theta_l N\right) \end{pmatrix} \tag{SI138}$$

where the θ_l stated in Eq. (SI125) satisfies the boundary conditions of the atomic chain. The purpose of using the linear combination of V_i for the initial eigenvector C_1 is to achieve the simplest form of the vector components. We can also choose $C_1 = (\widetilde{c}_0, \widetilde{c}_1) = (0, 1)$ since this initial condition also fulfills the restrictions imposed by the atomic chain system. However, the $C_1 = (0, 1)$ choice gives an additional factor of $\frac{1}{\sin(\theta_l)}$ to the eigenvector $\widetilde{C}_l$ in Eq. (SI138) when you carry out the same process from Eq. (SI129).

The eigenenergies E for the atomic chain can also be solved using another method known as "judicious guess" like the eigenvalue problem of the atomic ring from the previous section.

We can make an experienced guess for the eigenvector with a similar form as Eq. (SI138):

$$\widetilde{C} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_{N-1} \\ c_N \end{pmatrix} = \begin{pmatrix} \sin(k) \\ \sin(k2) \\ \sin(k3) \\ \sin(k4) \\ \vdots \\ \sin(k(N-1)) \\ \sin(kN) \end{pmatrix} \tag{SI139}$$

where k is the electron momentum in the atomic chain. We implement the boundary conditions to the additional eigenvectors along the edges of the atomic chain similar to Eq. (SI113), i.e.

$$\widetilde{c}_0 = \sin(k \cdot 0) = \widetilde{c}_{N+1} = \sin(k(N+1)) = 0 \tag{SI140}$$

The eigenvalue problem of the Hamiltonian matrix is

$$H\widetilde{C} = E\widetilde{C}$$

$$\begin{pmatrix} 0 & \gamma & 0 & 0 & \dots & 0 & 0 \\ \gamma & 0 & \gamma & 0 & \dots & 0 & 0 \\ 0 & \gamma & 0 & \gamma & \dots & 0 & 0 \\ 0 & 0 & \gamma & 0 & \dots & 0 & 0 \\ \vdots & & & & \ddots & & \\ 0 & 0 & 0 & 0 & \dots & 0 & \gamma \\ 0 & 0 & 0 & 0 & \dots & \gamma & 0 \end{pmatrix} \begin{pmatrix} \sin(k) \\ \sin(k2) \\ \sin(k3) \\ \sin(k4) \\ \vdots \\ \sin(k(N-1)) \\ \sin(kN) \end{pmatrix} = E \begin{pmatrix} \sin(k) \\ \sin(k2) \\ \sin(k3) \\ \sin(k4) \\ \vdots \\ \sin(k(N-1)) \\ \sin(kN) \end{pmatrix} \tag{SI141}$$

that can be explicitly written as a simultaneous set of equations:

$$\begin{aligned}
-E\sin(k)+\gamma\sin(k2) &= 0;\\
\gamma\sin(k)-E\sin(k2)+\gamma\sin(k3) &= 0;\\
\gamma\sin(k2)-E\sin(k3)+\gamma\sin(k4) &= 0;\\
&\vdots\\
\gamma\sin(k(N-2))-E\sin(k(N-1))+\gamma\sin(kN) &= 0;\\
\gamma\sin(k(N-1))-E\sin(kN) &= 0;
\end{aligned} \quad . \tag{SI142}$$

By imposing the boundary conditions in Eq. (SI140), these set of equations in Eq. (SI142) can be reduced to:

$$\begin{aligned}
\gamma\sin(0)-E\sin(k)+\gamma\sin(k2) &= 0;\\
\gamma\sin(k)-E\sin(k2)+\gamma\sin(k3) &= 0;\\
\gamma\sin(k2)-E\sin(k3)+\gamma\sin(k4) &= 0;\\
&\vdots\\
\gamma\sin(k(N-2))-E\sin(k(N-1))+\gamma\sin(kN) &= 0;\\
\gamma\sin(k(N-1))-E\sin(kN)+\gamma\sin(k(N+1)) &= 0;
\end{aligned} \tag{SI143}$$

that can be condensed into one equation:

$$\gamma\sin(k(j-1))-E\sin(kj)+\gamma\sin(k(j+1))=0,\ \text{for } j=1,2,3,...,N \tag{SI144}$$

Taking into account the boundary conditions, the eigenenergies of the atomic chain are then:

$$E=\frac{\gamma}{\sin(kj)}\left(\sin(kj-k)+\sin(kj+k)\right) \tag{SI145}$$

$$E=\frac{\gamma}{\sin(kj)}\left(\sin(kj)\cos(k)-\cos(kj)\sin(k)+\sin(kj)\cos(k)+\cos(kj)\sin(k)\right) \tag{SI146}$$

$$E=\frac{\gamma}{\sin(kj)}\left(2\sin(kj)\cos(k)\right) \tag{SI147}$$

$$E = 2\gamma \cos(k) \tag{SI148}$$

To explicitly determine the k values, we take the boundary conditions from the Eq. (SI140):

$$\sin(k(N+1)) = 0$$

$$k(N+1) = \pi l \tag{SI149}$$

$$k = \frac{\pi l}{N+1}, \text{ for } l = 1, 2, 3, ..., N \tag{SI150}$$

Thus, the eigenenergies of the atomic chain are

$$E_l = 2\gamma \cos\left(\frac{\pi l}{N+1}\right), \text{ for } l = 1, 2, 3, ..., N \tag{SI151}$$

SI.1.3 Matching the eigenenergies of an atomic ring to a finite atomic chain

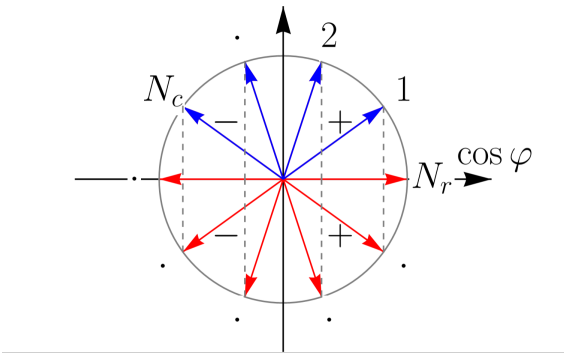
By inspection, the eigenenergies of the atomic ring system in Eq. (SI73) and the atomic chain structure from Eq. (SI151) would have the same energy level values when the phases are equal:

$$(E_l)_{\text{ring}} = (E_l)_{\text{chain}} \tag{SI152}$$

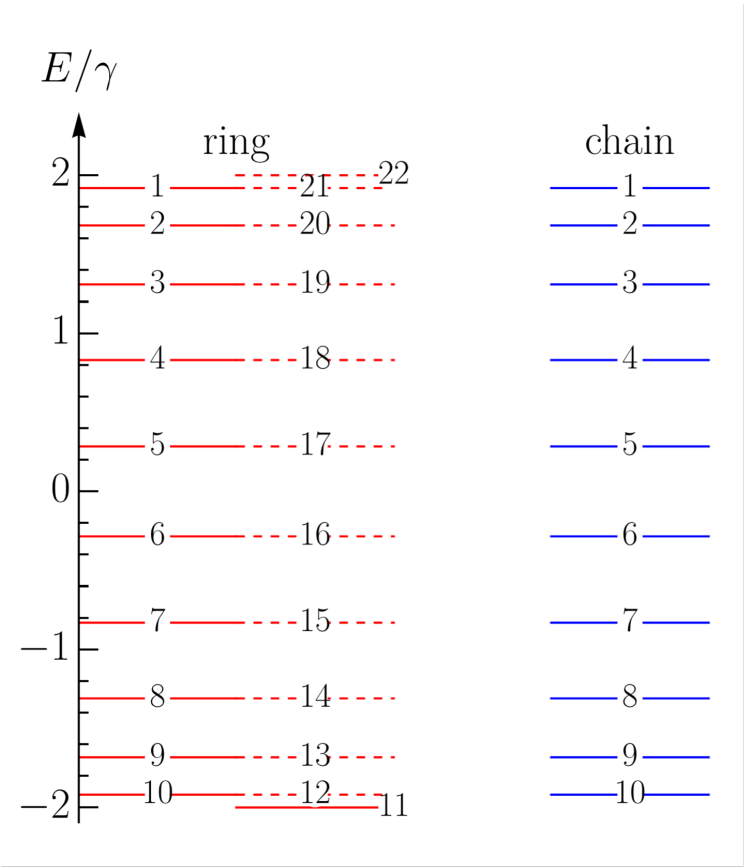
$$E_{l,\text{chain}} = 2\gamma \cos\left(\frac{\pi l_{\text{chain}}}{N_{\text{chain}}+1}\right) = E_{l,\text{ring}} = 2\gamma \cos\left(\frac{2\pi l_{\text{ring}}}{N_{\text{ring}}}\right), \text{ for } \begin{matrix} l_{\text{chain}} = 1, 2, 3, ..., N_{\text{chain}} \\ l_{\text{ring}} = 1, 2, 3, ..., N_{\text{ring}} \end{matrix} \tag{SI153}$$

$$\varphi_{\text{ring}} = \frac{2\pi l}{N_{\text{ring}}} = \varphi_{\text{chain}} = \frac{\pi l}{N_{\text{chain}}+1} \tag{SI154}$$

$$N_{\text{ring}} = 2N_{\text{chain}} + 2 \tag{SI155}$$



(a)



(b)

Figure SI3: Matching the eigenenergies between an atomic ring and a finite atomic chain. (a) A unit circle representation of the eigenenergies as a phase of the cosine function for the atomic ring (red arrows) and chain (blue arrow) cases, where $N_{\rm r} = 2N_{\rm c} + 2$ and $N_{\rm r}$ and $N_{\rm c}$ are the number of atoms in a ring and chain, respectively. (b) The red dashes/lines and blue lines represent the eigenenergies of an atomic ring number with $N_{\rm r} = 22$ and the finite atomic chain number $N_{\rm c} = 10$, respectively. The red dashed lines of the atomic ring levels show energy level degeneracies. All the energy values of the atomic chain fit the corresponding double degenerate energy levels of the atomic ring, except at the boundary points $\frac{E}{\gamma} = \pm 2$ which are only present in the atomic ring.

or the energy levels are equal when the number of atoms in a ring N_{ring} is about twice the number of atoms in the chain N_{ring} added with two more atoms. Consequently, the number of energy levels in the atomic ring l_{ring} is twice the number of atomic chains l_{chain}. But the phase of the atomic ring φ_{ring} encompasses the interval $(0, 2\pi)$ while the phase of the chain structure φ_{chain} is limited only on the interval $(0, \pi)$. Since the cos function is an even function from the center of the interval $(0, 2\pi)$ (in this case, the y-axis), the phases of the atomic ring φ_{ring} result to a double degeneracy except for the two phases $\varphi_{1,2} = \pi, 2\pi$ $\left(\frac{E}{\gamma} = \pm 2\right)$. Thus, the energy levels of the atomic ring are double degenerate and equal to the energy levels of the atomic chain, except for the two energies corresponding to the phases $\varphi_{1,2} = \pi, 2\pi$ $\left(\frac{E}{\gamma} = \pm 2\right)$ as shown in Fig. SI3. These results hold true to other carbon allotropes such as graphene nanoribbons and carbon nanotubes.[7,14–16]

SI.2 Optical properties of atomic structures

With the electronic results from the analytical tight-binding model, the optical properties of the atomic ring and finite chain are defined by their respective optical matrix elements. The optical matrix elements show the probability rate of transitions in the quantum mechanical system which leads us to the optical selection rules. The Fermi's golden rule gives the probability of transition induced by an electromagnetic wave per unit time[17,18] where the probability rate is proportional to the absolute value squared of the matrix elements in the interaction part of the Hamiltonian. For our atomic structures, we consider the interaction of an electron in a solid with an external electric field. Then, the interaction potential is described by $U = e\boldsymbol{E} \cdot \boldsymbol{r} = \boldsymbol{d} \cdot \boldsymbol{E}$, where $\boldsymbol{E}$ is the strength of the electric field of the electromagnetic wave, $\boldsymbol{r}$ is the electron position, and $\boldsymbol{d} = e\boldsymbol{r}$ is the dipole moment of the system. The calculation of optical properties in finite atomic-sized structures can then be reduced to the position or dipole moment operator matrix elements.

SI.2.1 Atomic ring

For the optical matrix elements of an atomic ring system, the electric field of an incident electromagnetic wave can be simplified by $\boldsymbol{E} = E\hat{\mathbf{e}}_p$, where E is the magnitude of the electric field of the electromagnetic wave and $\hat{\mathbf{e}}_p = (1, 0)$ is the constant vector chosen without losing generality to be along the Ox-axis. Then, the matrix elements of the interaction potential in the Hamiltonian is

$$\langle \Psi_n | U | \Psi_m \rangle = \int_V \Psi_n U \Psi_m d^3\mathbf{r} = eE \int_V \Psi_n \left(\hat{\mathbf{e}}_p \cdot \boldsymbol{r}\right) \Psi_m d^3\mathbf{r} = eE \int_V \Psi_n x \Psi_m d^3\mathbf{r} \tag{SI156}$$

where the integration should be evaluated over all space. In this case, the integration can be reduced to the projection of the position operator to the plane wave polarization vector, that is along the x coordinate. The integral in Eq. (SI156) can be compactly written in the tight-binding model form

$$\langle \Psi_n | U | \Psi_m \rangle = eE \int_V \Psi_n x \Psi_m d^3\mathbf{r} = eE x_{nm} \tag{SI157}$$

where the x coordinate matrix element is defined by

$$x_{nm} = \int \Psi_n x \Psi_m d^3\mathbf{r} \tag{SI158}$$

We can expand the electron wavefunction Ψ_i over a complete orthonormal basis set:

$$\Psi_i = \sum_{j=1}^{N} c_{ij} \psi_j \tag{SI159}$$

Substituting Eq. (SI159) into Eq. (SI158) results to

$$x_{nm} = \sum_{i=1}^{N} \sum_{j=1}^{N} c_{nj}^* c_{mi} \int \psi_j^* x \psi_i d^3\mathbf{r} \tag{SI160}$$

where the corresponding wavefunctions are $\Psi_n = \sum_{j=1}^{N} c_{nj}\psi_j$ and $\Psi_m = \sum_{i=1}^{N} c_{mi}\psi_i$. Under the tight-binding model, we can assume that the electrons are strongly bounded to their respective atomic nuclei and simplify the integral as

$$\int \psi_j^* x \psi_i d^3\mathbf{r} = x_i \delta_{ij} \tag{SI161}$$

or the x operator in the tight binding model equivalently be written as

$$\boldsymbol{X} = x_i\delta_{ij} = \begin{pmatrix} x_1 & 0 & 0 & 0 & \dots & 0 & 0 \\ 0 & x_2 & 0 & 0 & \dots & 0 & 0 \\ 0 & 0 & x_3 & 0 & \dots & 0 & 0 \\ 0 & 0 & 0 & x_4 & \dots & 0 & 0 \\ \vdots & & & & \ddots & & \vdots \\ 0 & 0 & 0 & 0 & \dots & x_{N-1} & 0 \\ 0 & 0 & 0 & 0 & \dots & 0 & x_N \end{pmatrix} \tag{SI162}$$

where x_i are the locations of the atoms in the ring structure. The coefficients of the expansion in Eq. (SI159) are related to the components of the eigenvectors $\widetilde{C}_l$ given by Eq. (SI93). We can then take a set of normalized eigenvectors $\widetilde{C}_m$ with coefficients c_{mi} given by

$$\widetilde{C}_m = \frac{1}{\sqrt{N}} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_{N-1} \\ c_N \end{pmatrix} = \frac{1}{\sqrt{N}} \begin{pmatrix} \mathrm{e}^{i\theta_m} \\ \mathrm{e}^{i\theta_m 2} \\ \mathrm{e}^{i\theta_m 3} \\ \mathrm{e}^{i\theta_m 4} \\ \vdots \\ \mathrm{e}^{i\theta_m (N-1)} \\ \mathrm{e}^{i\theta_m N} \end{pmatrix} \tag{SI163}$$

where $\theta_m = \frac{2\pi m}{N}$ with $m = 1, 2, 3, \ldots, N-1, N$. Since the eigenvectors in Eq. (SI93) are not normalized, a normalization constant $A = \frac{1}{\sqrt{N}}$ is multiplied to the non-normalized eigenvectors $\widetilde{C}_l$ by applying the condition $|A|^2 \widetilde{C}_l^{\dagger} \widetilde{C}_l = 1$, where the symbol † refers to the Hermitian conjugation. To explicitly show these computations, we take the expansion of the eigenvector coefficients and their corresponding conjugate terms:

$$|A|^2 \widetilde{C}_l^{\dagger} \widetilde{C}_l = |A|^2 \begin{pmatrix} \mathrm{e}^{-i\theta_l} & \mathrm{e}^{-i\theta_l 2} & \mathrm{e}^{-i\theta_l 3} & \cdots & \mathrm{e}^{-i\theta_l (N-1)} & \mathrm{e}^{-i\theta_l N} \end{pmatrix} \begin{pmatrix} \mathrm{e}^{i\theta_l} \\ \mathrm{e}^{i\theta_l 2} \\ \mathrm{e}^{i\theta_l 3} \\ \vdots \\ \mathrm{e}^{i\theta_l (N-1)} \\ \mathrm{e}^{i\theta_l N} \end{pmatrix} = 1 \tag{SI164}$$

$$|A|^2 \left(\mathrm{e}^{-i\theta_l} \mathrm{e}^{i\theta_l} + \mathrm{e}^{-i\theta_l 2} \mathrm{e}^{i\theta_l 2} + \mathrm{e}^{-i\theta_l 3} \mathrm{e}^{i\theta_l 3} + \ldots + \mathrm{e}^{-i\theta_l N} \mathrm{e}^{i\theta_l N} \right) = |A|^2 N = 1 \tag{SI165}$$

$$|A|^2 N = 1 \Rightarrow A = \frac{1}{\sqrt{N}} \tag{SI166}$$

By substituting the normalized eigenvectors of Eq. (SI163) and the x operator matrix in Eq. (SI162) into Eq. (SI160) gives us the matrix of x_{nm}:

$$x_{nm} = \widetilde{C}_n^{\dagger} X \widetilde{C}_m \tag{SI167}$$

$$x_{nm} = \frac{1}{\sqrt{N}} \begin{pmatrix} \mathrm{e}^{-i\theta_n} & \mathrm{e}^{-i\theta_n 2} & \cdots & \mathrm{e}^{-i\theta_n N} \end{pmatrix} \begin{pmatrix} x_1 & 0 & \cdots & 0 \\ 0 & x_2 & \cdots & 0 \\ \vdots & & \ddots & \vdots \\ 0 & 0 & \cdots & x_N \end{pmatrix} \frac{1}{\sqrt{N}} \begin{pmatrix} \mathrm{e}^{i\theta_m} \\ \mathrm{e}^{i\theta_m 2} \\ \vdots \\ \mathrm{e}^{i\theta_m N} \end{pmatrix} \tag{SI168}$$

which then results to

$$x_{nm} = \frac{1}{N} \sum_{j=1}^{N} x_j \exp\left[\frac{i2\pi (m-n)}{N} j \right] \tag{SI169}$$

From the location of atomic positions in Fig. SI1, the factor x_j can be expressed as

$$x_j = R\cos\phi_j = R\cos\left(\frac{2\pi}{N}j\right) \tag{SI170}$$

where the angle ϕ_j is measured from the starting point on the ring towards the j-th atom. Substituting the expression of x_j in Eq. (SI170) to the x coordinate matrix elements x_{nm} in Eq. (SI169) and then expanding the terms give us the following results

$$x_{nm} = \frac{1}{N}\sum_{j=1}^{N} R\cos\left(\frac{2\pi}{N}j\right)\exp\left[\frac{i2\pi\,(m-n)}{N}j\right] \tag{SI171}$$

$$x_{nm} = \frac{R}{N}\sum_{j=1}^{N}\frac{1}{2}\left(\exp\left[\frac{i2\pi}{N}j\right] + \exp\left[-\frac{i2\pi}{N}j\right]\right)\exp\left[\frac{i2\pi\,(m-n)}{N}j\right] \tag{SI172}$$

$$x_{nm} = \frac{R}{2N}\sum_{j=1}^{N}\left(\exp\left[\frac{i2\pi\,(m-n+1)}{N}j\right] + \exp\left[\frac{i2\pi\,(m-n-1)}{N}j\right]\right) \tag{SI173}$$

The summation in Eq. (SI173) is a finite geometric series with geometric sequence $b_n = b_1 q^{n-1}$ that leads us to the n-th partial sum $S_n = \frac{b_1(1-q^n)}{(1-q)}$. The common ratio of a geometric sequence in Eq. (SI173) is then $q = \exp\left[\frac{i2\pi(m-n+1)}{N}\right]$ for the first term and $q = \exp\left[\frac{i2\pi(m-n-1)}{N}\right]$ for the second term, which is also equal to their respective initial term b_1. Evaluating the sum shows that the x coordinate matrix element is

$$x_{mn} = \frac{R}{2N}\left\{\frac{1-\exp\left(i2\pi\,(m-n+1)\right)}{\exp\left[-\frac{i2\pi(m-n+1)}{N}\right]-1} + \frac{1-\exp\left(i2\pi\,(m-n-1)\right)}{\exp\left[-\frac{i2\pi(m-n-1)}{N}\right]-1}\right\} \tag{SI174}$$

When we take the case $m-n+1=0$, the second term of Eq. (SI174) is equal to zero due to the numerator equal to $(1-e^{-4\pi i})$ while the denominator is a finite value. On the other hand, the first term is an indeterminate form of $\frac{0}{0}$ which can be easily worked on by applying L'Hospital's rule: $\lim_{x\to 0}\frac{f(x)}{g(x)} = \lim_{x\to 0}\frac{f'(x)}{g'(x)}$. If we take a new variable $\eta = 2\pi\,(m-n+1)$ as an expression to the argument of the exponential in the first term, then the x coordinate

matrix element is simply

$$x_{mn} = \frac{R}{2N}\left[\lim_{\eta\to 0}\frac{1-\exp\left(i\eta\right)}{\exp\left(-\frac{i\eta}{N}\right)-1}\right] = \frac{R}{2N}\left[\lim_{\eta\to 0}\frac{-i\exp\left(i\eta\right)}{-\frac{i}{N}\exp\left(-\frac{i\eta}{N}\right)}\right] = \frac{R}{2N}N = \frac{R}{2} \tag{SI175}$$

A similar scenario occurs for the case of $m-n-1=0$, where the first term of Eq. (SI174) is equal to zero due to the numerator equal to $(1-e^{4\pi i})$ while the denominator is a finite value. The second term is an indeterminate form of $\frac{0}{0}$ where we again employ L'Hospital's rule. The x coordinate matrix element is

$$x_{mn} = \frac{R}{2N}\left[\lim_{\varsigma\to 0}\frac{1-\exp\left(i\varsigma\right)}{\exp\left(-\frac{i\varsigma}{N}\right)-1}\right] = \frac{R}{2N}\left[\lim_{\varsigma\to 0}\frac{-i\exp\left(i\varsigma\right)}{-\frac{i}{N}\exp\left(-\frac{i\varsigma}{N}\right)}\right] = \frac{R}{2N}N = \frac{R}{2} \tag{SI176}$$

where we take $\varsigma = 2\pi\left(m-n-1\right)$. As for the other cases when $m-n \neq \pm 1$, the values of x coordinate matrix element in Eq. (SI174) are equal to zero due to numerators of both terms equate to zero.

From the analytical results above, we get the following optical selection rules for an atomic ring:

1. Transitions are allowed when the eigenstate indices n and m follow $n-m=\pm 1$. Otherwise, transitions are forbidden.

2. When transitions are allowed, the position operator matrix element is equal to $\frac{R}{2}$. Also, the dipole moment operator matrix element has an entry corresponding to $\frac{eR}{2}$.

Interestingly, the same selection rules are found in the continuous ring model of a semiconductor quantum ring which is also known as the effective mass approximation.[19]

SI.2.2 Finite atomic chain

Unlike the atomic ring, a finite atomic chain lacks circular symmetry. Then, in-plane anisotropy of optical properties is expected to occur for an atomic chain. We consider again a plane electromagnetic wave incident to the atomic chain with an electric field $\boldsymbol{E} = E\hat{\mathbf{e}}_p$,

where E is the magnitude of the electric field of the electromagnetic wave and $\hat{\mathbf{e}}_p = (1, 0)$ is the polarization vector chosen to be along the Ox-axis and parallel to the chain, see Fig. SI2. When the polarization vector is directed normally to the atomic chain, the projection of the radius vector from the atomic locations onto the polarization vector is $\hat{\mathbf{e}}_p$ is zero. Thus, the optical transitions for a normal incident electromagnetic wave are forbidden while transitions for polarization vector parallel to the atomic chain are allowed and considered as a non-trivial case.

We take the atomic chain eigenvectors from Eq. (SI138) given by:

$$\widetilde{C}_l = \begin{pmatrix} \sin(\theta_l) \\ \sin(\theta_l 2) \\ \sin(\theta_l 3) \\ \sin(\theta_l 4) \\ \vdots \\ \sin(\theta_l (N-1)) \\ \sin(\theta_l N) \end{pmatrix} \tag{SI177}$$

where $\theta_l = \frac{\pi l}{(N+1)}$ with $l = 1, 2, 3, \ldots, N-1, N$. To normalize these eigenvectors, we apply the normalization condition $|A|^2 \widetilde{C}_l^{\dagger} \widetilde{C}_l = 1$, where the symbol " $\dagger$ " refers again to the Hermitian conjugation. Then, the normalization constant A for the non-normalized eigenvectors of atomic chains is expressed as

$$A = \frac{1}{\sqrt{\sum_{j=1}^{N} \sin^2(\theta_l j)}} = \frac{1}{\sqrt{\frac{1}{2}\left(N - \cos\left[\theta_l (N+1)\right] \frac{\sin(\theta_l N)}{\sin\theta_l}\right)}} \tag{SI178}$$

Compared to the atomic ring, the normalization constant of an infinite chain in Eq. (SI178) depends on l which would result in a different set of eigenvectors. However, we find that the normalization constant is not truly dependent on l but on N as seen by evaluating the factor inside the parenthesis of Eq. (SI178) and substituting the value of θ_l

into $\sin\left[\theta_l\left(N+1\right)\right]=\sin\left(\pi l\right)$ that results to 0. With that being said, consider the following expansion of $\sin\left(\theta_l N\right)$:

$$\begin{aligned}\sin\left(\theta_l N\right) &= \sin\left(\theta_l N+\theta_l-\theta_l\right)\\ &= \sin\left[\left(\theta_l\left(N+1\right)-\theta_l\right)\right]\\ &= \sin\left[\theta_l\left(N+1\right)\right]\cos\theta_l-\cos\left[\theta_l\left(N+1\right)\right]\sin\theta_l\\ &= \sin\left[\pi l\right]\cos\theta_l-\cos\left[\theta_l\left(N+1\right)\right]\sin\theta_l\\ &= -\cos\left[\theta_l\left(N+1\right)\right]\sin\theta_l\end{aligned} \tag{SI179}$$

Substituting the result from Eq. (SI179) into the Eq. (SI178) shows that the normalization constant of a finite atomic chain depends only on N:

$$A=\frac{1}{\sqrt{\frac{1}{2}\left(N-\cos\left[\theta_l\left(N+1\right)\right]\frac{-\cos[\theta_l(N+1)]\sin\theta_l}{\sin\theta_l}\right)}} \tag{SI180}$$

$$A=\frac{1}{\sqrt{\frac{1}{2}\left(N+\cos^2\left[\theta_l\left(N+1\right)\right]\right)}}=\frac{1}{\sqrt{\frac{1}{2}\left(N+\frac{1}{2}\left\{\cos\left[2\theta_l\left(N+1\right)\right]+1\right\}\right)}} \tag{SI181}$$

$$A=\frac{1}{\sqrt{\frac{1}{2}\left(N+\frac{1}{2}\left\{\cos\left[2\frac{\pi l}{(N+1)}\left(N+1\right)\right]+1\right\}\right)}}=\frac{1}{\sqrt{\frac{1}{2}\left(N+\frac{1}{2}\left[\cos\left(2\pi l\right)+1\right]\right)}} \tag{SI182}$$

$$A=\frac{1}{\sqrt{\frac{1}{2}\left(N+\frac{1}{2}\left[1+1\right]\right)}}=\frac{1}{\sqrt{\frac{1}{2}\left(N+1\right)}} \tag{SI183}$$

$$A=\sqrt{\frac{2}{N+1}} \tag{SI184}$$

We now evaluate the x coordinate matrix element by substituting the normalized eigenvectors of the atomic chain in Eq. (SI177) and the x coordinate operator in Eq. (SI162) into

the x_{nm} in Eq. (SI167):

$$x_{nm} = \widetilde{C}_n^{\dagger} X \widetilde{C}_m = \frac{2}{N+1} \begin{pmatrix} \sin(\theta_n) & \cdots & \sin(\theta_n N) \end{pmatrix} \begin{pmatrix} x_1 & 0 & \cdots & 0 \\ \vdots & \ddots & & \vdots \\ 0 & 0 & \cdots & x_N \end{pmatrix} \begin{pmatrix} \sin(\theta_m) \\ \vdots \\ \sin(\theta_m N) \end{pmatrix} \tag{SI185}$$

$$x_{nm} = \frac{2}{N+1} \sum_{j=1}^{N} \sin(\theta_n j) \sin(\theta_m j)\, x_j = \frac{2}{N+1} \sum_{j=1}^{N} \frac{1}{2} \left\{ \cos\left[(\theta_n - \theta_m) j\right] - \cos\left[(\theta_n + \theta_m) j\right] \right\} x_j \tag{SI186}$$

$$x_{nm} = \frac{1}{N+1} \sum_{j=1}^{N} \left\{ \cos\left[(\theta_n - \theta_m) j\right] - \cos\left[(\theta_n + \theta_m) j\right] \right\} a_0 j \tag{SI187}$$

$$x_{nm} = \frac{a_0}{N+1} \left\{ \sum_{j=1}^{N} j \cos\left[(\theta_n - \theta_m) j\right] - \sum_{j=1}^{N} j \cos\left[(\theta_n + \theta_m) j\right] \right\} \tag{SI188}$$

where we used the product of sines and the variable length of an atomic chain as $x_j = j a_0$. The two sums in the expression of x_{nm} above can be evaluated exactly by expanding the cosine function into a sum of its complex components:

$$\sum_{j=1}^{N} j \cos(\beta_{\pm} j) = \frac{1}{2} \left[\sum_{j=1}^{N} j \exp(i \beta_{\pm} j) + \sum_{j=1}^{N} j \exp(-i \beta_{\pm} j) \right] \tag{SI189}$$

where $\beta_{\pm} = \theta_n \pm \theta_m = \pi (n \pm m) / (N+1)$. The summation of exponentials in Eq. (SI189) is a sum of an arithmetic-geometric series with an arithmetic-geometric sequence of the k-th element defined as $(a_1 + kr)\, q^k$, where a_1 is the first element in the sequence, r is the constant difference and q is the constant multiplier. By comparison, the expressions in Eq. (SI189) have the following relations with the said arithmetic-geometric sequence: $a_1 = 0$, $r = 1$, $q = \exp(\pm i \beta_{\pm})$, and $k = j$. Then, the sums of Eq. (SI189) can be evaluated by using the formula of the n-th partial sum:[20]

$$S_n = \frac{a_1 - [a_1 + (n-1) r]\, q^n}{1 - q} + \frac{r q \left(1 - q^{n-1}\right)}{(1-q)^2} \tag{SI190}$$

$$S_N = \frac{-(N-1)\,\mathrm{e}^{\pm i\beta_\pm N}}{1-\mathrm{e}^{\pm i\beta_\pm}} + \frac{\mathrm{e}^{\pm i\beta_\pm}\left(1-\mathrm{e}^{\pm i\beta_\pm(N-1)}\right)}{\left(1-\mathrm{e}^{\pm i\beta_\pm}\right)^2} \tag{SI191}$$

Thus, the resulting summation of the right-hand side in Eq. (SI189) is

$$\sum_{j=1}^{N} j\cos(\beta_\pm j) = \frac{(N+1)\cos(N\beta_\pm) - N\cos[(N+1)\beta_\pm] - 1}{2(1-\cos\beta_\pm)} \tag{SI192}$$

Before we proceed with the substitution process of the right-hand side expression from Eq. (SI192) to the x_{nm} matrix element in Eq. (SI188), let us consider first the factor $\cos(N\beta_\pm)$ in the numerator. The factor $\cos(N\beta_\pm)$ can be conveniently represented into $\cos[(N+1)\beta_\pm]$, where the relation $(N+1)\beta_\pm = \pi(n\pm m)$ is replaced in the argument as follows:

$$\begin{aligned}
\cos(N\beta_\pm) &= \cos(N\beta_\pm + \beta_\pm - \beta_\pm) \\
&= \cos[(N+1)\beta_\pm - \beta_\pm] \\
&= \cos[(N+1)\beta_\pm]\cos\beta_\pm + \sin[(N+1)\beta_\pm]\sin\beta_\pm \\
&= \cos[\pi(n\pm m)]\cos\left[\tfrac{\pi(n\pm m)}{N+1}\right] + \sin[\pi(n\pm m)]\sin\left[\tfrac{\pi(n\pm m)}{N+1}\right] \\
&= \cos[\pi(n\pm m)]\cos\left[\tfrac{\pi(n\pm m)}{N+1}\right]
\end{aligned} \tag{SI193}$$

where we have evaluated $\sin[(N+1)\beta_\pm] = \sin[\pi(n\pm m)] = 0$ for all integers n and m. Using this expression of $\cos(N\beta_\pm)$ in Eq. (SI192), the summation becomes:

$$\sum_{j=1}^{N} j\cos(\beta_\pm j) = \frac{(N+1)\cos[\pi(n\pm m)]\cos\left[\tfrac{\pi(n\pm m)}{N+1}\right] - N\cos[\pi(n\pm m)] - 1}{2\left(1-\cos\left[\tfrac{\pi(n\pm m)}{N+1}\right]\right)} \tag{SI194}$$

The factor $\cos[\pi(n\pm m)]$ can be rewritten as $(-1)^p$ where $p = n-m$ regardless of the sign from $n\pm m$. If p is even, then the integers n and m are both either even or odd which makes their sum even. When p is odd, on the other hand, one integer is even while another is odd which leads to an odd sum of the n and m integers. Thus, the value p is even (odd) when

$n \pm m$ is even (odd). The sum in Eq. (SI194) can now be succinctly written as

$$\sum_{j=1}^{N} j \cos \beta_{\pm} j = \frac{(N+1)(-1)^p \cos \beta_{\pm} - N(-1)^p - 1}{2(1 - \cos \beta_{\pm})} \tag{SI195}$$

This expression of the sum is substituted to the x coordinate matrix element expression in Eq. (SI188) and then evaluated to get the following results:

$$x_{nm} = \frac{a_0}{N+1} \left[\sum_{j=1}^{N} j \cos(\beta_- j) - \sum_{j=1}^{N} j \cos(\beta_+ j) \right] \tag{SI196}$$

$$x_{nm} = \frac{a_0}{N+1} \left[\frac{(N+1)(-1)^p \cos \beta_- - N(-1)^p - 1}{2(1 - \cos \beta_-)} - \frac{(N+1)(-1)^p \cos \beta_+ - N(-1)^p - 1}{2(1 - \cos \beta_+)} \right] \tag{SI197}$$

$$\begin{aligned} x_{nm} = \quad & a_0 \{ (1 - \cos \beta_+) [(N+1)(-1)^p \cos \beta_- - N(-1)^p - 1] - \\ & - (1 - \cos \beta_-) [(N+1)(-1)^p \cos \beta_+ - N(-1)^p - 1] \} \times \\ & \times [2(N+1)(1 - \cos \beta_+)(1 - \cos \beta_-)]^{-1} \end{aligned} \tag{SI198}$$

$$\begin{aligned} x_{nm} = \quad & a_0 [(N+1)(-1)^p \cos \beta_- \cancel{- N(-1)^p - 1} - (N+1)(-1)^p \cos \beta_+ + \\ & \cancel{+ N(-1)^p + 1} \cancel{- \cos \beta_+ (N+1)(-1)^p \cos \beta_-} + \cos \beta_+ N(-1)^p + \\ & + \cos \beta_+ \cancel{+ \cos \beta_- (N+1)(-1)^p \cos \beta_+} - \cos \beta_- N(-1)^p - \cos \beta_-] \times \\ & \times [2(N+1)(1 - \cos \beta_+)(1 - \cos \beta_-)]^{-1} \end{aligned} \tag{SI199}$$

$$\begin{aligned} x_{nm} = \quad & a_0 [(N+1)(-1)^p (\cos \beta_- - \cos \beta_+) + \\ & + N(-1)^p (\cos \beta_+ - \cos \beta_-) + \cos \beta_+ - \cos \beta_-] \times \\ & \times [2(N+1)(1 - \cos \beta_+)(1 - \cos \beta_-)]^{-1} \end{aligned} \tag{SI200}$$

$$\begin{aligned} x_{nm} = \quad & a_0 \left[\cancel{N(-1)^p (\cos \beta_- - \cos \beta_+)} \cancel{- N(-1)^p (\cos \beta_- - \cos \beta_+)} + \right. \\ & \left. + (-1)^p (\cos \beta_- - \cos \beta_+) + \cos \beta_+ - \cos \beta_- \right] \times \\ & \times [2(N+1)(1 - \cos \beta_+)(1 - \cos \beta_-)]^{-1} \end{aligned} \tag{SI201}$$

$$x_{nm} = \frac{a_0\left[(-1)^p - 1\right]\left(\cos\beta_- - \cos\beta_+\right)}{2\left(N+1\right)\left(2\sin^2\frac{\beta_+}{2}\right)\left(2\sin^2\frac{\beta_-}{2}\right)} \tag{SI202}$$

$$x_{nm} = \frac{a_0\left[(-1)^p - 1\right]}{8\left(N+1\right)}\frac{\left[1 - \cos\beta_+ - 1 + \cos\beta_-\right]}{\sin^2\frac{\beta_+}{2}\sin^2\frac{\beta_-}{2}} \tag{SI203}$$

$$x_{nm} = \frac{a_0\left[(-1)^p - 1\right]}{8\left(N+1\right)}\frac{\left(2\sin^2\frac{\beta_+}{2} - 2\sin^2\frac{\beta_-}{2}\right)}{\sin^2\frac{\beta_+}{2}\sin^2\frac{\beta_-}{2}} \tag{SI204}$$

$$x_{nm} = \frac{a_0\left[(-1)^p - 1\right]}{4\left(N+1\right)}\left(\frac{1}{\sin^2\frac{\beta_-}{2}} - \frac{1}{\sin^2\frac{\beta_+}{2}}\right) \tag{SI205}$$

where we have used the cosine double angle relation given by:

$$1 - \cos\theta = 2\sin^2\frac{\theta}{2} \tag{SI206}$$

in Eq. (SI202) and Eq. (SI204). Also, we can rewrite the arguments of the *sin* functions in terms of variable p such that $n - m = p$ while $n + m = 2m + p$. The matrix x_{nm} finally results to:

$$x_{nm} = \frac{a_0\left[(-1)^p - 1\right]}{4\left(N+1\right)}\left(\frac{1}{\sin^2\frac{\pi p}{2(N+1)}} - \frac{1}{\sin^2\frac{\pi(2m+p)}{2(N+1)}}\right) = x_{m\to m+p} \tag{SI207}$$

where p can be interpreted as the transition order. Thus, the transitions between states m and n are transformed to transitions between m and $m + p$ states in Eq. (SI207).

There are at least three practical issues worth considering in Eq. (SI207). They are as follows:

1. When $p = 0$, the $x_{m,m}$ results to a counter-intuitive factor of the first term in Eq. (SI207) where we get an indeterminate form of $\frac{0}{0}$. With the application of the L'Hospital's rule, Eq. (SI207) becomes:

$$x_{m,m} = -\frac{a_0\left(N+1\right)}{2\pi^2} \tag{SI208}$$

which has an additional 'spurious' factor of $\frac{1}{\pi^2}$ that is carried over from the $\cos\left[\pi\left(n \pm m\right)\right]$ representation as $(-1)^p$ in Eq. (SI192). This result can be easily checked by doing the

same calculations with $(-1)^p$ replaced by $\cos(\pi p)$ that gives us a physically manageable outcome:

$$x_{m,m} = -\frac{a_0 (N+1)}{2} \tag{SI209}$$

2. An extra negative sign can also be observed on the expressions above compared to Eq. (SI186). This minus sign factor comes from the definition of $p = n - m$ in $\cos(\pi p) = \cos[\pi (n-m)]$ instead of $\cos[\pi (n+m)]$. However, this minus sign discrepancy is inessential since a minus sign factor does not affect the absolute value of the position matrix element x_{nm}.

3. Only the integer values of p from the expression in Eq. (SI207) coincide with the ones in Eq. (SI186). For a fractional number of p, the $(-1)^p$ factor may return a complex value such as $(-1)^{\frac{5}{6}}$ or $(-1)^{\frac{1}{6}}$.

These technical issues can impede the plotting of the matrix elements for our further theoretical investigation. We can then safely take the $\cos(\pi p)$ instead of the $(-1)^p$ to avoid complications. Thus, the final expression of the position matrix x_{nm} is in the following form:

$$x_{nm} = x_{m\to m+p} = \frac{a_0 [\cos(\pi p) - 1]}{4 (N+1)} \left(\frac{1}{\sin^2 \frac{\pi p}{2(N+1)}} - \frac{1}{\sin^2 \frac{\pi (2m+p)}{2(N+1)}} \right) \tag{SI210}$$

The position operator matrix element x_{nm} is zero when $p = n - m$ is an even number. We get the following results from the optical selection rules for an atomic chain:

1. Optical transitions are forbidden if the differences between n and m are even. Otherwise, transitions are allowed.

2. Higher order transitions with odd differences are allowed in an atomic finite chain while these higher transitions are forbidden in the atomic ring.

To estimate the strength of higher transitions in an atomic chain, a plot of $x_{m\to m+p}$, which can be written as $x_{m,m+p}$, as a function of p is shown in Fig. SI4 based on the Eq.

(SI210). The matrix elements of the position operator $x_{m,m+p}$ have weaker magnitude at higher order transitions than that of the lower order. Also, the magnitude quickly diminishes with increasing values of p. Indeed, for $p \gg m$ the parentheses in Eq. (SI210) converges to zero, since $\sin^2 \frac{\pi(2m+p)}{2(N+1)} \approx \sin^2 \frac{\pi(p)}{2(N+1)}$. The zero-order transitions, which are in fact the expectation values of the position operator, i.e. $x_{m\to m+p}|_{p=0}$ from Eqs. (SI186) and (SI210) shown by the solid and dashed curves, respectively, have equal magnitude but have different signs. These results agree well with our discussion above regarding the practical issues.

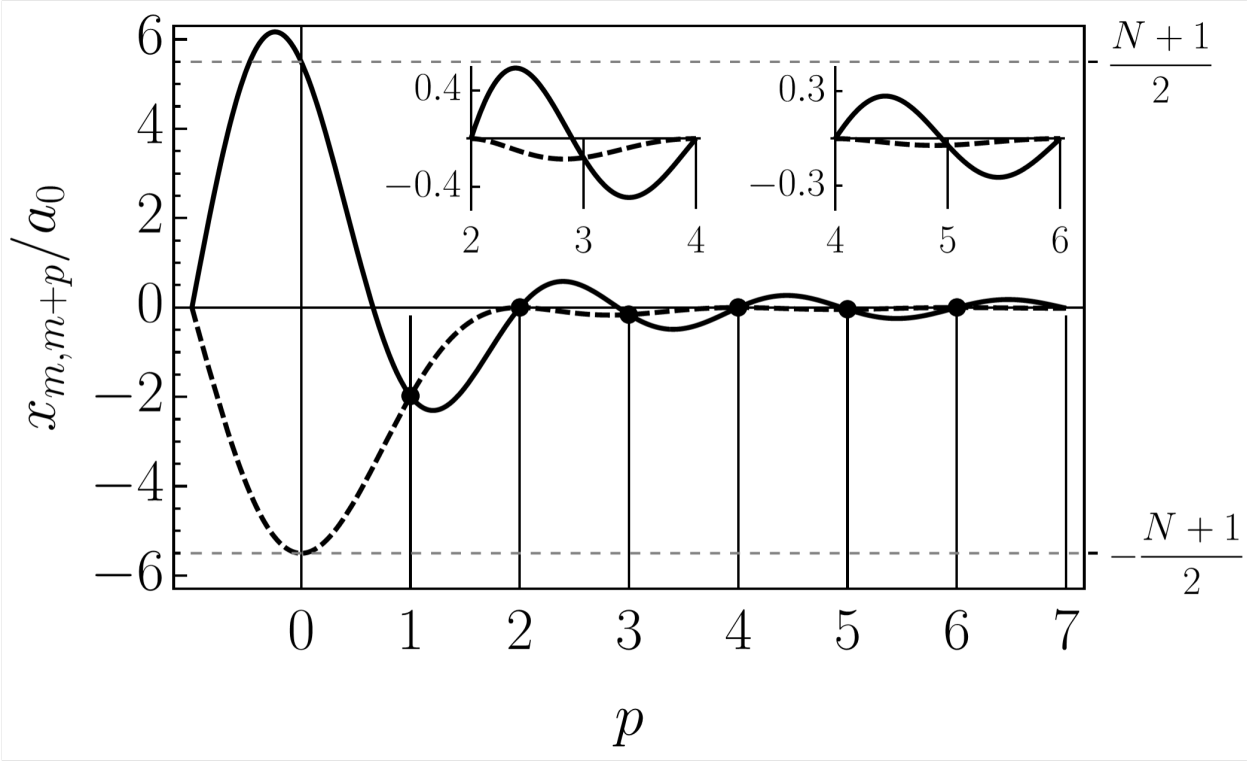


Figure SI4: Matrix element $x_{m,m+p}$ as a function of p for a finite atomic chain with $m = 1$ and $N_c = 10$ atoms. The plot of the solid curve is obtained from Eq. (SI186) while the dashed line curve comes from Eq. (SI210). Only the integer values of p from $x_{m,m+p}$ have the physical relevance while the higher order transitions diminish as p increases.

SI.2.3 Summary: Optical properties of finite structures

The optical transitions for an atomic ring and finite atomic chain have almost similar selection rules between states the n and m. Both the atomic ring and finite atomic chain allow

transitions between states n and m where the difference between them is ± 1, i.e. $p = n - m = \pm 1$. In contrast to the ring, the finite atomic chain has higher order odd transitions such as those with $p = \pm 3, \pm 5, \ldots$, albeit the probability of the higher order odd transitions rapidly decreases to zero as p increases. The additional transitions from the finite atomic chain are much weaker compared to the transitions with $p = \pm 1$. Therefore, the absorption spectra of the atomic ring and finite chain are expected to be similar as the energy levels match when the number of atoms in the ring is twice of that in the chain with two extra atoms.

SI.3 Time Dependent Density Functional Theory (TD-DFT)

SI.3.1 Analysis of electronic charge density of cyclo[18]carbon

The energy diagram of the cyclo[18]carbon and carbynes $N = 7$ and 8 optimized structures from DFT is shown in Fig. SI5. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap also differ for all three allotropes. The energy gaps are shown in each diagram, specifically carbynes $N = 7$ and 8, and cyclo[18]carbon have energy gaps of 3.47 eV, 6.85 eV and 4.73 eV, respectively.

SI.3.2 Analysis of wave functions of cyclo[18]carbon

Since cyclo[18]carbon has two-fold degeneracies, the two diagrams below (Fig. SI6 and Fig. SI7) illustrate the two configurations of molecular orbital (MO) wave functions and their corresponding transitions. We can observe similar MO transitions, MO wave functions and the corresponding square of subtraction illustrations with only the fractional weights of the configuration composition as the only factor that differs between them. This result is expected for degenerate ground state energies with one band transition in the absorption spectra.

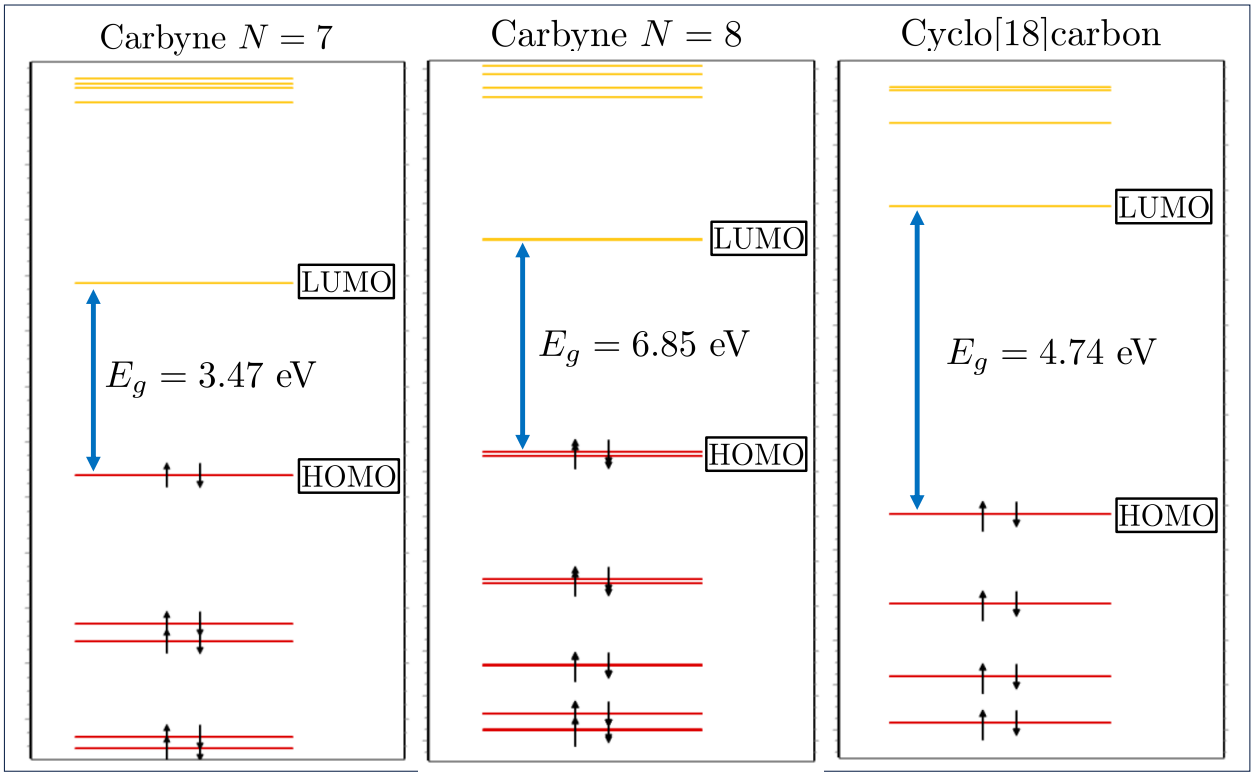


Figure SI5: Energy diagrams of carbynes $N = 7$ and 8, and cyclo[18]carbon, where their corresponding H-L gap is shown at the center of each diagram.

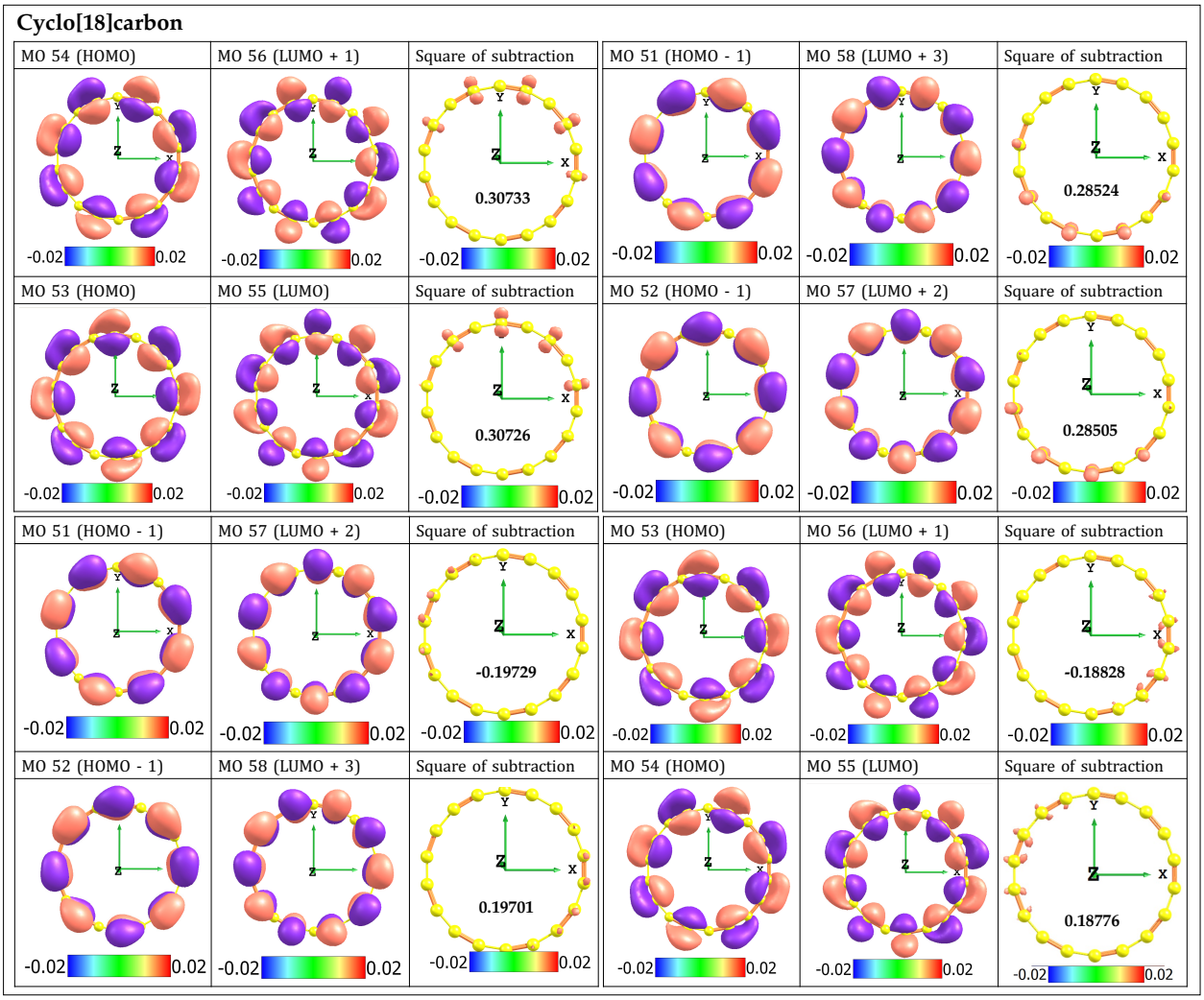


Figure SI6: One configuration (degeneracy 1) of electronic charge density in each molecular orbital states of cyclo[18]carbon represented as wave functions in 3D isovalue surfaces where the areas painted in orange show positive values while the areas shaded as violet are negative values. The values in the square of subtraction are corresponding weights of the configuration compositions to the cyclo[18]carbon MO transitions given in Table SI1 as the amount of percent contribution to the absorption peak.

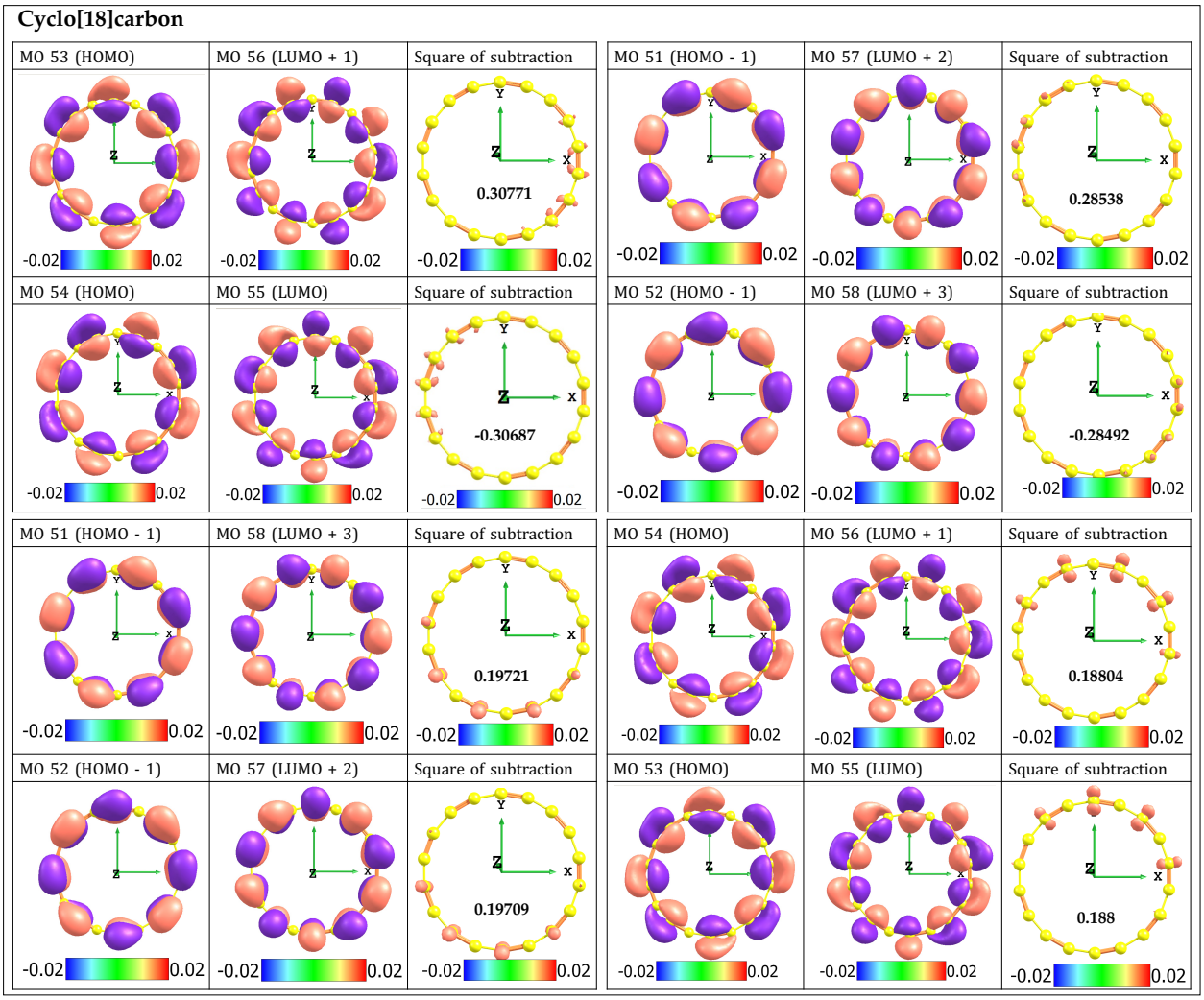


Figure SI7: Second configuration (degeneracy 2) of electronic charge density in each molecular orbital states of cyclo[18]carbon represented as wave functions in 3D isovalue surfaces where the areas painted in orange show positive values while the areas shaded as violet are negative values. The values in the square of subtraction are corresponding weights of the configuration compositions to the cyclo[18]carbon MO transitions given in Table SI1 as the amount of percent contribution to the absorption peak.

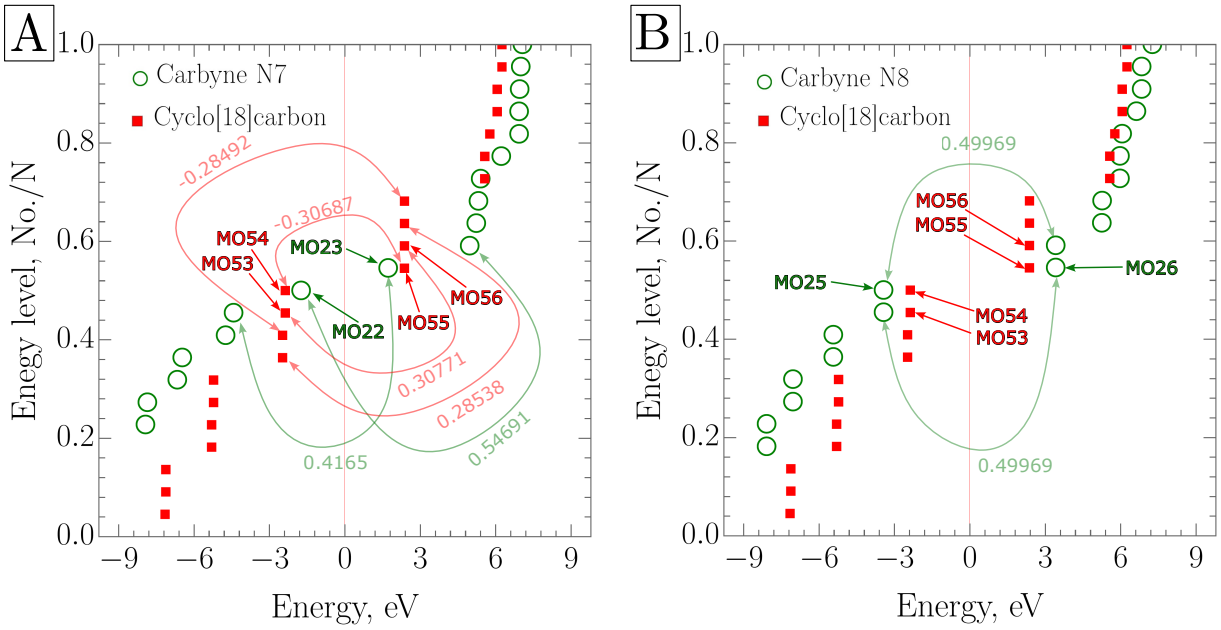


Figure SI8: Comparison of the electronic energy levels of (A) carbyne $N = 7$ and cyclo[18]carbon, and (B) carbyne $N = 8$ and cyclo[18]carbon. Single-headed arrows show correspondence to MO numbering. Half-toned double-headed arrows show dominant optical transitions together with their configuration coefficients contributing to the most intense peaks in the absorption spectra of the structures.

Table SI1: Electronic absorption spectrum of carbynes $N = 7$ and 8, and cyclo[18]carbon calculated by TD-DFT CAM-B3LYP/6-311++g(3d,3p). Most prominent transitions highlighted in bold are visualized in Fig. SI8. Selection rules are given in terms of H: HOMO and L: LUMO.

Carbon allotrope	Wavelength (nm)	Excitation Energy (eV)	Oscillation Strength (a.u.)	Configuration composition (orbitals: selection rules)
Carbyne $N = 7$	403.72	3.0711	0.0124	$+0.55222\,(\mathrm{MO21} \rightarrow \mathrm{MO23} : \mathrm{H}-1 \rightarrow \mathrm{L})$ $-0.043058\,(\mathrm{MO22} \rightarrow \mathrm{MO24} : \mathrm{H} \rightarrow \mathrm{L}+1)$
	235.66	5.2611	0.0173	$+0.668\,(\mathrm{MO22} \rightarrow \mathrm{MO27} : \mathrm{H} \rightarrow \mathrm{L}+4)$ $+0.16134\,(\mathrm{MO22} \rightarrow \mathrm{MO31} : \mathrm{H} \rightarrow \mathrm{L}+8)$ $+0.12303\,(\mathrm{MO20} \rightarrow \mathrm{MO26} : \mathrm{H}-2 \rightarrow \mathrm{L}+3)$
	225.13	5.5073	3.2121	$+\mathbf{0.54691}\,(\mathrm{MO22} \rightarrow \mathrm{MO24} : \mathrm{H} \rightarrow \mathrm{L}+1)$ $+\mathbf{0.4165}\,(\mathrm{MO21} \rightarrow \mathrm{MO23} : \mathrm{H}-1 \rightarrow \mathrm{L})$ $+0.13883\,(\mathrm{MO22} \rightarrow \mathrm{MO33} : \mathrm{H} \rightarrow \mathrm{L}+10)$ $+0.10408\,(\mathrm{MO20} \rightarrow \mathrm{MO30} : \mathrm{H}-2 \rightarrow \mathrm{L}+7)$
Carbyne $N = 8$	209.56	5.9164	3.971	$+\mathbf{0.49969}\,(\mathrm{MO24} \rightarrow \mathrm{MO26} : \mathrm{H}-1 \rightarrow \mathrm{L})$ $+\mathbf{0.49969}\,(\mathrm{MO25} \rightarrow \mathrm{MO27} : \mathrm{H} \rightarrow \mathrm{L}+1)$
	181.85	6.8178	0.02	$+0.63869\,(\mathrm{MO24/MO25} \rightarrow \mathrm{MO29} : \mathrm{H}-1 \rightarrow \mathrm{L}+3)$ $-0.19244\,(\mathrm{MO24/MO25} \rightarrow \mathrm{MO33} : \mathrm{H}-1 \rightarrow \mathrm{L}+7)$ $-0.18873\,(\mathrm{MO22/MO23} \rightarrow \mathrm{MO28} : \mathrm{H}-3 \rightarrow \mathrm{L}+2)$ $-0.10325\,(\mathrm{MO24/MO25} \rightarrow \mathrm{MO41} : \mathrm{H}-1 \rightarrow \mathrm{L}+15)$
Cyclo[18]carbon	507.77	2.4417	0.0037	set 1 : $+\mathbf{0.30771}\,(\mathrm{MO53} \rightarrow \mathrm{MO56} : \mathrm{H} \rightarrow \mathrm{L}+1)$ $-\mathbf{0.30687}\,(\mathrm{MO54} \rightarrow \mathrm{MO55} : \mathrm{H} \rightarrow \mathrm{L})$ $+\mathbf{0.28538}\,(\mathrm{MO51} \rightarrow \mathrm{MO57} : \mathrm{H}-1 \rightarrow \mathrm{L}+2)$ $-\mathbf{0.28492}\,(\mathrm{MO52} \rightarrow \mathrm{MO58} : \mathrm{H}-1 \rightarrow \mathrm{L}+3)$ $+0.19721\,(\mathrm{MO51} \rightarrow \mathrm{MO58} : \mathrm{H}-1 \rightarrow \mathrm{L}+3)$ $+0.19709\,(\mathrm{MO52} \rightarrow \mathrm{MO57} : \mathrm{H}-1 \rightarrow \mathrm{L}+2)$ $+0.18804\,(\mathrm{MO54} \rightarrow \mathrm{MO56} : \mathrm{H} \rightarrow \mathrm{L}+1)$ $+0.188\,(\mathrm{MO53} \rightarrow \mathrm{MO55} : \mathrm{H} \rightarrow \mathrm{L})$
				set 2 : $+\mathbf{0.30733}\,(\mathrm{MO54} \rightarrow \mathrm{MO56} : \mathrm{H} \rightarrow \mathrm{L}+1)$ $+\mathbf{0.30726}\,(\mathrm{MO53} \rightarrow \mathrm{MO55} : \mathrm{H} \rightarrow \mathrm{L})$ $+\mathbf{0.28524}\,(\mathrm{MO51} \rightarrow \mathrm{MO58} : \mathrm{H}-1 \rightarrow \mathrm{L}+3)$ $+\mathbf{0.28505}\,(\mathrm{MO52} \rightarrow \mathrm{MO57} : \mathrm{H}-1 \rightarrow \mathrm{L}+2)$ $-0.19729\,(\mathrm{MO51} \rightarrow \mathrm{MO57} : \mathrm{H}-1 \rightarrow L+2)$ $+0.19701\,(\mathrm{MO52} \rightarrow \mathrm{MO58} : \mathrm{H}-1 \rightarrow \mathrm{L}+3)$ $-0.18828\,(\mathrm{MO53} \rightarrow \mathrm{MO56} : \mathrm{H} \rightarrow \mathrm{L}+1)$ $+0.18776\,(\mathrm{MO54} \rightarrow \mathrm{MO55} : \mathrm{H} \rightarrow \mathrm{L})$

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