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Localization–delocalization phenomena in a cyclic box

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Abstract   The localization–delocalization of a particle in a cyclic box is studied by examination of its Shannon information entropy and standard deviation. These results are compared to the particle in a box model, in ground and also in excited states. We show how a cyclic symmetry imposes that the ground state is more delocalized in the cyclic box as compared to the particle in a box. However, excited states in both models exhibit the same localization. The differences between the Shannon entropy and the standard deviation are discussed and the analysis is then extended to consider multiple particles in both models.

1 Introduction

Localization–delocalization phenomena exhibited by quantum systems is an important aspect in several fields in chemistry and physics [1–5]. In physics, it is common to find this kind of phenomena in confined systems where particles are confined in one, two or three dimensions. A quantum dot is currently one of the most revolutionary and technologically useful examples of this kind of confined system. In chemistry, aromatic compounds are those in which many important properties depend on the delocalization of π electrons [6]. In both cases, the study of localization–delocalization phenomena has a very important role in the development of new concepts and applications.

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The localization (delocalization) inherent in a distribution can be quantified by the Shannon information entropy [7], taken from information theory [8]. This information entropy has been applied to the study of atomic and molecular systems [9–17]. It is defined for continuous variables as

$$S_x = - \int \rho(x) \ln \rho(x) dx \qquad (1)$$

where the probability density $\rho(x)$ is defined in terms of the wave function of the system

$$\rho(x) = |\Psi(x)|^2. \qquad (2)$$

The density is normalized to unity,

$$\int \rho(x) dx = 1. \qquad (3)$$

Larger values of the Shannon entropy are indicative of a more delocalized density while smaller values are associated with localized distributions. Recently, a discrete Shannon entropy has been used to study aromaticity [18].

The Shannon information entropy can be compared to another measure of the localization, the standard deviation, defined as

$$\Delta x = \left(\langle x^2 \rangle - \langle x \rangle^2 \right)^{\frac{1}{2}}, \qquad (4)$$

and the moments are

$$\langle x^2 \rangle = \int \rho(x) x^2 dx, \quad \langle x \rangle = \int \rho(x) x dx. \qquad (5)$$

Smaller (larger) values of Δx are associated with a more localized (delocalized) distribution.

The particle in a box or infinite well model (B) with wave functions and energies in atomic units, for a box length L

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{n^2 \pi^2}{2mL^2}, \quad n = 1, 2, 3, \ldots \qquad (6)$$

has been studied from an information theoretic perspective [19,20]. The dependence of the Shannon entropy on the quantum number, n, has been analyzed and shown to be a constant as a function of quantum number. That is, the localization–delocalization does not vary in ground or excited states [21]. It is dependent on the box length [19,21] as

$$S_B = \ln(L) - (1 - \ln 2). \qquad (7)$$

In contrast, the standard deviation does depend on the quantum number as [20,22]

$$\Delta x_B = \frac{L}{2\sqrt{3}}\sqrt{1 - \frac{6}{\pi^2 n^2}}. \tag{8}$$

Thus, Δx_B increases with quantum number, in contrast to S_B, with the interpretation that excitation induces delocalization. In the limit of very large n, which according to the correspondence principle is the classical limit, $\Delta x_B \rightarrow \frac{L}{2\sqrt{3}}$.

These results prompt the question of which is the superior measure of localization, how are they different, and what would occur if the symmetry of the system were to change, i.e. if the particle was confined to a ring instead of the box. In which system would the particle be more delocalized? These models have been applied to chemical systems where the particle can be used to represent the behavior of a π electron in an alkene (box) or cyclic conjugated molecule (ring) and go by the name of Free Electron Molecular Orbital (FEMO) model [23].

The natural coordinates of the particle on a ring [24,25] are polar ones where the wave functions are dependent on the polar angle, θ, and are given as $\frac{1}{\sqrt{2\pi}}e^{im\theta}$ with $m = \pm 1, \pm 2, \ldots$. Thus the density is constant, independent of the quantum number and θ, and yields an entropy of $\ln 2\pi$. However, our coordinate system must be consistent in the two models, in order to compare results, since the measures are dependent on the coordinate system that is employed [8].

Wave functions for the ring can be obtained in cartesian coordinates by imposing the necessary boundary conditions [25,26]. This model is referred to as the cyclic box (CB). The wave functions and energies are

$$\Phi_{k=0}(x) = \sqrt{\frac{1}{L}}$$

$$\Phi_k^+(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{2k\pi x}{L}\right), \quad k = 1, 2, 3, \ldots$$

$$\Phi_k^-(x) = \sqrt{\frac{2}{L}}\cos\left(\frac{2k\pi x}{L}\right), \quad k = 1, 2, 3, \ldots$$

$$E_k = \frac{(2k)^2\pi^2}{2mL^2} \tag{9}$$

where k is the quantum number and L is the cyclic box length which is equivalent to the circumference of the ring. There is degeneracy in this model since $\Phi_k^-(x)$, $\Phi_k^+(x)$ yield the same energy.

FEMO [4,23] has been used to discuss the role of the spatial symmetry by defining a delocalization energy as the difference between the energies of the two models. Thus, the observed stability of aromatic molecules could be attributed to the stability of the ground state of the cyclic box as compared to the box. These models have also been used to discuss Aromaticity/Antiaromaticity in cyclic conjugated hydrocarbons [24].

The purpose of this work is to examine the differences in (de)localization of the probability density, in the two models, from analysis of the Shannon entropies and standard deviations. Hence, instead of an energetic perspective, we focus on the behavior of the probability densities which is more directly related to the localization–delocalization concept in quantum mechanics. Atomic units are used throughout.

2 Results and discussion

2.1 Ground state

We begin the study by examining the localization–delocalization in the ground states of the B and CB models. We plot the respective probability densities as a function of x in Fig. 1. One can see that the CB ground state density is flat and thus more delocalized as compared to the B model which exhibits a maximum.

The localization can be quantified by calculating the Shannon entropies and standard deviations. In the CB model

$$
S_{CB} = \ln(L)
$$
$$
\Delta x_{CB} = \frac{L}{2\sqrt{3}}. \tag{10}
$$

These expressions can be compared to and contrasted to those in Eqs. (7) and (8) for the box with $n = 1$, corresponding to the ground state. Both the Shannon entropy and the standard deviation yield that the particle in the box is more localized than in the cyclic box or equivalently that the particle in the cyclic box is more delocalized than in the box. Figures 2 and 3 illustrate this as a function of box length, L. One can see that the curve of cyclic box is always above that of the box. These results illustrate that the symmetry of the system plays an important role in the delocalization of the particle.

The difference between Figs. 2 and 3 is that the difference between Shannon entropies in Fig. 2 is constant and independent of L, whereas the difference between the standard deviations in Fig. 3 is linear with L.

It is also noteworthy that the standard deviation of the ground state in the cyclic box is the same as that of the classical limit in the box when n is very large.

2.2 Excited states

Figure 4 shows the probability density of the two degenerate excited state CB functions corresponding to $k = 1$. The $\Phi_k^+(x)$ function has the same form as the B function, with $n = 2k$, thus the entropy of this CB function is the same as the B one [Eq. (7)].

One can also verify that degenerate functions, $\Phi_k^+(x)$ and $\Phi_k^-(x)$, yield the same value of entropy, equal to that of Eq. (7). This is not the case for the standard deviation. One obtains that the two degenerate functions for the excited states of the CB model do not yield the same standard deviation. Equation (8) for these states is generalized to
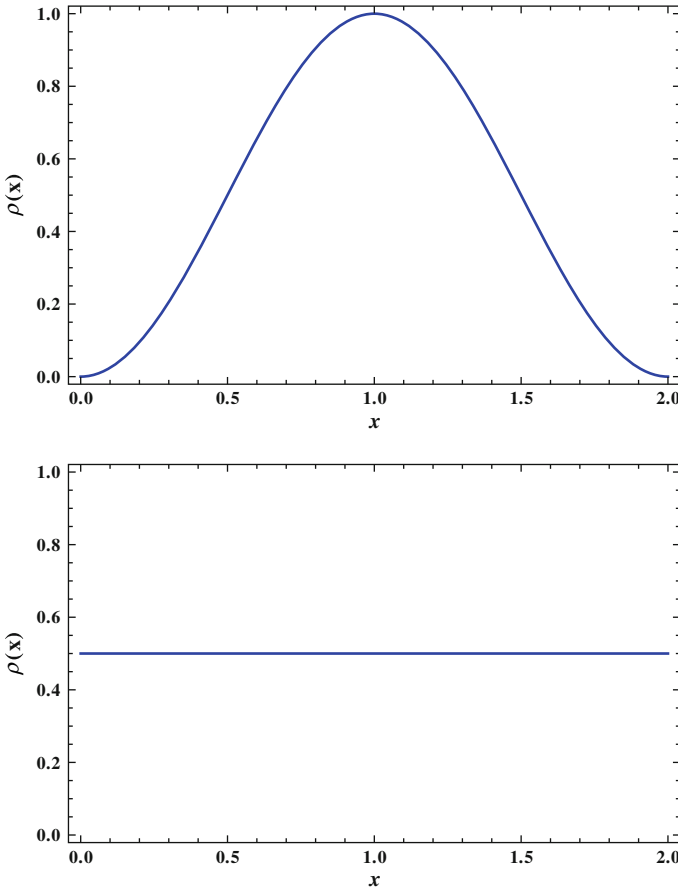
Fig. 1 Probability density of the particle in a box (*upper curve*) and the cyclic box (*lower curve*) in the ground state for $L = 2$

$$\Delta x_{CB} = \frac{L}{2\sqrt{3}}\sqrt{1 \pm \frac{3}{2\pi^2 k^2}}, \tag{11}$$

where the + corresponds to the $\Phi_k^-(x)$ functions and − to the $\Phi_k^+(x)$ functions. Thus although degenerate, the standard deviation for the $\Phi_k^-(x)$ function is larger than that of the $\Phi_k^+(x)$ function. This is a salient difference from the Shannon entropy where both are equal. We believe that this behavior of the standard deviation stems from inconsistencies in defining expectation values of x for a periodic system, and is connected to the choice of origin in the coordinate system. For example, the $\sin[\Phi_k^+(x)]$ and $\cos[\Phi_k^-(x)]$ functions in Fig. 4 are phase-shifted. An in-depth analysis of this effect will be presented elsewhere.
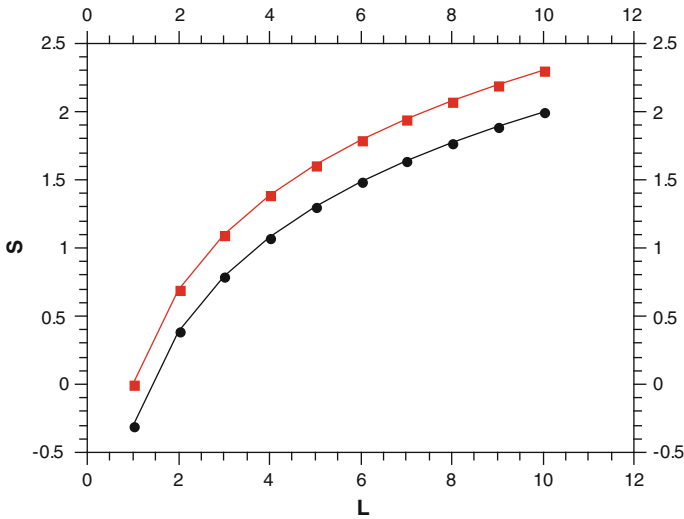
Fig. 2 Shannon entropy for the particle in a box (*circles*) and a cyclic box (*squares*) in their ground states as a function of box length, L
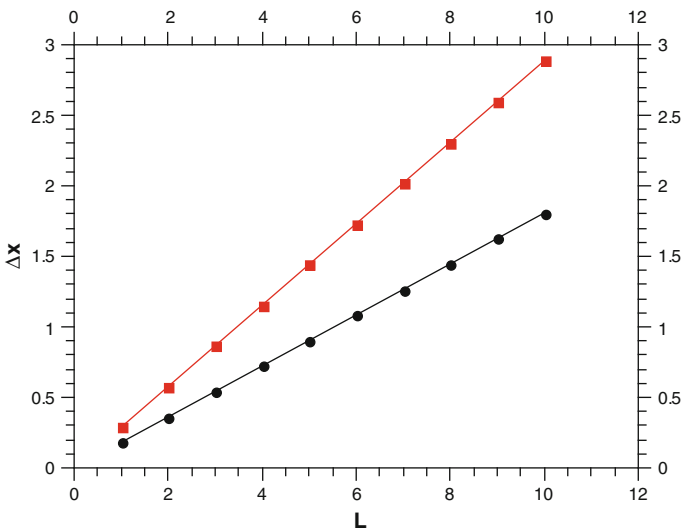

Fig. 3 Standard deviation values for the particle in a box (*circles*) and a cyclic box (*squares*) in their ground states as a function of box length, L

Comparing the first excited state of the CB model ($k = 1$) to that of the B model ($n = 2$), with the same L, one observes that their Shannon entropies are equal, i.e. they are equally (de)localized. The reason for this is that Eq. (7) does not depend on the quantum number. This is also true for the second, third, …, excited states. A striking observation is that the differences in localization between the two models previously seen in the ground state, is lost when one examines excited states.
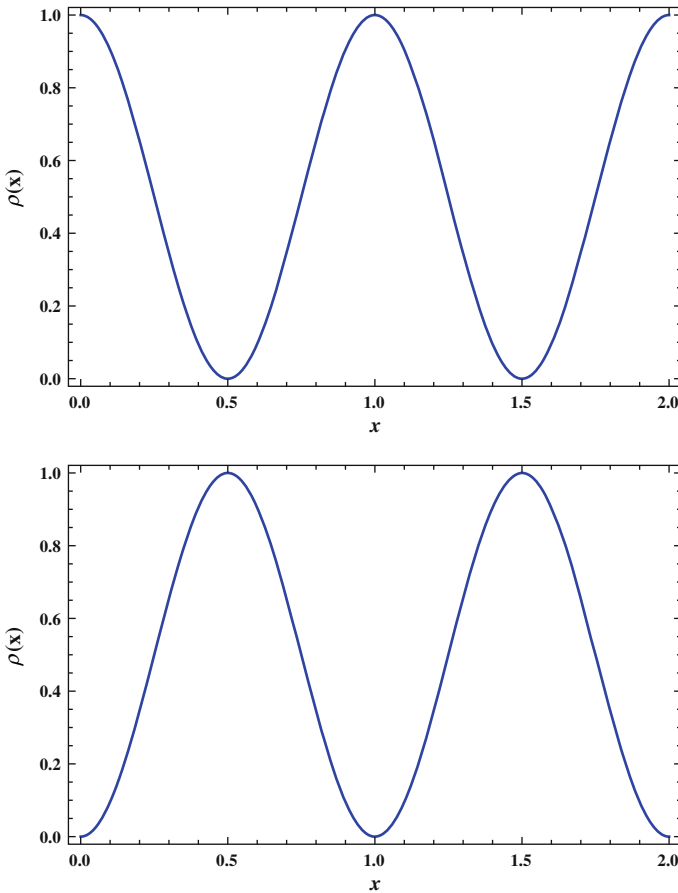
Fig. 4 Probability density of the degenerate first excited states of the cyclic box, $\Phi_1^-(x)$ (*upper curve*), $\Phi_1^+(x)$ (*lower curve*), with $L = 2$

Analogously, the standard deviation of the CB model for $\Phi_k^+(x)$ can be compared to the B model with the use of Eqs. (8) and (11). In the first excited state of the box, $n = 2$ while in the cyclic box, $k = 1$. Thus both models yield the same standard deviation in these states. The interpretation in this case is consistent with that obtained from the Shannon entropy, i.e. both models in the first excited state are equally (de)localized.

This behavior is also examined in other excited states. For $n > 2$ and $k > 1$, Eqs. (8) and (11) show that the CB particle is more delocalized than the B particle in these states, similar to the ground state. This also holds for the $\Phi_k^-(x)$ functions (and in the first excited state). Thus, there are differences in interpretation according to which measure one employs.

The differences in the measures can be summarized and clarified by examining the (second) excited state densities for both models in Fig. 5 for $n = 3$ in the box and $k = 2$ (effective quantum number 4) in the cyclic box. One notes that the nodal structure in the CB model is more pronounced. However, independent of this, the Shannon
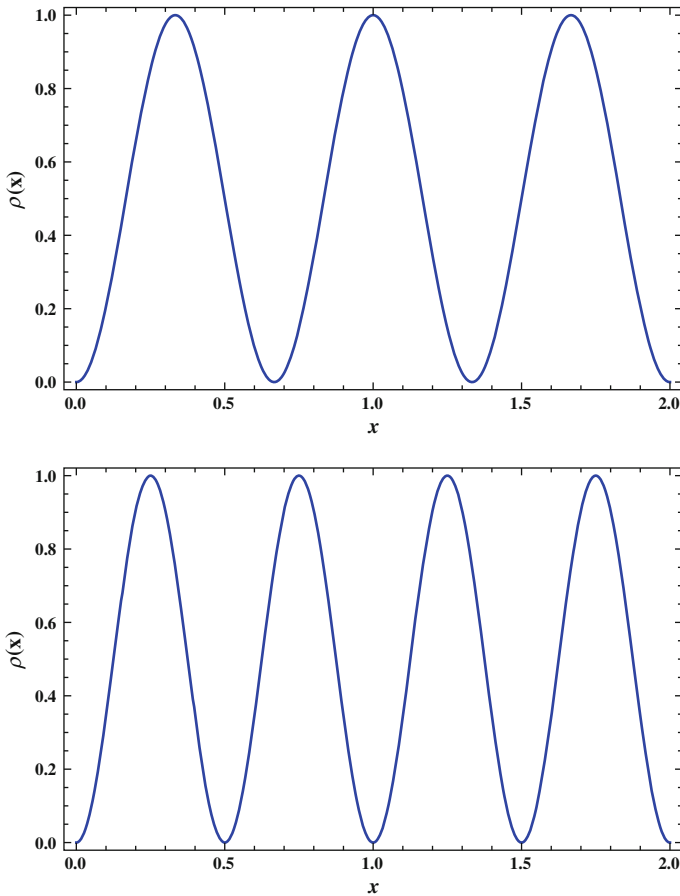
Fig. 5 Probability density for states $n = 3$ in the box (*upper curve*) and $k = 2$ in the cyclic box (*lower curve*), with $L = 2$

entropy quantifies the (de)localization to be equal in both models while the standard deviation yields that the CB model is more delocalized.

Examination of the energy expressions in Eqs. (6) and (9) show that the energies of the two models are equal in the first excited state, in contrast to the ground state where the lower energy of the CB model was argued to be due to delocalization. Hence the arguments and interpretation for the energy, Shannon entropy and standard deviation are congruent. That is, there is no difference between the B and CB models in the first excited state. For other excited states the B model energies are lower than the CB model.

2.3 Momentum space

In this section we will explore the momentum space formulation of the particle in a cyclic box since the momentum space Shannon entropy has been studied for the

particle in a box [19,20]. To our knowledge, the cyclic box in momentum space has not been previously studied or applied to study chemical systems. The Shannon entropies in position and in momentum space together define an entropic uncertainty relation [27]

$$S_t = S_x + S_p \geq 1 + \ln \pi, \tag{12}$$

where the momentum space Shannon entropy is defined as

$$S_p = -\int \pi(p) \ln \pi(p) dp \tag{13}$$

and $\pi(p)$ is the momentum space density. This density is defined in terms of the wave function in momentum space as

$$\pi(p) = |\varphi(p)|^2. \tag{14}$$

The wave function in momentum space is connected to that in position space by the Dirac-Fourier transform

$$\varphi(p) = \frac{1}{\sqrt{2\pi}} \int_0^L \Phi(x) e^{-ipx} dx. \tag{15}$$

Using the above expression, we transformed the functions given in Eq. (9) to,

$$\varphi_{k=0}(p) = \frac{i(e^{-ipL} - 1)}{p\sqrt{2\pi L}}$$

$$\varphi_k^+(p) = 2k\sqrt{\pi L} \left[\frac{\cos(pL) - i\sin(pL) - 1}{(pL)^2 - (2\pi k)^2} \right]$$

$$\varphi_k^-(p) = \frac{ipL^{\frac{3}{2}}}{\sqrt{\pi}} \left[\frac{\cos(pL) - i\sin(pL) - 1}{(pL)^2 - (2\pi k)^2} \right]. \tag{16}$$

The $\langle p^2 \rangle$ expectation value gives twice the kinetic energy which in this case is twice the total energy. Calculating $\langle p^2 \rangle$ using the above functions,

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} p^2 |\varphi(p)|^2 dp, \tag{17}$$

one finds that the $\varphi_{k=0}$ and φ_k^- functions do not correctly reproduce the energy, while the φ_k^+ function does give the correct energy. Thus, the $\varphi_{k=0}$ and φ_k^- functions are not valid representations in momentum space even though they are the transforms of the position space functions. Their common trait in position space is that they do not
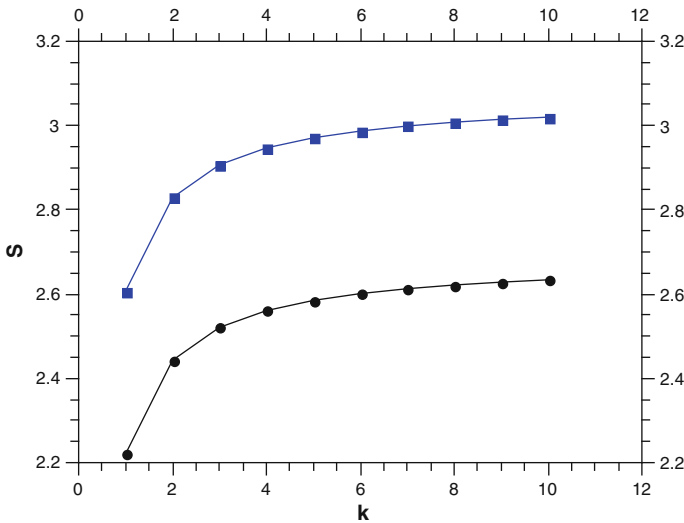
Fig. 6 S_p (*circles*) and S_t (*squares*) of the cyclic box as a function of quantum number with $L = 2$

vanish at the boundaries of the cyclic box, in contrast to the φ_k^+ function which does vanish.

S_p, calculated from the $\varphi_k^+(p)$ functions via numerical integration, is shown in Fig. 6 along with S_t. S_p increases with quantum number, in sharp contrast to position space where S_x is constant. Thus, the behavior of S_t is governed by S_p. The behavior of S_p with quantum number in the cyclic box mimics that of the particle in a box [19,20]. Hence, the momentum density in the cyclic box is more delocalized than the box in corresponding (first, second, third, …) excited states.

Figure 7 shows the variation of S_x, S_p and S_t with L. S_p decreases, or the momentum density localizes, while S_x increases. Note that S_t is a constant and its value is above that of the bound established in Eq. (12). This bound also holds for S_t in Fig. 6.

The standard deviation of the momentum density,

$$\Delta p = \left(\langle p^2 \rangle - \langle p \rangle^2 \right)^{\frac{1}{2}} = \sqrt{2E_k} = \frac{2k\pi}{L}, \tag{18}$$

is related to the energy since $\langle p \rangle = 0$. From Eq. (18), one sees that Δp grows linearly with quantum number k. This differs from the behavior of S_p in Fig. 6 where S_p approaches an asymptotic value. This difference has been previously discussed in the box (B) model [19].

2.4 Multiple particles

We now focus the attention on the behavior of the two models in position space but now with multiple particles. The wave functions of a system of N non-interacting
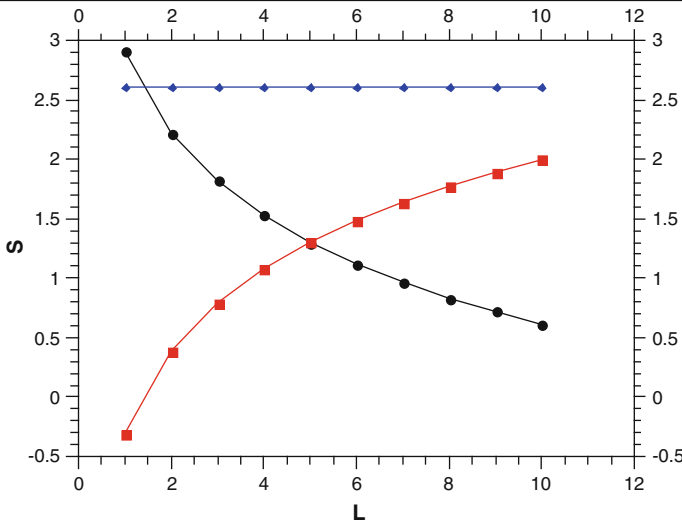
Fig. 7 S_p (*circles*), S_x (*squares*) and S_t (*diamonds*) of the cyclic box as a function of box length, L, for $k = 1$

and indistinguishable particles for these models are (anti)symmetrized products of the one-particle functions (orbitals)

$$\Omega_B(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} |\Psi_{n1}(x_1)\Psi_{n2}(x_2), \ldots, \Psi_{nN}(x_N)|$$

$$\Lambda_{CB}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} |\Phi_{k1}(x_1)\Phi_{k2}(x_2), \ldots, \Phi_{kN}(x_N)|. \qquad (19)$$

The one-particle density is obtained by integration over $N - 1$ variables

$$\rho_B(x) = \int |\Omega_B(x_1, x_2, \ldots, x_N)|^2 dx_2 \ldots dx_N$$

$$\rho_{CB}(x) = \int |\Lambda_{CB}(x_1, x_2, \ldots, x_N)|^2 dx_2 \ldots dx_N \qquad (20)$$

which gives

$$\rho_B(x) = \frac{1}{N} \sum_n |\Psi_n(x)|^2$$

$$\rho_{CB}(x) = \frac{1}{N} \sum_k |\Phi_k(x)|^2, \qquad (21)$$

where the subscript under x_1 has been dropped to reflect the indistinguishability of particles.

Electron spin is introduced into the models by allowing for double occupancy of the orbitals and hence respecting the Pauli exclusion principle. The densities are
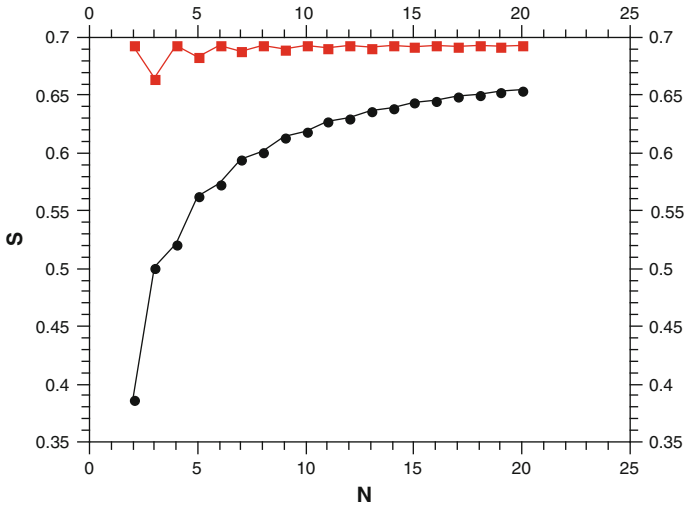
Fig. 8 Shannon entropy of the box (*circles*) and cyclic box (*squares*) with multiple particles and $L = 2$

normalized to unity and the entropies were obtained via numerical integration. Hund's rule was used in the orbital filling of the cyclic box. For example, ground state densities of the cyclic box are [26]

$$
\begin{aligned}
\rho_{CB}^2(x) &= \frac{1}{2}\left(2|\Phi_0(x)|^2\right) \\
\rho_{CB}^3(x) &= \frac{1}{3}\left(2|\Phi_0(x)|^2 + |\Phi_1^{\pm}(x)|^2\right) \\
\rho_{CB}^4(x) &= \frac{1}{4}\left(2|\Phi_0(x)|^2 + |\Phi_1^{+}(x)|^2 + |\Phi_1^{-}(x)|^2\right)
\end{aligned} \tag{22}
$$

while in the box

$$
\begin{aligned}
\rho_{B}^2(x) &= \frac{1}{2}\left(2|\Psi_1(x)|^2\right) \\
\rho_{B}^3(x) &= \frac{1}{3}\left(2|\Psi_1(x)|^2 + |\Psi_2(x)|^2\right) \\
\rho_{B}^4(x) &= \frac{1}{4}\left(2|\Psi_1(x)|^2 + 2|\Psi_2(x)|^2\right),
\end{aligned} \tag{23}
$$

where the superscript corresponds to the number of particles. It should be emphasized that although the particles are non-interacting, there is a *pseudo* force between them due to the antisymmetry of the wave function and respect of the Pauli principle.

Figure 8 shows the behavior of the entropies of the two models as a function of N. First, $S_{CB} > S_B$, that is the cyclic box is always more delocalized than the box, independent of the number of particles. This reaffirms the previous result for the one-particle ground state.
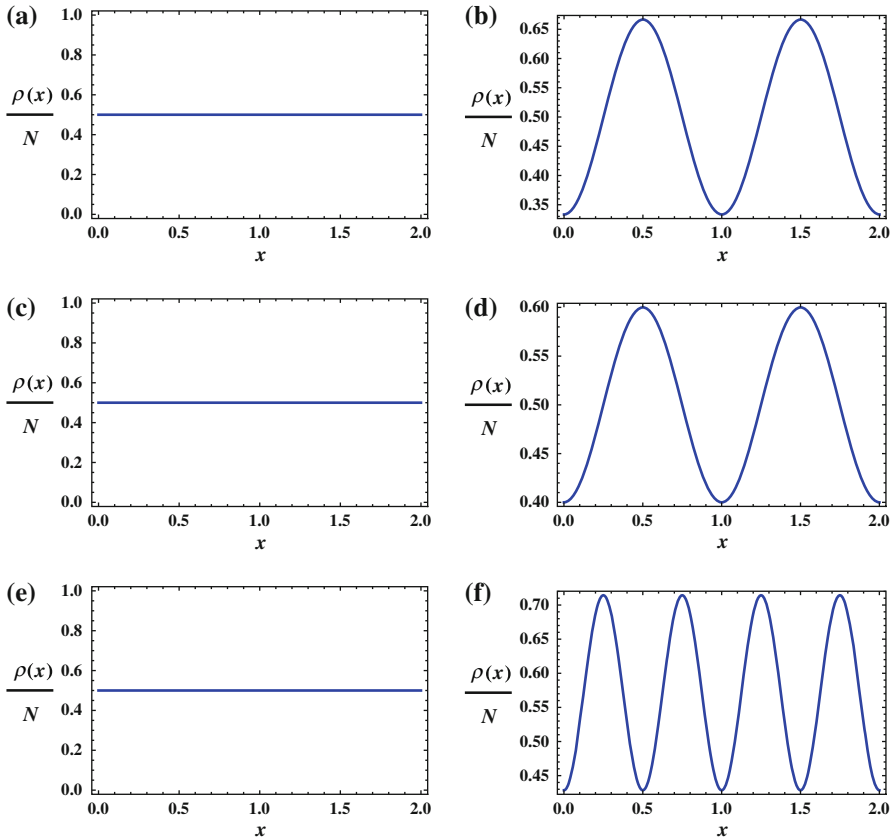
Fig. 9 Probability density of the cyclic box with $L = 2$ for $N = 2 - 7$, (**a**)–(**f**)

Second, the density of the box delocalizes with N, i.e. the entropy increases. The interpretation of this is that the *pseudo* force between particles causes them to avoid each other which results in a delocalization of the density.

On the other hand, the entropy of the cyclic box remains virtually the same, localizing slightly for an odd number of particles. That is, the density localizes and the entropy decreases when a new orbital is filled. We present in Fig. 9 plots of the densities for different particle number where one can observe how adding a particle changes the structure of the probability density. The oscillations in the entropy of the cyclic box decrease for larger N, and are not present in the box model. Also, the effect of the *pseudo* repulsion with N is greater in the box than in the cyclic box.

As N increases, the entropies of the two models tend to one another, and it is plausible to believe that they would be equal in the asymptotic limit of very large N. In this limit which one can consider as classical (uniform distribution of particles), the density would be constant and written as
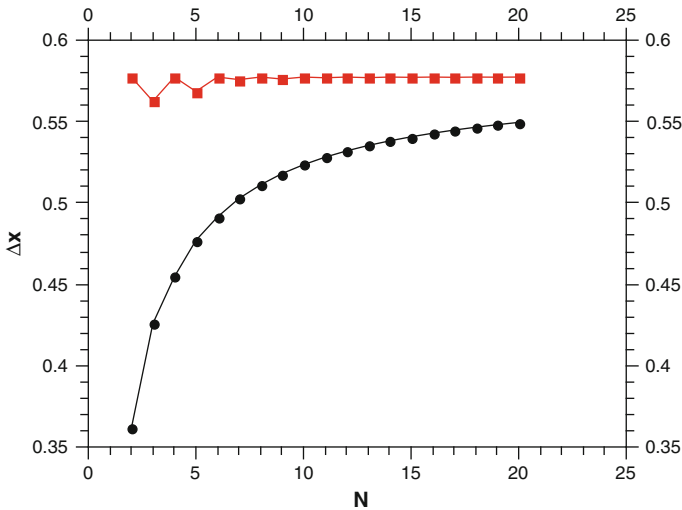
$$\rho_c(x) = \frac{N}{L}. \tag{24}$$

Fig. 10 Standard deviation of the box (*circles*) and cyclic box (*squares*) with multiple particles and $L = 2$

Such a density when normalized to unity gives $\frac{1}{L}$, and yields an entropy of $\ln(L)$, which are the same as those in the ground state of the particle in a cyclic box. The important point here is that in the limit of very large N, both models exhibit the same (de)localization as measured by the entropies.

The behavior of the standard deviation is given in Fig. 10 and is similar to that of the Shannon entropy. Thus the previous arguments and interpretations hold in the analysis of multiple particles. In the limit of large N, one can use the expression for the density in Eq. (24) to calculate the standard deviation, which gives $\frac{L}{2\sqrt{3}}$, and is the same as the standard deviation of the particle in a cyclic box in its ground state.

The energies of the models as a function of N, calculated by using orbital filling and the respective expressions in Eqs. (6) and (9), are presented in Fig. 11. One observes that the energy of the CB model is always below that of the B model, independent of the number of particles. Note that this is different from the one-particle case where the B model has a lower energy for higher excited states. The added stability of the CB model can be justified by the larger delocalization of its probability density, seen in the Shannon entropy and standard deviation.

3 Conclusions

Shannon information entropies and standard deviations are used to quantify, compare and contrast the localization of the probability density of the particle in a cyclic box with that of a one-dimensional box. In the ground state, the particle in a cyclic box is more delocalized than in the one-dimensional box. In excited states, the situation is different since there is an equal (de)localization of the particles in both models according to the Shannon entropy analysis. This result is in agreement with the
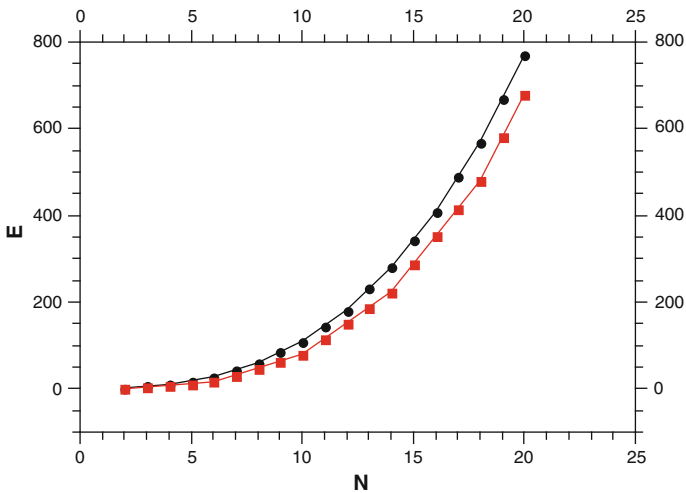
Fig. 11 Energies of the box (*circles*) and cyclic box (*squares*) models in units of $\frac{\pi^2}{2mL^2}$ as a function of number of particles

standard deviation analysis in the first excited states. In other excited states, the standard deviation gives that the cyclic box model is more delocalized than the one-dimensional box, similar to ground state results. Analysis of the ground states corresponding to multiple particles in these models show that the cyclic box density is more delocalized than the one-dimensional box with the differences decreasing as the number of particles is increased. Thus independent of the number of (non-interacting) particles, the cyclic box is more delocalized than the one-dimensional box. The cyclic box in momentum space is also discussed.

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