United Nations Educational Scientific and Cultural Organization  
and  
International Atomic Energy Agency  

THE ABDUS SALAM INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS  

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Abstract  

The Bose-Einstein energy spectrum of a quantum gas, confined in a rigid cubic box, is shown to become discrete and strongly dependent on the box geometry (size L), temperature, \( T \) and atomic mass number, \( A \), in the region of small \( \gamma = A T V^{1/3} \). This behavior is the consequence of the random state degeneracy in the box. Furthermore, we demonstrate that the total energy does not obey the conventional law any longer, but a new law, which depends on \( \gamma \) and on the quantum gas fugacity. This energy law imposes a faster decrease to zero than it is classically expected, for \( \gamma \to 0 \). The lighter the gas atoms, the higher the temperatures or the box size, for the same effects in the discrete Bose-Einstein regime.  

MIRAMARE – TRIESTE  
March 2001  

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1. Introduction

Einstein introduced the brilliant hypothesis that the particles (atoms, molecules with rest mass and without limit for level occupation) of a gas are, like photons, indistinguishable from each other and calculated the gas statistics almost in the same way as for photons. The specific feature of the particle gas is the finite number of particles, which leads to a non-zero chemical potential [1-4]. This model became one of the pillars of modern physics and prompted the research of Bose-Einstein condensation (BEC) and its challenges. An excellent review of this matter was recently presented by Tino and Inguscio [5]. The Bose-Einstein distribution law is described by a continuous function, which is dependent on kinetic energy, temperature and chemical potential, but is independent on the container size and shape (considering the quantum gas in a large container).

Will this remain true when the box size and the temperature are smaller and smaller? Following Einstein’s line of thinking, can the results obtained with photons in a small box be generalized to the problem of atoms in a small box?

The ideal classical box may be defined as a closed surface with a perfectly smooth and unitary reflection interior wall. The quantum counterpart of this classical definition is the concept of an infinite potential well, ensuring a vanishing probability for the atom presence outside its surface.

The quantum version of the atom confinement is actually an eigenvalue problem, the discrete spectrum of the atom energies being a direct consequence of the volume finiteness and of the shape of limiting surface. For a free particle with rest mass, the energy equation (with the corresponding quantum operators) can lead to a Schrödinger-Helmholtz equation. The rigid box introduces a Dirichlet boundary condition. The history of these types of problems is very rich [6]. Gutierrez and Yanez [7] and Pathria [8] gave good accounts of it. The previous attempts to calculate the effects of the container size on the boson gas thermodynamics have used the (Weyl-Pleijel) asymptotic state density corrections only. These corrections were relatively small, but increasing with the box size decrease. More recently, a number of papers calculated the effect of trap dimension and size on BEC [5, 9-12].

If we refer definitely to the Bose-Einstein energy spectrum (BEES), we show that the effect of the geometrical confinement upon the energy spectrum of the particles stored inside the box may be assigned to an additional quantisation, similar to the case of photons in a small box. In this case, not only the atom internal energy is quantified, but also its kinetic energy, through the agency of the discrete spatial directions of the allowed wave-vectors (as a result of the confinement) [13-18]. We name this quantum device as double quantized box (DQB). The effect of the additional energy quantisation is controlled by the factor $\gamma = A_{at}TV^{2/3}$ ($A_{at}$ - atomic mass number, $T$ - absolute temperature and $V$ - the allowed volume), which is proportional to the adiabatic invariant and by the chemical potential (or alternatively, by the particle number). For $2.28 \times 10^{-14} \leq \gamma \leq 76 \times 10^{-14} \text{[cm}^3\text{K]}$, we show that BEES presents a discrete pattern (of lines with irregular intensities). For larger $\gamma$, the asymptotic region is reached and the continuous BEES is obtained by averaging over many non-resolvable spectrum lines.

Furthermore, the total energy, obtained in this case by summing up the exact contributions of the eigenvalues and their weights, for well-defined values of $\gamma$, does not obey the conventional law any longer. We demonstrate that the new total energy law is depending on $\gamma$ and on the chemical potential (fugacity) and imposes a faster decrease to zero than it is classically expected, for $\gamma \to 0$. 

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2. Schrödinger-Helmholtz eigenvalue problem for bosons confined in a box

The energy levels, $\varepsilon_n$, of a particle of mass $m$, in a box, can be obtained from the energy eigenfunctions of the time-dependent Schrödinger equation [2,6,7]:

$$
-\left(\frac{\hbar^2}{2m}\right) \nabla^2 \psi(r,t) + V(r)\psi(r,t) = i\hbar \frac{\partial \psi}{\partial t} \quad (1)
$$

with $\psi(r,t) = \phi(r)e^{-\frac{i\varepsilon nt}{\hbar}}$, $\varepsilon = \bar{p}^2 / 2m$ - the particle kinetic energy. In Eq.(1), we can take $V(r) = 0$ and impose a Dirichlet condition on the box boundary. The solution of this problem is similar to that obtained in the case of the three-dimensional harmonic oscillator, which is better realized in the present experimental conditions [6,11]). Eq.(1) can be separated on the spatial and temporal variables. The spatial part has the form of Helmholtz equation:

$$(\nabla^2 + K^2)\phi(r) = 0; \quad K^2 = 2m\varepsilon / \hbar^2 \quad (2)$$

with Dirichlet boundary condition for a rigid (reflecting) box: $\psi_s = 0$. \quad (3)

For a cubic box with size $L$, Eq.(2) can be separated on the independent variables and the corresponding energy eigenfunctions have the form [2,17]:

$$
\phi_k(x_k) = \frac{2}{\sqrt{L}} \sin \left[ \frac{2\pi}{L} q_k x_k \right]; \quad (k = 1,2,3); \quad [\phi_k(\pm L/2) = 0] \quad (4)
$$

where the quantum numbers, $q_k$, are integers and zero. The allowed wave-vectors in the cubic box are:

$$
K^2 = (4\pi^2 / L^2)(q_1^2 + q_2^2 + q_3^2) \quad (5)
$$

and the kinetic energies in the cubic box can be written as:

$$
\varepsilon = \frac{\hbar^2}{2m} K^2 = \frac{\hbar^2}{2m L^2} (q_1^2 + q_2^2 + q_3^2) = \frac{\hbar^2}{2m L^2} q = \varepsilon_0 \cdot q \quad (6)
$$

where $q$ is an integer state number and $\varepsilon_0$ – the ground level energy.

The energies of the box states, $\varepsilon(q)$, are distributed in a discrete spectrum defined by the spatial quantisation rule:

$$
q_1^2 + q_2^2 + q_3^2 = q \quad (7)
$$

The allowed triplets of integers of the Diophantine equation (7) are all numbers which do not lead to state numbers of the form (Gauss solution) [13,16]:

$$
q (p, l) = 4p \cdot (8l + 7), \quad (p \text{ and } l \text{ positive integers}) \quad (8)
$$
We have observed that the number of degenerate states in the box is strongly and randomly fluctuating. The degeneracy occurs due to the discrete spatial orientations of the state wave-vectors with the same quantum number \( q \). The exact weights, \( g(q) \), resulted from Eq.(7), are given in Table 1 and are represented in Fig.1 as a graph with jointed points.

The weight (degeneracy) of state with a quantum number \( q \) can be found, for large level numbers (asymptotic case), as [13,16]:

\[
g_{\text{asy}} = \frac{4\pi V}{h^3} \sqrt{2m^*} \epsilon = 2\pi \sqrt{q} . \tag{9}
\]

The average of the distribution \( g(q) \) follows the asymptotic trend from Eq.(9).

There are combinations of integers, which did not satisfy Eq.(7) leading to "antiresonances" in the spectrum [13,16]. The antiresonance frequencies can be identified in Fig.1 as points on the \( q \)-axis (\( g(q) = 0 \)). It is interesting to point out that (1/6) of the box energy spectrum is emptied by antiresonances.

For particle confinement in relatively small volumes and at relatively small temperatures (we shall define later what "relatively small" means), we have to face the random distribution of the eigenvalue intervals and/or degeneracy. One can expect that the selection rules imposed by the boundary conditions and eigenvalue ortho-normalization will lead to allowed states and forbidden states (antiresonances), i.e. a discrete and irregular spectrum of the S-H operator.

We can define the quantum degeneracy factor:

\[
\zeta(q) = \frac{g(q)}{g_{\text{asy}}(q)} = \frac{g(q)}{2\pi \sqrt{q}} , \tag{10}
\]

which includes the spatial quantization effects. We have checked that the factor \( \zeta(q) \) is randomly fluctuating around the value 1 by the calculation of the average number of states on constant frequency intervals. The result from Fig.1 is very convincing: although the degeneracy fluctuations are large for a box with a small number of states (and must be taken into account), the average number of states tends to the asymptotic value very rapidly. For a number of states larger than \( \approx 100 \), the classical equation (9) can be safely used.

For bosons with non-zero rest mass and chemical potential, the energy density spectrum can be deduced from the Bose-Einstein law for particle distribution [1-4]:

\[
\delta E = \frac{g \cdot q}{e^{(\epsilon + \mu)/kT} - 1} = \frac{g \cdot q}{e^{(\mu)/kT} \cdot e^{\epsilon/kT} - 1} = \frac{g \cdot q}{A^{-1} \cdot \exp(\alpha \cdot q / A_mL^2T) - 1} . \tag{11}
\]

with \( g \) - the level degeneracy, \( \mu \) - the chemical potential, \( k \) – the Boltzmann constant and \( T \) – the absolute temperature of the boson quantum gas, \( A = \exp(\mu / kT) \) - the fugacity, \( \mu \) - the chemical potential (\( < 0 \)), \( \alpha = h^2 / 2m_0p \approx 9.5060 \cdot 10^{-14} [cm^2 \cdot K] \) and \( A_m \) – the atomic mass number (\( m = A_m m_0p \)). Using the quantum degeneracy factor defined in (10), the boson spectrum (11) can be put in the form:

\[
\frac{\delta E}{\delta \epsilon} \frac{2p12}{A^{-1} \cdot \exp(\alpha \cdot q / A_mL^2T) - 1} = \zeta(q) . \tag{12}
\]
\[ Q(q) = \frac{g(q)}{2n \sqrt{q}} \]

Fig. 1. (a) The random fluctuations of the level degeneracy, \( g(q) \), around the curve \( 2\pi \sqrt{q} \), for state numbers, \( q \), including the first antiresonant doublet \((111,112)\). (b) The random fluctuation of the weight factor, \( \xi(q) \), around the unit value (graph with jointed points); the dots represent the calculated average number of modes on constant frequency intervals and show that the classical (asymptotic) mode density can be reached when \( q > 110 \), by the averaging of the actual mode density.
We define double quantized cubic cavities (DQB) as cavities with a small number of states, more precisely, with a special upper limit on the highest significant state number in the box: $q_T < 100$. In this case, the energy density spectrum of the boson gas does depend upon the box size (volume), i.e. upon the boundary conditions, (which is a non-classical effect).

The Bose-Einstein energy spectrum, from Eq.(12), is discrete for a small number of states in the cubic box, as shown in Fig.2 and Fig.3. From these graphs, one can observe that the quantum effects may occur in cubic cavities with micrometer sizes, at temperatures around $\mu$K, which are presently reached by evaporation and laser cooling [5]. These spectra show that, for specified particles (atoms), the higher the adiabatic invariant, $L^2T$, the higher the number of levels in the DQB. At a certain resolution limit, the spectrum is obtained by averaging the energy lines ($\zeta \to 1$) and the continuous BEES is reached (dashed graphs in Fig.2 and 3).

We can introduce a reasonable superior limit of the number of states in the box, $q_T$, which brings a significant contribution to the BEES. Observing that, at high energies, in Eq.(12), the exponential term dominates and $\zeta(q)$ goes to 1, the total energy density can be brought to the form: $u(x) = Bx^3 \exp(-x)$, with $x = \left(\alpha / A_m L^2 T\right)q = \left(\alpha / \gamma\right) \cdot q$. If we consider that $A < 0.99$ and we neglect the levels which bring to BEES a contribution of less than $10^{-2}$, one can truncate Bose-Einstein distribution at the highest significant level number (HSL) in the box:

$$q_T \approx 12.5 \cdot \left(\frac{A_m L^2 T}{\alpha}\right)^q = 12.5 \cdot \left(\frac{\gamma}{\alpha}\right). \quad (13)$$

One can observe that, in the above conditions, the fugacity plays a minor role in this truncation and for any of its values, Eq.(13) ensures an over-evaluated value for $q_T$.

For $A_e = 87$ (Rubidium), $L = 10^{-4}$ cm and $T = 10^{-6}$ K, Eq.(16) leads to: $q_T = 114$. For Li, one can find some more convenient conditions for DQB, namely: $L = 10$ $\mu$m and $T \approx 120$ nK. For a precision of $10^{-3}$, one can take: $q_T \approx 15(\gamma / \alpha) \approx 137$.

The state with the maximum total energy density can be evaluated at:

$$q_{max} \approx \frac{3}{2} \left(\frac{\gamma}{\alpha}\right) \left[1 - 0.223A\right] = 1.58 \cdot 10^{13} [cm^{-2} K^{-1}] \cdot (A_m L^2 T [1 - 0.223A]); \quad (14)$$

Thus, for the same parameter values as in the first example and for $A \approx 0.99$ (quasi-degenerate gas), one can find $q_{max} = 10$ and the ratio between HSL and the maximum (peak) state numbers as: $q_T / q_M = 14$ (the truncation precision was taken to be $10^{-2}$). The graphs in Figs. 2 and 3 show indeed, that the higher the parameter $\gamma$, the higher the level of the BEES peak (at constant fugacity, $A$). Furthermore, the closer the fugacity to 1, the lower the BEES peak coordinate (at constant $\gamma$).
Fig. 2. Some conventional Bose-Einstein spectra (dashed lines) and discrete Bose-Einstein spectra (solid lines, joining the tops of the energy spectrum lines), for $\gamma = 0.99$ (quasi-degenerated gas) and for the values of $\gamma = A_{\text{at}} L^2 T$ which are shown in each graph.
**Fig. 3.** Some conventional Bose-Einstein spectra (dashed lines) and discrete Bose-Einstein spectra (solid lines, joining the tops of the energy spectrum lines), for $A = 0.2$ (almost classical gas) and for the values of $\gamma = A_{at} L^2 T$ which are shown in each graph.
3. The total energy of boson gas in the double quantified cubic box

The total energy and the total number of particles of the free boson gas (in CGS-Gauss unit system) are [3]:

\[
E = \frac{g L^3 m^{3/2}}{\sqrt{2\pi^2 h^3}} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{\exp\left(\frac{\varepsilon - \mu}{kT}\right) - 1} ; \quad \varepsilon = \varepsilon_0 \cdot q ; \quad \varepsilon_0 = \frac{\alpha}{A_w L^2 T} \cdot kT ;
\]

\( (15) \)

\[
N = \frac{g L^3 m^{3/2}}{\sqrt{2\pi^2 h^3}} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{\exp\left(\frac{\varepsilon - \mu}{kT}\right) - 1} .
\]

\( (16) \)

One can find that [18]:

\[
A \rightarrow 0 , \quad E \rightarrow 3/2 N k T (1 - f_1 (A)) = \frac{3}{2} N k T (1 - 0.1767767 \cdot A - 0.0658001 \cdot A^2 - 0.0364655 \cdot A^3 - 0.0239014 \cdot A^4 - 0.0171965 \cdot A^5) .
\]

\( (17) \)

Introducing the new normalized variable \( z = \varepsilon / kT \), one can write Eq. (15) and (16) in the form:

\[
E = g L^3 (m k T)^{3/2} \int_0^\infty \frac{z^{3/2} \cdot e^{-z}}{A^1 - e^{-z}} d z ;
\]

\( (18) \)

\[
N = g L^3 (m k T)^{3/2} \int_0^\infty \frac{z^{1/2} \cdot e^{-z}}{A^1 - e^{-z}} d z = \left( \frac{\pi A_w L^2 T}{\alpha} \right)^{3/2} \cdot f_2 (A) .
\]

\( (19) \)

Solving the integral Eq.(19) to obtain the particle number in function of fugacity, we have generalized the result from [2] as[18]:

\[
N \left( \frac{\pi \cdot Y}{\alpha} \right)^{-3/2} = f_2 (A) = A + 2^{-3/2} A^2 + 3^{-3/2} A^3 + 4^{-3/2} A^4 + 5^{-3/2} A^5 + ....
\]

\( (20) \)

One can invert this function in order to obtain the dependences of the fugacity and of the chemical potential on \( N \) and \( \gamma \), which are shown in Fig. 4. However, the present cooling procedure, which is based on evaporation, eliminates progressively the particles with the highest kinetic energy. Consequently, we prefer to consider a variable particle number in the system and to calculate this number in function of a given fugacity and \( \gamma \) (Fig. 5). One can remark that \( N \) increases monotonically with \( A \) and \( \gamma \). The higher the fugacity in the DQB, the stronger the increase of \( N \) with \( \gamma \).
Fig. 4. (a) The 3D plot of fugacity, $A$, in function of the particle numbers in the box, $N$ and $y = A/a L^2 T$ [cm$^2$-K]. (b) The dependence of chemical potential on $y$ [cm$^2$-K], for different fixed values of $N$. 
In DQB, the total energy should be written by summing the state energies up to the highest significant one (characterized by $q_r$):

$$
\frac{E}{kT} = \frac{gL^3(mkT)^{3/2}}{2\pi^2 \hbar^3} \cdot \left(\frac{e_0}{kT}\right)^{3/2} \cdot \sum_{q=1}^{3/2} \frac{q^{3/2}}{A^{-1}} \cdot e^{-q\gamma/kT} \cdot \zeta(q) = 2\pi \frac{\alpha}{\gamma} \sum_{q=1}^{3/2} \frac{q^{3/2}}{A^{-1}} \cdot e^{(\alpha/\gamma)q} - 1 \cdot \zeta(q)
$$

We can calculate the ratio of total energies of the particle gas in DQB and in a conventional (large) container:

$$
F(A, \frac{\alpha}{\gamma}) = \frac{E}{(3/2)NkT[1 - f_1(A)]} = \frac{4\pi}{3N[1 - f_1(A)]} \left(\frac{\alpha}{\gamma}\right)^{3/2} \sum_{q=1}^{3/2} \frac{q^{3/2}}{A^{-1}} \cdot e^{(\alpha/\gamma)q} - 1 \cdot \zeta(q)
$$

In the asymptotic limit, $\zeta(q)$ goes to 1 (by averaging over many and very close modes), $F$ tends to 1, and one arrives to the conventional formalism. The corrective factor is represented in Fig.6, in function of the parameter $\gamma$, for two characteristic values of the fugacity, one close to the maximum admissible value $A = 1$ and the second, close to the classical (Maxwell- Boltzmann) regime.

Calculating the corrective factor $F$ from (22) with the exact degeneracy provided by the Diophantine equation (10) and with the asymptotic degeneracy, $g(q) = 2\pi\sqrt{q}$, we found out maximum differences of the order of $\approx 2 \cdot 10^{-3}$, for $A = 0.2$, which are small differences with respect to those expected in the DQB.

We can put the total energy density law of DQB into a new form:

$$
E = 2\pi \cdot \left(\frac{\alpha}{\gamma}\right) \cdot \sum_{q=1}^{3/2} \frac{q^{3/2}}{A^{-1}} \cdot e^{(\alpha/\gamma)q} - 1 \cdot kT
$$

and observe that the small number of states in the box (up to $q_T$, i.e. small $\gamma = A_{st}L^2T$) plays the key role in the dependency $E(\gamma)$ and not the exact degeneracy.

Thus, with specified atoms and box size, the total energy in DQCB has a stronger dependence on temperature than was predicted by the conventional law. As the box is emptied of states, its total energy is strongly decreasing according a new law derived in Eq.(23).

We have shown that the positions of the energy density peak and of HSL depend on the product $\gamma_q = A_{st}L^2T$ (and in some respect, on $A$). Eq. (22) and Fig. 6 show that the asymptotic limit can be set for $F(\alpha/\gamma) = 1$, at a conventional limit of $\gamma_{q_{max}} \alpha = 8$, which leads to $\gamma_{q_{max}} = 76 \cdot 10^{-14}$ [cm$^2$.K] and to $q_{T_{max}} = 100$.

On the other hand, the lowest box mode (1,1,1) imposes an inferior limit to the level number at: $q_{T_{min}} = 12.5 \cdot (\gamma/\alpha) = 3$ leading to $\gamma_{q_{min}} = 2.28 \cdot 10^{-14}$ [cm$^2$.K]. Thus, we can define the double quantization regime of the cubic box in the range:

$$
3 \leq q \leq 100
$$

$$
2.28 \cdot 10^{-14} \leq \gamma \leq 7.6 \cdot 10^{-13} \text{ [cm}^2\text{.K].}
$$
Fig. 5. The particle number in the DQB in function of a given fugacity, \( A \) (shown in the graph label) and \( \gamma \text{[cm}^2\text{.K]} \).

Fig. 6. The ratio between the total energy of the particles in DQB and the total energy in a conventional container, \( F \), in function of \( \gamma \text{[cm}^2\text{.K]} \) for two values of the fugacity, \( A \), shown in the graph label.

The following **reciprocity rule** holds: for given atoms, the box size and the temperature are reciprocal parameters in the DQB, i.e. the same effects (in the thermodynamics of the boson gas) can be obtained either by varying \( L^2 = V^{2/3} \) or by varying \( T \), if their product remain constant.

We can remark that BEES are produced by a small number of particles. From Eq. (20) and (22), represented in Fig. 5 and 6, respectively, it is possible to calculate the number of particles at \( \gamma = 10^{-13} \text{[cm}^2\text{.K]} \), where the correction factor of the total energy is \( F \approx 0.9 \), for \( A = 0.99 \) and \( F \approx 0.96 \), for \( A = 0.2 \). In the specified quasi-degenerate gas, there are \( N = 9 \) particles and in the quasi-classical gas, \( N = 1 \) particle.
It is clear that the discrete Bose-Einstein effects are stronger for the quasi-degenerate quantum gases.

Previous calculations with photons have shown that the double quantization regime of the spherical box is qualitatively similar to that of the cubic box [16,17]. However, this regime is extended to values of the principal quantum numbers, which are almost ten times higher than those obtained for the cubic box. The calculations for the discrete Bose-Einstein spectra are in progress and we expect more favorable conditions of observation of these effects for bosons in spherical boxes.

4. Conclusions

We have shown that the energy spectrum of a boson gas, which is confined in a rigid cubic box, in the regime of small $\gamma = A_0 T V^{1/3}$, is discrete and depends strongly on the box size and temperature. The complex aspect of the spectrum, is the consequence of the random degeneracy distribution in the cubic box, which introduces an additional energy quantisation controlled by $\gamma$ and by gas fugacity (or alternatively, by the particle number). This quantum system was called by us double quantised box (DQB). The discrete Bose-Einstein spectra in DQB also show forbidden energies.

Furthermore, the total energy, obtained in this case by summing up the exact contributions of the eigenvalues and their weights, for well-defined values of $\gamma$, does not obey the conventional law any longer. We have demonstrated that the new total energy law depends on $\gamma$ and on fugacity and imposes a faster decrease to zero than it is classically expected, for $\gamma \rightarrow 0$.

We have defined DQB by the conditions: $2.28 \times 10^{-14} \leq \gamma \leq 76 \times 10^{-12}$ [cm$^2$-K]. Thus, in this regime, the box size and the temperature are reciprocal parameters in the sense that the same effects (in the boson gas) can be obtained either by varying $L$ or by varying $T$, if their product remain constant. The lighter the gas atoms, the higher the temperatures or the box size, for the same effects in DQB.

The number of particles, which create the discrete behavior of DQB, is small (not exceeding ≈100). The discrete effects in DQB are stronger with respect to the Bose-Einstein continuous distribution for the quasi-degenerate quantum gases, in which the number of particles is higher (at fixed $A$ and $\gamma$).

Acknowledgements. One of the authors (V.I.V.) thanks The Abdus Salam International Centre for Theoretical Physics, Trieste (Italy) for the working stages at the Centre as a Regular Associate Member. Particularly, he wishes to thank Prof. Gallieno Denardo and Prof. Giuseppe Furlan for their support in these visits, which have offered the optimum conditions for thinking and writing this and other papers. He wishes to acknowledge also Prof. Herbert Walther for the useful discussions and for the privilege to be an external collaborator of Max Planck Institut für Quantenoptik.
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Table 1. The weights $g(q)$ in the box-shaped box for state numbers up to 350

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