

Title: New Foundations for Quantum Statistical Mechanics

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Abstract: A new microcanonical equilibrium state is introduced for quantum systems with finite-dimensional state spaces. Equilibrium is characterised by a uniform distribution on a level surface of the expectation value of the Hamiltonian. The distinguishing feature of the proposed equilibrium state is that the corresponding density of states is a continuous function of the energy, and hence thermodynamic functions are well defined for finite quantum systems. The density of states, however, is not in general an analytic function. It is demonstrated that generic quantum systems therefore exhibit second-order phase transitions at finite temperatures. The talk is based on work carried out in collaboration with D.W. Hook and L.P. Hughston.

# Related papers

- Brody, D.C. and Hughston, L.P. (1998) "The quantum canonical ensemble" *Journal of Mathematical Physics* **39**, 6502-6508.
- Brody, D.C. and Hughston, L.P. (1999) "Thermalisation of quantum states" *Journal of Mathematical Physics* **40**, 12-18.
- Brody, D.C. and Hughston, L.P. (1999) "Geometrisation of statistical mechanics" *Proceedings of the Royal Society London A***455**, 1683-1715.
- Brody, D.C. and Hughston, L.P. (2000) "Information content for quantum states" *Journal of Mathematical Physics* **41**, 2586-2592.
- Brody, D.C., Hook, D.W., and Hughston, L.P. (2005) "Microcanonical distributions for quantum systems" [quant-ph/0506163](#).
- Bender, C.M., Brody, D.C. and Hook, D.W. (2005) "Solvable model of quantum microcanonical states" *Journal of Physics A***38** L607-L613.
- Brody, D.C., Hook, D.W., and Hughston, L.P. (2007) "Quantum phase transitions without thermodynamic limits" *Proceedings of the Royal Society London A***463** 2021-2030.
- Brody, D.C., Hook, D.W., and Hughston, L.P. (2007) "On quantum microcanonical equilibrium" *Journal of Physics: Conference Series* **67** 012025-1~6.

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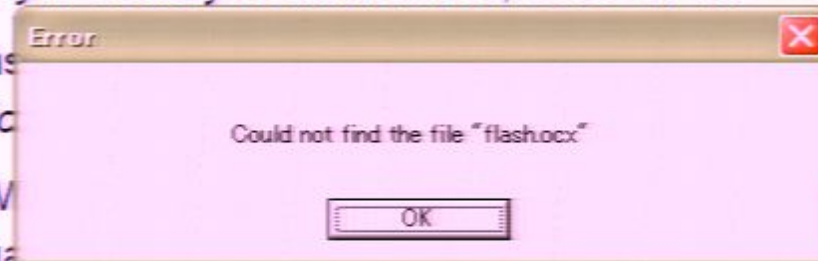


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# QM vs Quantum Stat-Mech

Erwin Schrödinger:

“ . . . this assumption is irreconcilable with the very foundations of quantum mechanics.”

“ . . . to adopt this view is to think along severely ‘classical’ lines.”

*Statistical Thermodynamics* (CUP, 1952)

# Old-fashioned approach (1)

In the usual heuristic approach to quantum statistical mechanics, one tries to develop the idea of a 'microcanonical ensemble' in the following manner:

Number of microstates:

$$n_E = \# \text{ of energy eigenstates } \in [E, E + \Delta E].$$

Entropy:

$$S = k_B \ln n_E.$$

Temperature:

$$dE = TdS.$$



# Old-fashioned approach (2)

Some problems associated with the heuristic approach are:

- Entropy depends on the **arbitrary** energy band  $\Delta E$ .
- Entropy is a **discontinuous** function of  $E$ .
- Hence thermodynamic quantities are **not defined**.

These problems can to some extent be circumvented in thermodynamic limit:  $\text{Volume} \rightarrow \infty$  (Griffiths, 1965).

However, for finite quantum systems, there is no well-defined formulation of microcanonical equilibrium state. But . . .

We introduce a new approach to deal with these issues.

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# Quantum phase space (1)

In 1979 Kibble observed that the Schrödinger evolution on the Hilbert space  $\mathcal{H}^{n+1}$  is equivalent to Hamilton's dynamics on the space of rays ( $|\psi\rangle \sim \lambda|\psi\rangle$ ) through the origin of  $\mathcal{H}^{n+1}$ .

The space of rays is just the complex projective space  $\mathbb{C}\mathbb{P}^n$  endowed with a symplectic structure and a metric.

We parameterise the state space as:

$$|\psi\rangle = \sum_{i=1}^n \sqrt{p_i} e^{-iq_i} |E_i\rangle + (1 - \sum_{i=1}^n p_i)^{\frac{1}{2}} |E_{n+1}\rangle.$$

Then we have

$$H(q, p) = E_n + \sum_{i=1}^n \omega_i p_i.$$



# Quantum phase space (2)

The Schrödinger equations then become

$$\dot{q}_i = \frac{\partial H(q, p)}{\partial p_i} \quad \text{and} \quad \dot{p}_i = -\frac{\partial H(q, p)}{\partial q_i},$$

with solutions  $q_i(t) = q_i(0) + \omega_i t$  and  $p_i(t) = p_i(0)$ .

Thus  $\mathbb{C}\mathbb{P}^n$ , viewed as a real manifold  $\Gamma$ , is the phase space for quantum mechanics.

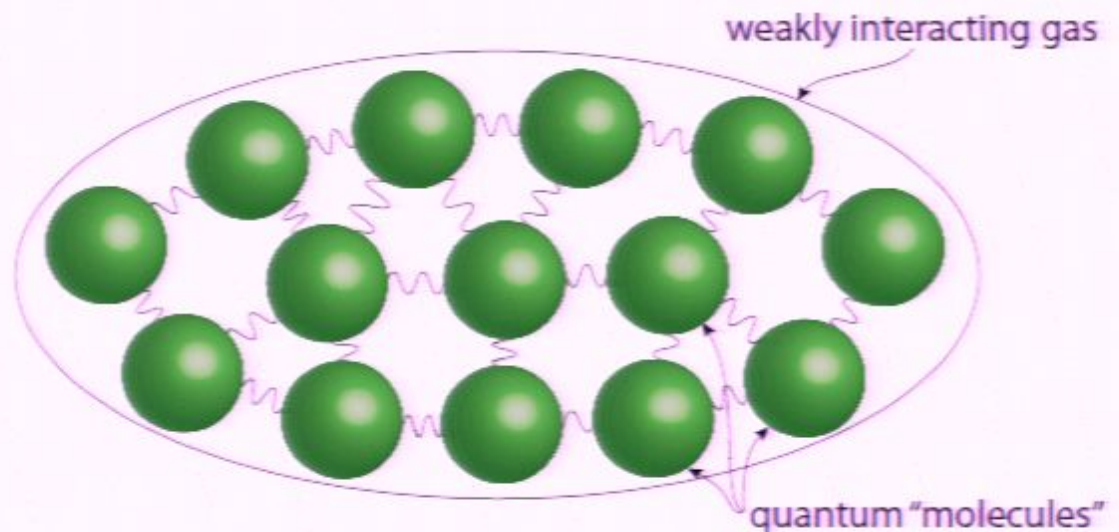
This allows us to examine equilibrium properties of quantum systems from an entirely new perspective.

# Ideal quantum gas (1)

We consider a system of a **large** number ( $N$ ) of identical quantum particles.

We assume that the interactions are very weak so that

$$\hat{H}_{\text{total}} \approx \sum_{i=1}^N \hat{H}_i.$$



(We ignore spin-statistics for simplicity.)



# Ideal quantum gas (2)

We also assume that the particles are approximately disentangled, so that the wave function of the gas is can be approximated by a product state.

For a system in isolation the total energy is fixed:

$$\langle \hat{H}_{\text{total}} \rangle = E_{\text{total}}.$$

We therefore have

$$\sum_{i=1}^N \langle \hat{H}_i \rangle = E_{\text{total}}.$$

# Ideal quantum gas (3)

Writing  $E = N^{-1}E_{\text{total}}$ , we conclude that in equilibrium the gas must have the property that

$$\langle \hat{H}_i \rangle = E.$$

⇒ The state of each constituent must lie on the energy surface  $\mathcal{E}_E$  in the pure state manifold for that particular constituent.

The energy surface  $\mathcal{E}_E$  is given by

$$\mathcal{E}_E = \left\{ |\psi\rangle \mid \langle \psi | \hat{H}_i | \psi \rangle = E \right\}.$$



# Microcanonical equilibrium

For an isolated system in equilibrium, we have a uniform distribution of states over the energy surface. Therefore, we have . . .

Density of states:

$$\Omega(E) = \int_{\Gamma} \delta(H(\psi) - E) dV_{\psi}.$$

⇒ The entropy is  $S(E) = k_B \ln \Omega(E)$ .

Temperature and specific heat are:

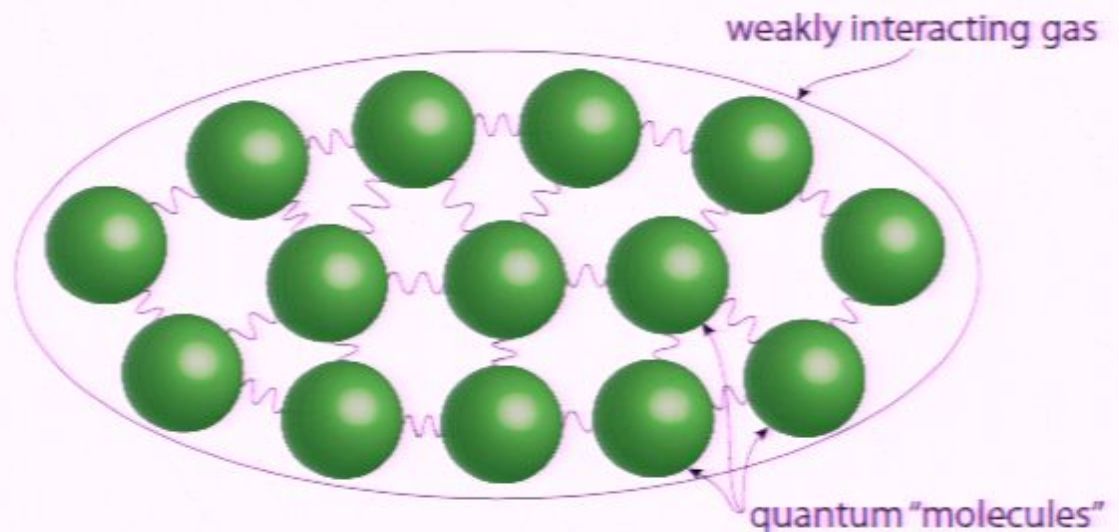
$$k_B T = \frac{\Omega(E)}{\Omega'(E)}, \quad C(T) = \frac{k_B (\Omega')^2}{(\Omega')^2 - \Omega \Omega''}.$$

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# Thermodynamic considerations

Consider two independent systems, each in equilibrium, with state densities  $\Omega_1(E_1)$  and  $\Omega_2(E_2)$ .

We let them interact for a period of time, during which energy is exchanged.

We let them relax to equilibrium and then separate them.

As a consequence of the interaction the state densities of the systems are now  $\Omega_1(E_1 + \epsilon)$  and  $\Omega_2(E_2 - \epsilon)$  for some  $\epsilon$ .

The value of  $\epsilon$  is determined by the requirement that the total entropy  $S(E) = k_B \ln[\Omega_1(E_1 + \epsilon)\Omega_2(E_2 - \epsilon)]$  is maximised.

This condition is satisfied if and only if  $\epsilon$  is such that the temperatures of the two systems are equal.



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# Density of states (1)

After a calculation, we find

$$\begin{aligned}\Omega(E) &= \int_{\Gamma} \delta(H(\psi) - E) dV_{\psi} \\ &= \frac{(-1)^{m-1} \pi^n}{(n-1)!} \prod_{j=1}^m \frac{1}{(\delta_j - 1)!} \left( \frac{d}{dE_j} \right)^{\delta_j - 1} \\ &\quad \times \sum_{k=1}^m \mathbb{1}_{\{E_k \geq E\}} (E_k - E)^{n-1} \prod_{l \neq k} \frac{1}{E_l - E_k},\end{aligned}$$

for the density of states ( $\delta_j$  is the # of degeneracies).

$\Omega(E)$  depends directly on the energy eigenvalue spectrum.



## Density of states (2)

In the case of a nondegenerate spectrum the expression simplifies to:

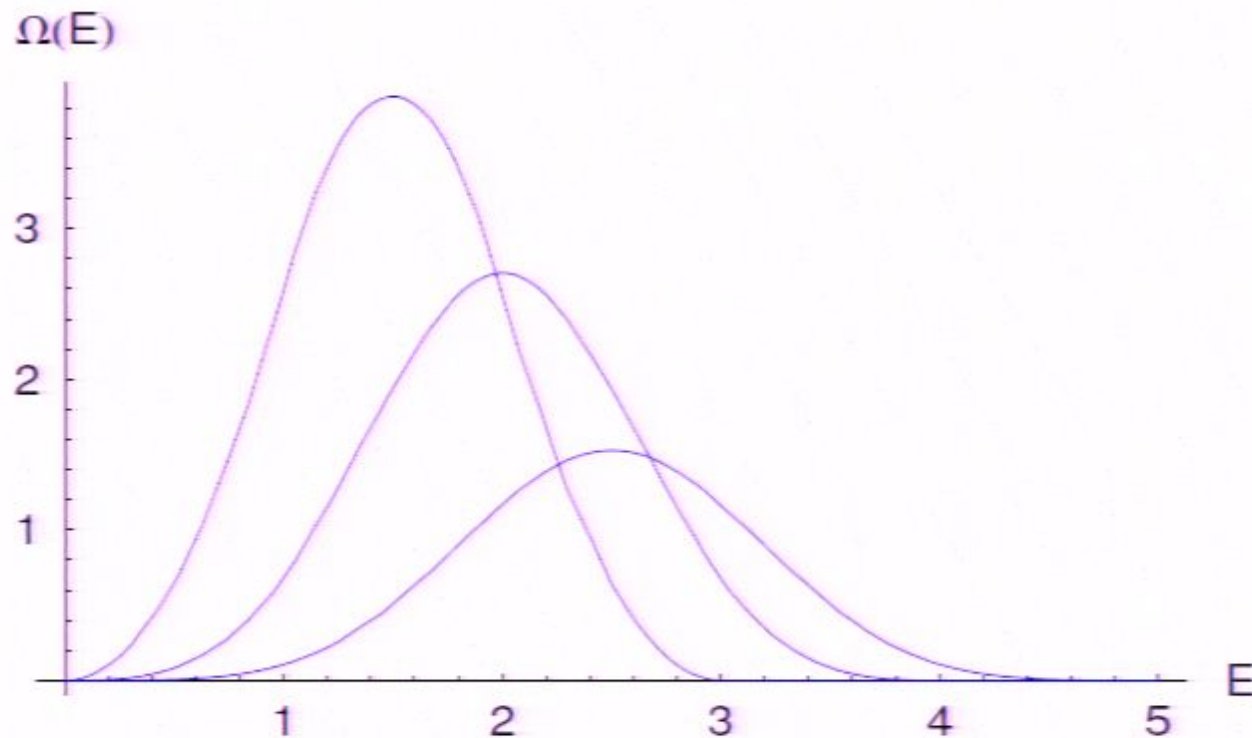
$$\Omega(E) = \frac{(-\pi)^n}{(n-1)!} \sum_{k=1}^{n+1} (E_k - E)^{n-1} \prod_{l \neq k}^{n+1} \frac{\mathbb{1}_{\{E_k > E\}}}{E_l - E_k}.$$

For an equally-spaced spectrum  $E_k = \varepsilon(k-1)$  we have

$$\Omega(E) = \varepsilon^{-1} \frac{(-\pi)^n}{(n-1)!} \sum_{k > E/\varepsilon}^n \frac{(-1)^k (k - E/\varepsilon)^{n-1}}{k!(n-k)!}.$$

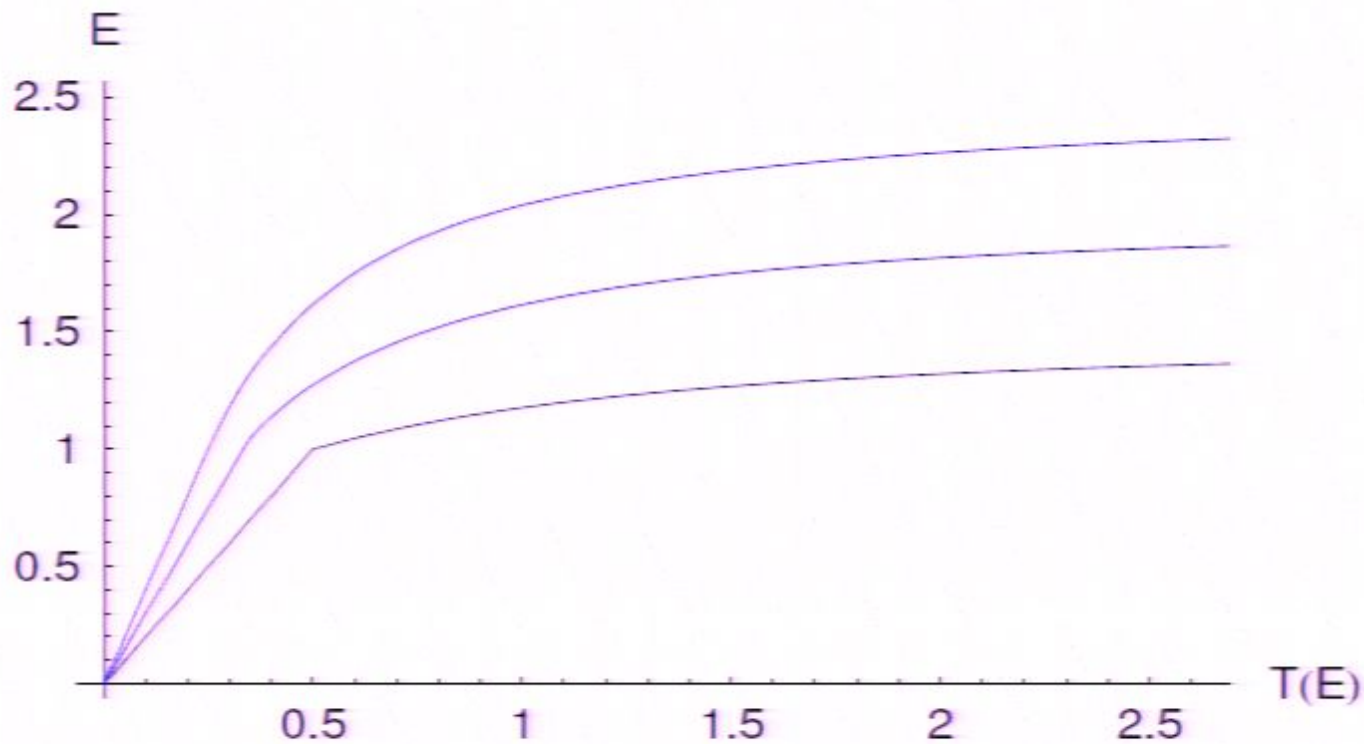
# $\Omega(E)$ for nondegenerate Hamiltonians

In the case of equally-spaced energy spectra we have (4-, 5-, and 6-level systems):



# Energy vs temperature

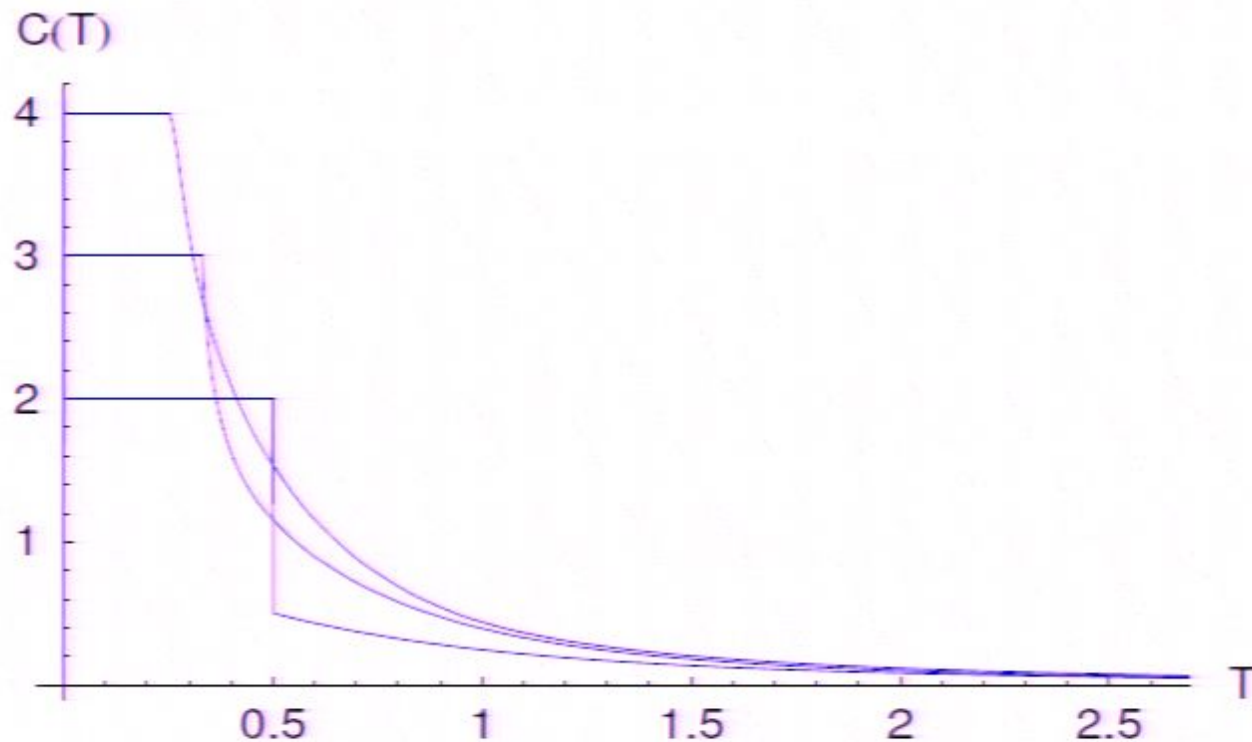
For the energy  $E(T)$  as a function of temperature we have (4-, 5-, and 6-level systems):





# Specific heat

In the case of equally-spaced energy spectra we have (4-, 5-, and 6-level systems):



# Quantum phase transitions

We observe that these systems exhibit second-order phase transitions.

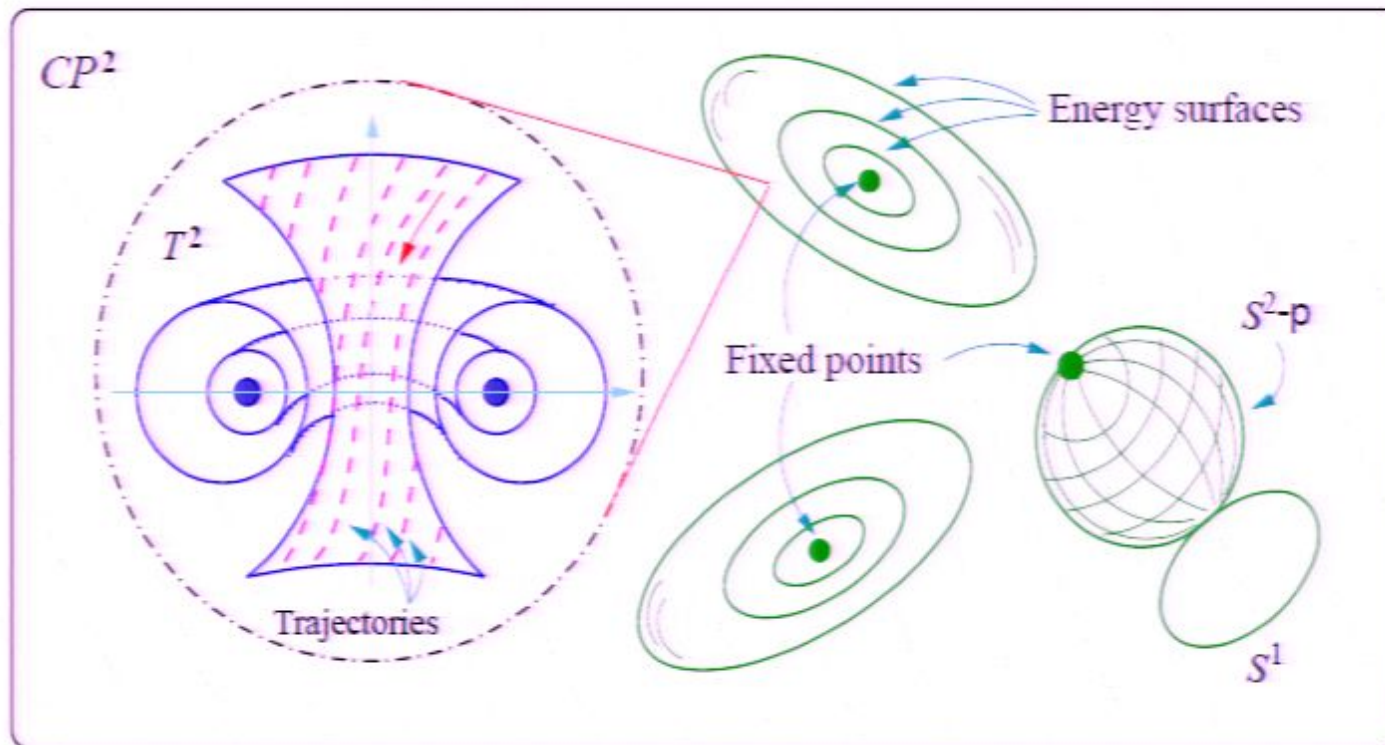
For example, in the case of a 4-level system the transition occurs at the following critical temperature and energy

$$k_B T_c = \frac{1}{2}\varepsilon, \quad E_c = \varepsilon.$$

This phenomenon is intimately related to the **topological structure** of the energy surface in the quantum state space.

# Structure of quantum state space

The quantum energy surfaces exhibit topological transitions. For example, for a 3-level (spin-1) system we have:



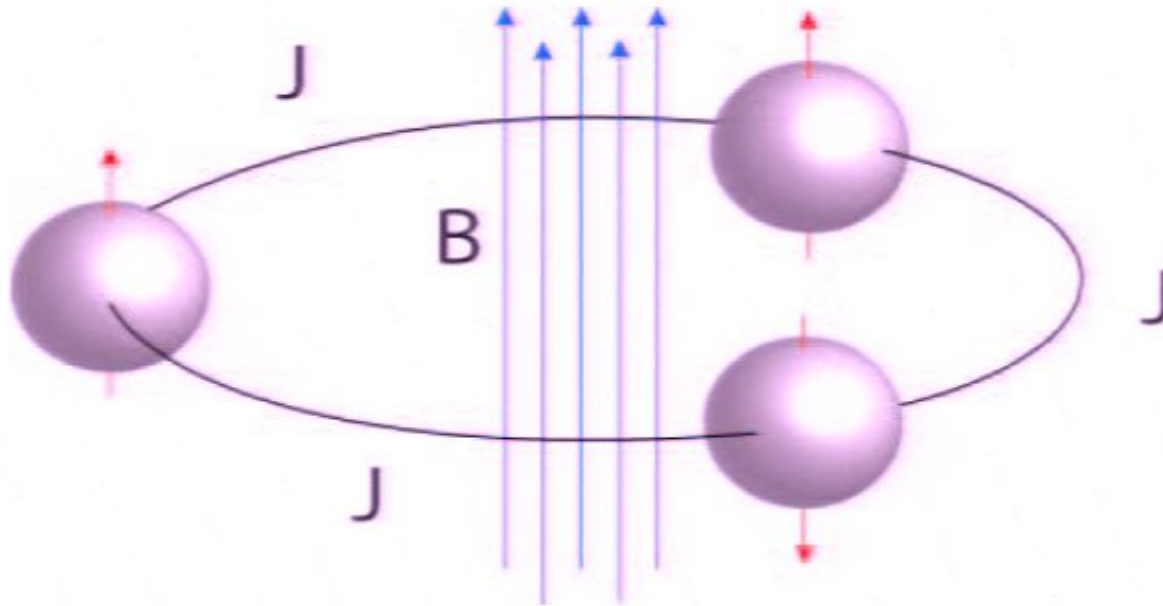
$$\text{Point} \rightarrow S^3 \rightarrow S^1 \times \mathbb{R}_{\#}^2 \rightarrow S^3 \rightarrow \text{Point}$$



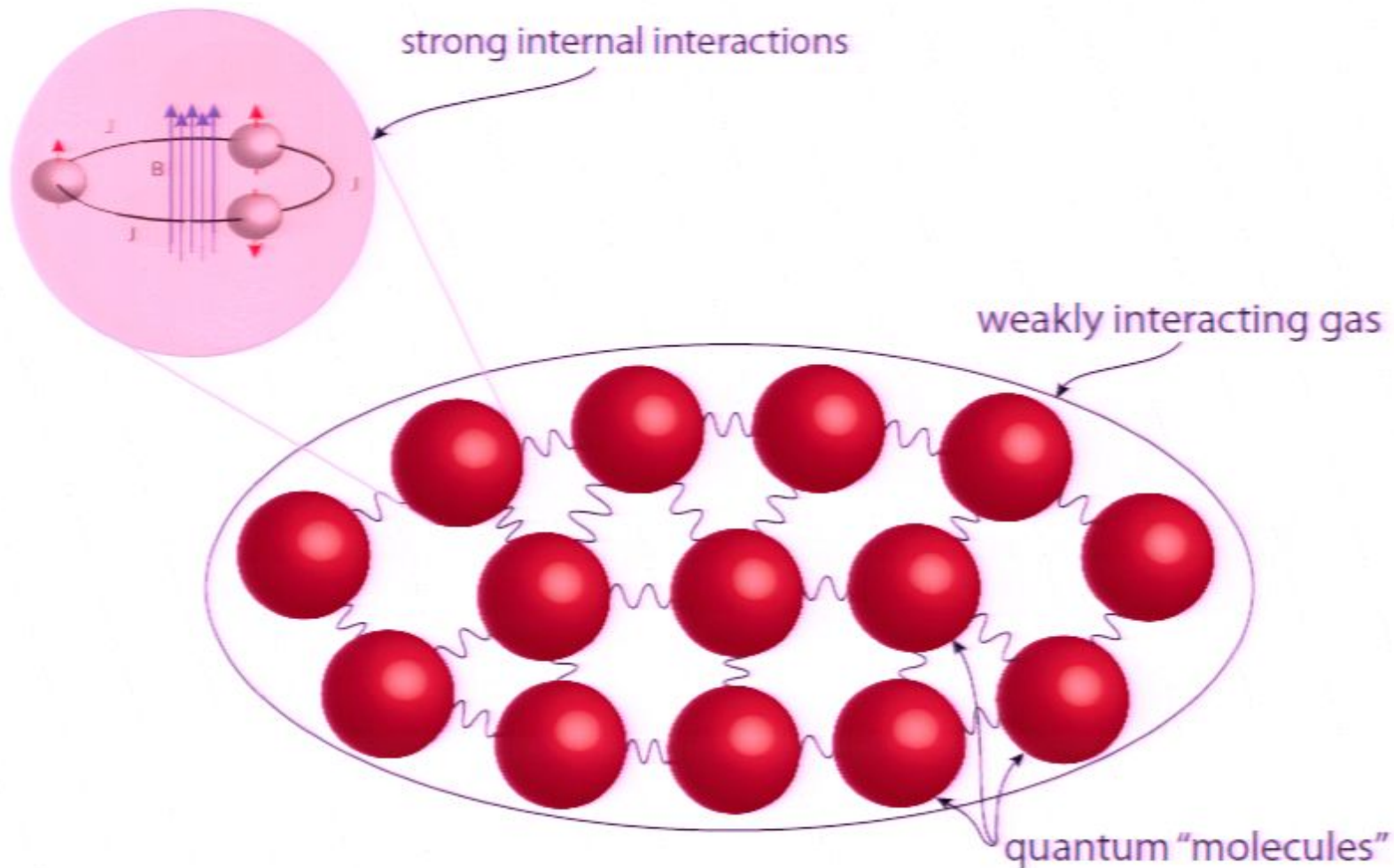
# Quantum Ising chain (1)

As a degenerate system, consider the Hamiltonian:

$$\hat{H} = -J \sum_{k=1}^3 \sigma_z^k \sigma_z^{k+1} - B \sum_{k=1}^3 \sigma_z^k,$$



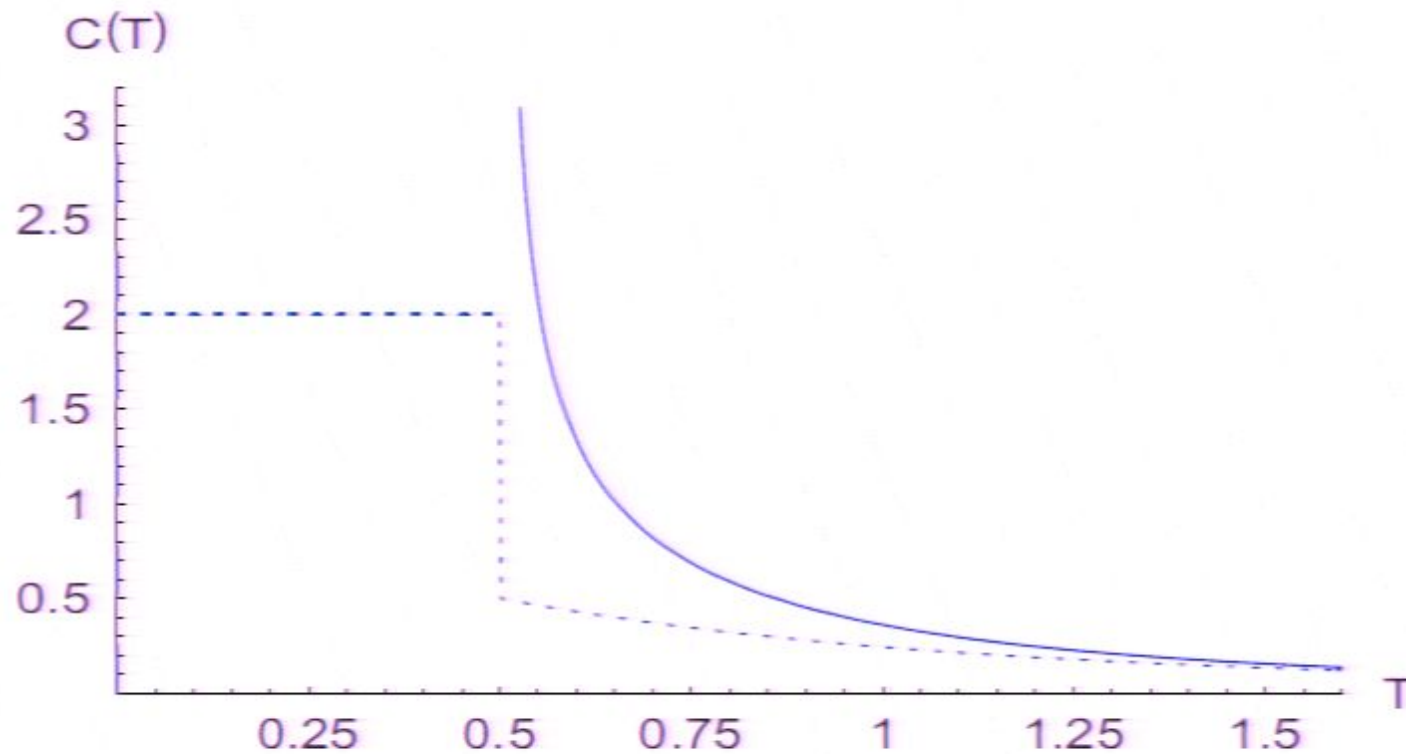
# Quantum Ising chain (2)



# Quantum Ising chain (3)

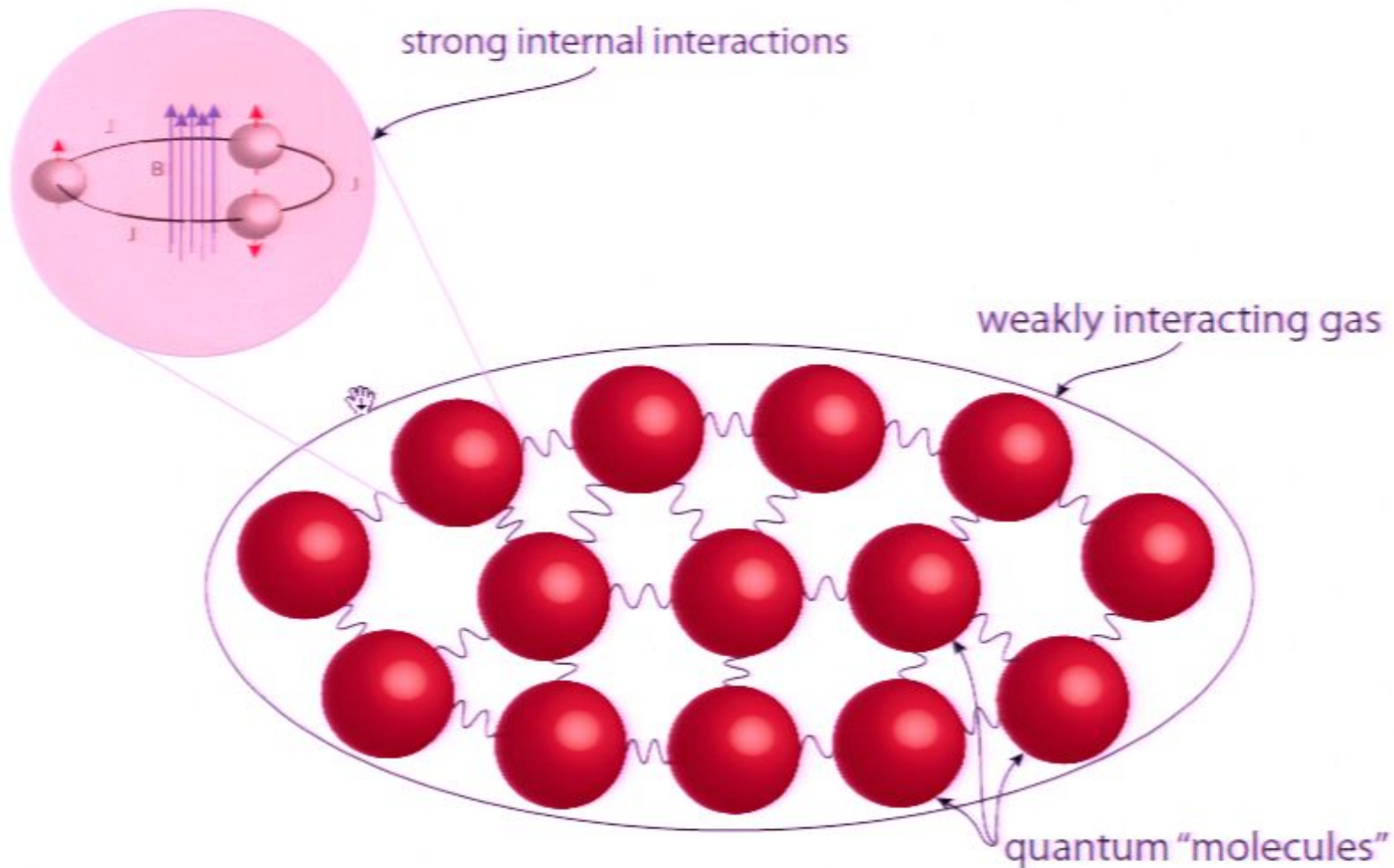
Specific heat for 4-level systems:

- dotted line: 4-level non-degenerate system;
- solid line: Ising model ( $T_c = (2J + B)/3k_B$ )





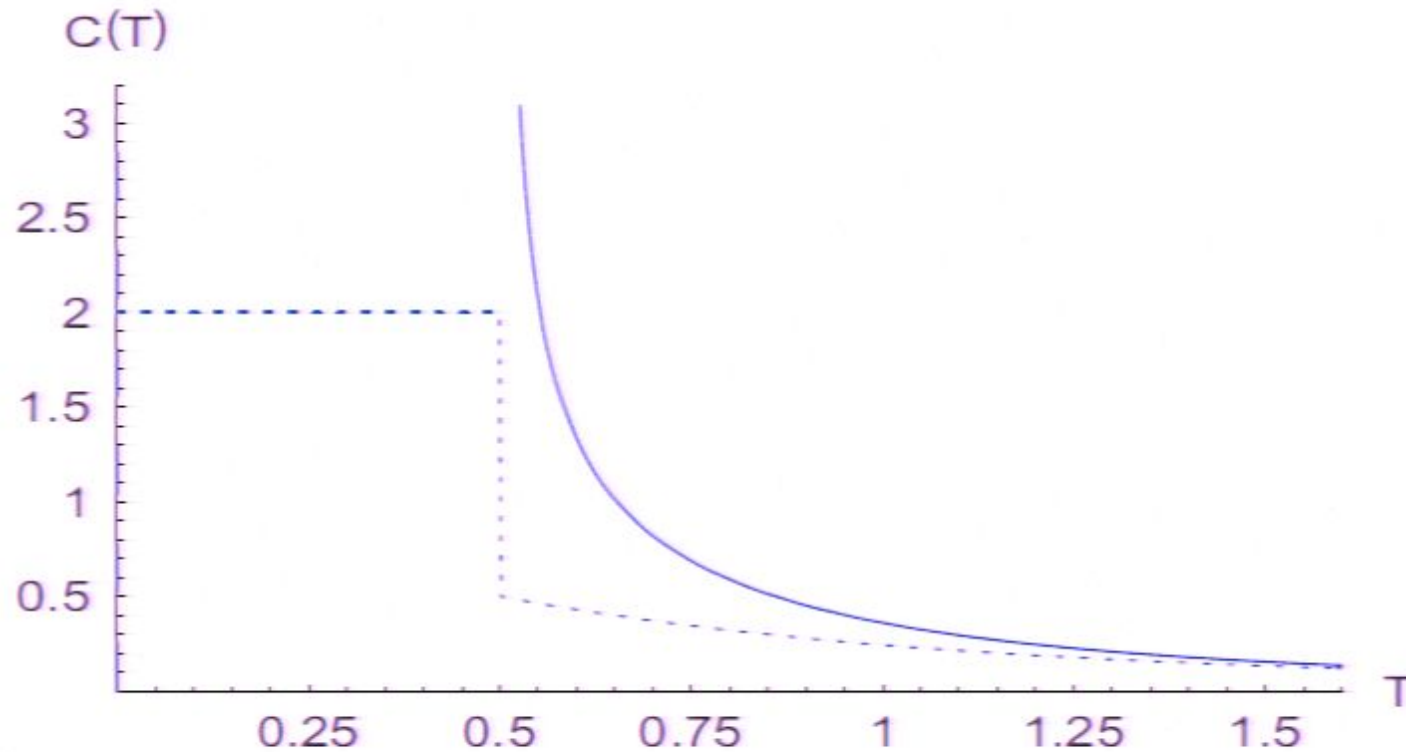
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# Density matrix & energy uncertainty

The density matrix of the microcanonical equilibrium is

$$\hat{\rho}_E = \frac{1}{\Omega(E)} \int_{\Gamma} \delta(H(\psi) - E) \hat{\Pi}(\psi) dV_{\Gamma}.$$

Here  $\hat{\Pi}(\psi) = |\psi\rangle\langle\psi|/\langle\psi|\psi\rangle$  denotes the projection operator.

The squared energy uncertainty is

$$(\Delta H)^2 = \frac{n+1}{\Omega(E)} \int_{E_{\min}}^E (\bar{H} - u) \Omega(u) du,$$

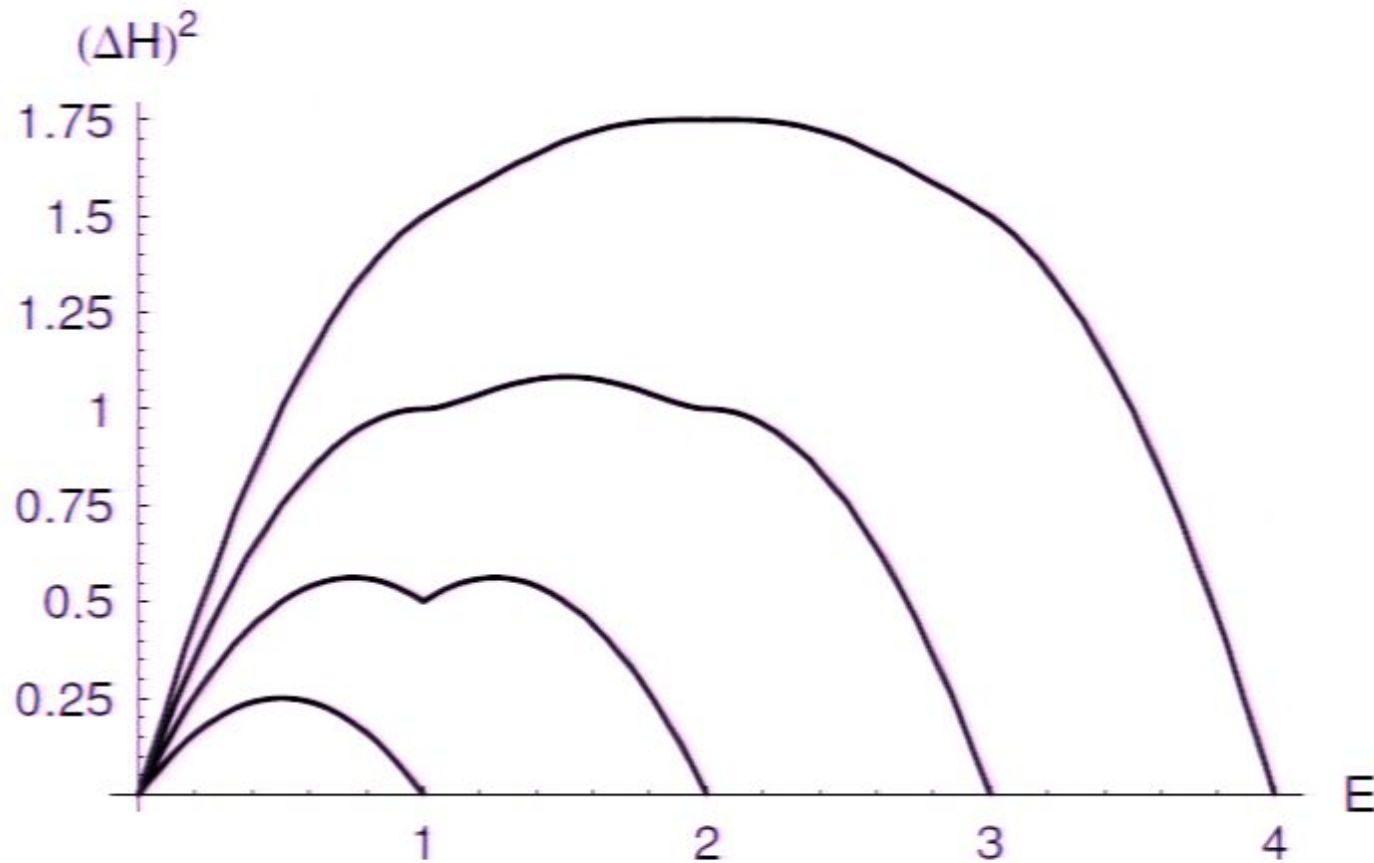
where  $\bar{H} = \text{tr}(\hat{H})/(n+1)$ .

There is a natural 'energy band'  $\Delta H$  associated with the microcanonical equilibrium.



# Microcanonical energy band $\Delta H$

The energy dispersion  $(\Delta H)^2$  in the microcanonical equilibrium for 2, 3, 4, and 5-level systems:



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The density matrix of the microcanonical equilibrium is

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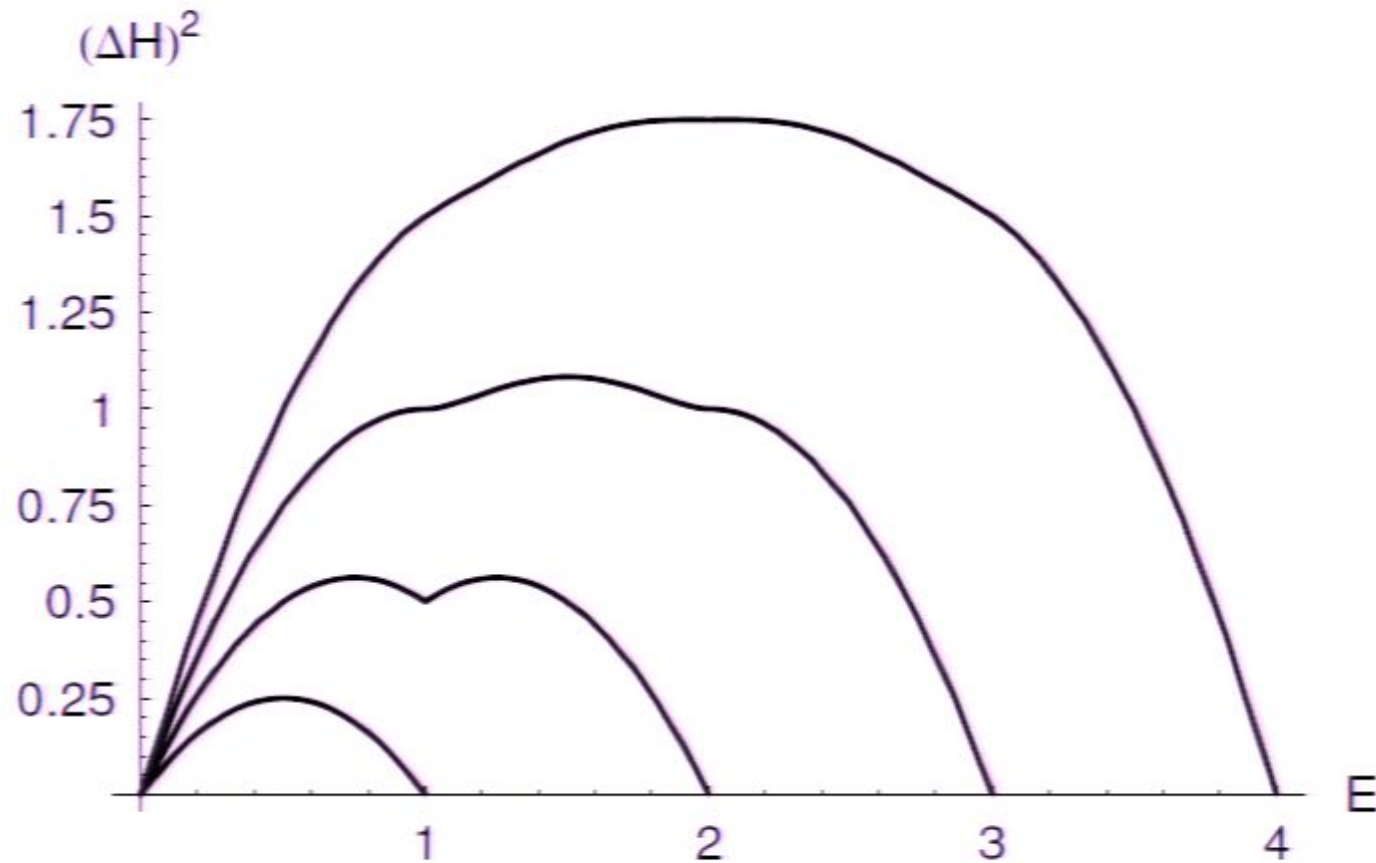
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# Density matrix & energy uncertainty

The density matrix of the microcanonical equilibrium is

$$\hat{\mu}_E = \frac{1}{\Omega(E)} \int_{\Gamma} \delta(H(\psi) - E) \hat{\Pi}(\psi) dV_{\Gamma}.$$

Here  $\hat{\Pi}(\psi) = |\psi\rangle\langle\psi|/\langle\psi|\psi\rangle$  denotes the projection operator.

The squared energy uncertainty is

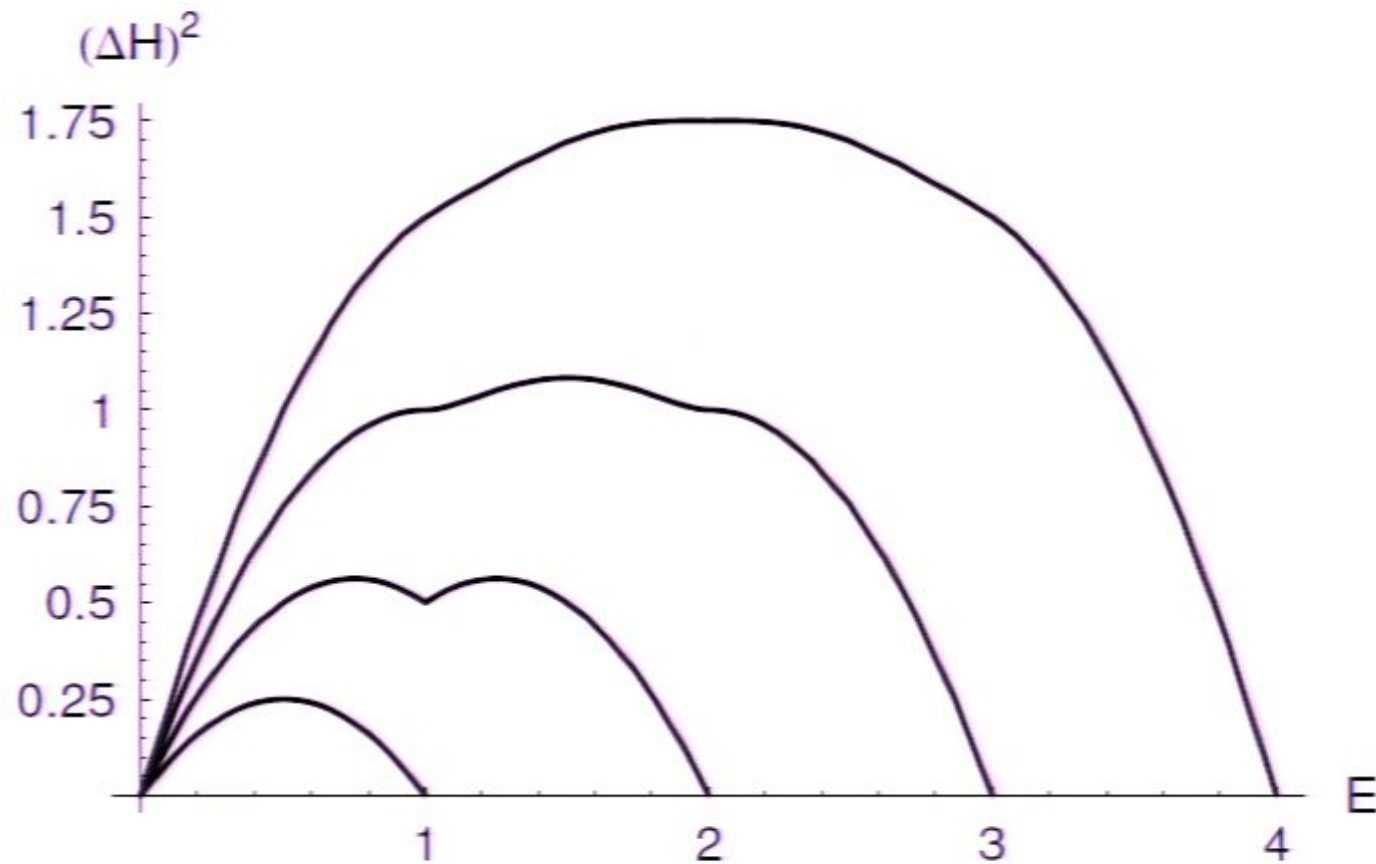
$$(\Delta H)^2 = \frac{n+1}{\Omega(E)} \int_{E_{\min}}^E (\bar{H} - u) \Omega(u) du,$$

where  $\bar{H} = \text{tr}(\hat{H})/(n+1)$ .

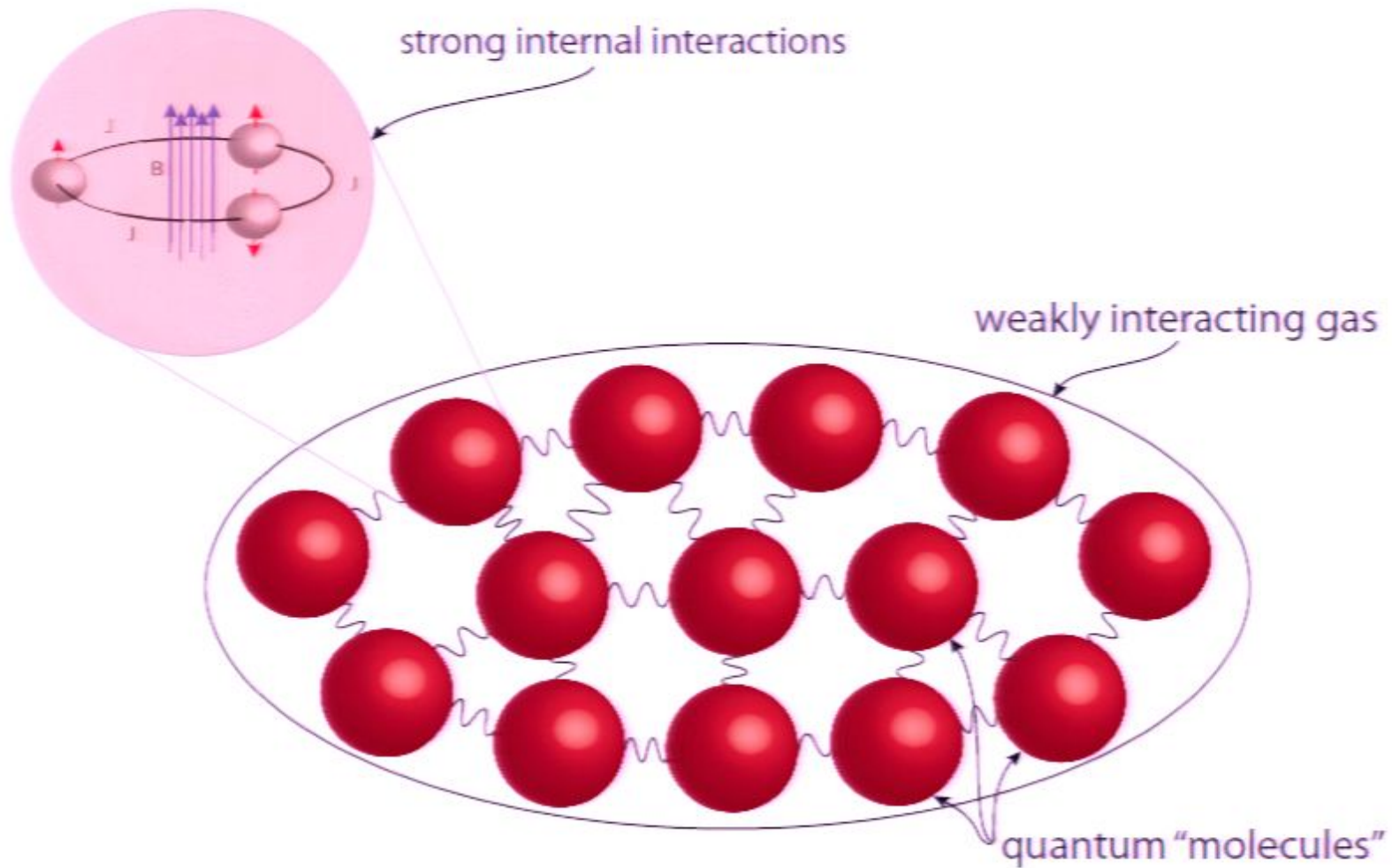
There is a natural 'energy band'  $\Delta H$  associated with the microcanonical equilibrium.

# Microcanonical energy band $\Delta H$

The energy dispersion  $(\Delta H)^2$  in the microcanonical equilibrium for 2, 3, 4, and 5-level systems:



# Quantum Ising chain (2)





# Density of states (1)

After a calculation, we find

$$\begin{aligned}\Omega(E) &= \int_{\Gamma} \delta(H(\psi) - E) dV_{\psi} \\ &= \frac{(-1)^{m-1} \pi^n}{(n-1)!} \prod_{j=1}^m \frac{1}{(\delta_j - 1)!} \left( \frac{d}{dE_j} \right)^{\delta_j - 1} \\ &\quad \times \sum_{k=1}^m \mathbb{1}_{\{E_k \geq E\}} (E_k - E)^{n-1} \prod_{l \neq k} \frac{1}{E_l - E_k},\end{aligned}$$

for the density of states ( $\delta_j$  is the # of degeneracies).

$\Omega(E)$  depends directly on the energy eigenvalue spectrum.

# Microcanonical equilibrium

For an isolated system in equilibrium, we have a uniform distribution of states over the energy surface. Therefore, we have . . .

Density of states:

$$\Omega(E) = \int_{\Gamma} \delta(H(\psi) - E) dV_{\psi}.$$

⇒ The entropy is  $S(E) = k_B \ln \Omega(E)$ .

Temperature and specific heat are:

$$k_B T = \frac{\Omega(E)}{\Omega'(E)}, \quad C(T) = \frac{k_B (\Omega')^2}{(\Omega')^2 - \Omega \Omega''}.$$

# Quantum phase space (1)

In 1979 Kibble observed that the Schrödinger evolution on the Hilbert space  $\mathcal{H}^{n+1}$  is equivalent to Hamilton's dynamics on the space of rays ( $|\psi\rangle \sim \lambda|\psi\rangle$ ) through the origin of  $\mathcal{H}^{n+1}$ .

The space of rays is just the complex projective space  $\mathbb{C}\mathbb{P}^n$  endowed with a symplectic structure and a metric.

We parameterise the state space as:

$$|\psi\rangle = \sum_{i=1}^n \sqrt{p_i} e^{-iq_i} |E_i\rangle + (1 - \sum_{i=1}^n p_i)^{\frac{1}{2}} |E_{n+1}\rangle.$$

Then we have

$$H(q, p) = E_n + \sum_{i=1}^n \omega_i p_i.$$



# Old-fashioned approach (2)

Some problems associated with the heuristic approach are:

- Entropy depends on the **arbitrary** energy band  $\Delta E$ .
- Entropy is a **discontinuous** function of  $E$ .
- Hence thermodynamic quantities are **not defined**.

These problems can to some extent be circumvented in thermodynamic limit:  $\text{Volume} \rightarrow \infty$  (Griffiths, 1965).

However, for finite quantum systems, there is no well-defined formulation of microcanonical equilibrium state. But . . .

We introduce a new approach to deal with these issues.

# Old-fashioned approach (1)

In the usual heuristic approach to quantum statistical mechanics, one tries to develop the idea of a 'microcanonical ensemble' in the following manner:

Number of microstates:

$$n_E = \# \text{ of energy eigenstates } \in [E, E + \Delta E].$$

Entropy:

$$S = k_B \ln n_E.$$

Temperature:

$$dE = TdS.$$

# Ideal quantum gas (3)

Writing  $E = N^{-1}E_{\text{total}}$ , we conclude that in equilibrium the gas must have the property that

$$\langle \hat{H}_i \rangle = E.$$

⇒ The state of each constituent must lie on the energy surface  $\mathcal{E}_E$  in the pure state manifold for that particular constituent.

The energy surface  $\mathcal{E}_E$  is given by

$$\mathcal{E}_E = \left\{ |\psi\rangle \mid \langle \psi | \hat{H}_i | \psi \rangle = E \right\}.$$



# Thermodynamic considerations

Consider two independent systems, each in equilibrium, with state densities  $\Omega_1(E_1)$  and  $\Omega_2(E_2)$ .

We let them interact for a period of time, during which energy is exchanged.

We let them relax to equilibrium and then separate them.

As a consequence of the interaction the state densities of the systems are now  $\Omega_1(E_1 + \epsilon)$  and  $\Omega_2(E_2 - \epsilon)$  for some  $\epsilon$ .

The value of  $\epsilon$  is determined by the requirement that the total entropy  $S(E) = k_B \ln[\Omega_1(E_1 + \epsilon)\Omega_2(E_2 - \epsilon)]$  is maximised.

This condition is satisfied if and only if  $\epsilon$  is such that the temperatures of the two systems are equal.

# Microcanonical equilibrium

For an isolated system in equilibrium, we have a uniform distribution of states over the energy surface. Therefore, we have . . .

Density of states:

$$\Omega(E) = \int_{\Gamma} \delta(H(\psi) - E) dV_{\psi}.$$

⇒ The entropy is  $S(E) = k_B \ln \Omega(E)$ .

Temperature and specific heat are:

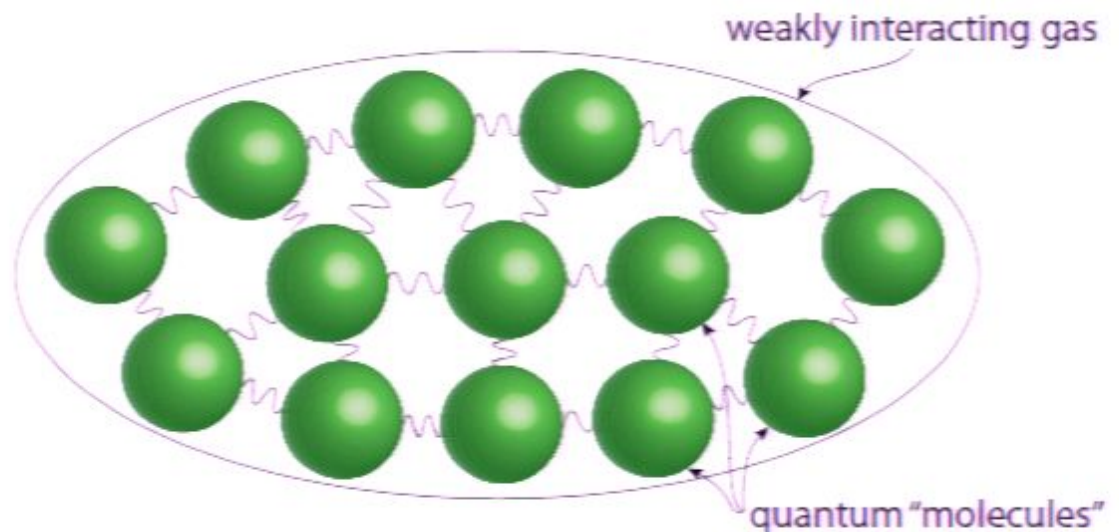
$$k_B T = \frac{\Omega(E)}{\Omega'(E)}, \quad C(T) = \frac{k_B (\Omega')^2}{(\Omega')^2 - \Omega \Omega''}.$$

# Ideal quantum gas (1)

We consider a system of a **large** number ( $N$ ) of identical quantum particles.

We assume that the interactions are very weak so that

$$\hat{H}_{\text{total}} \approx \sum_{i=1}^N \hat{H}_i.$$



(We ignore spin-statistics for simplicity.)



