

Quantum Statistics - Algebraic and Combinatorial Aspects

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Introduction

In their first statistical Mechanics course, students learn that for a system of N identical non-interacting fermions, the number of microstates with energy E subject to $\sum_{i=1}^N n_i = N$ is given by the Fermi-Dirac distribution,

$$\Omega^{\text{FD}} = \prod_i \binom{g_i}{n_i}. \quad (1)$$

where n_i is the number of particles with energy ε_i and g_i is the degeneracy of level i and the product is taken over all energy levels (i). The corresponding formula for a system of bosons is the Bose-Einstein formula:

$$\Omega^{\text{BE}} = \prod_i \binom{g_i + n_i - 1}{n_i}. \quad (2)$$

Typical derivations of (1) and (2) utilize models involving arrangements of indistinguishable balls in boxes [5]. The number of configurations (subject to the constraint of one particle per box for fermions) is then calculated to give the number of microstates. [6],[3]. A disadvantage of this approach is that students may be puzzled by the concept of indistinguishable particles since the macroscopic objects with which they are familiar can always be distinguished or labelled in some way. Indistinguishable objects appear to exist solely in the quantum realm. Moreover, in the case of fermions, the origin of the constraint of one particle per level does not arise naturally from the elementary combinatorial proof. There are already many good demonstrations of (1) and (2) at varying levels of sophistication, which overcome these difficulties by counting wave functions directly. [1] In what follows, standard theorems of linear algebra are used to highlight the algebraic nature of the problem and to give an intermediate route between pure combinatorics and a full treatment in the language of exterior/symmetric algebras [2], and which is accessible to the student with a basic knowledge of Quantum Mechanics who has completed a linear algebra course.

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Review of Quantum Mechanics

We start by reviewing some basic facts from elementary Quantum Mechanics. It is assumed that the state of a quantum system is described by a wave function. Indistinguishability of particles arises from the fact that the state of such a system is invariant, up to a sign change, under transpositions (and hence permutations²) of the coordinates of two particles. Under such a transposition the state of the system remains unchanged. Particles with wave functions symmetric under particle interchange are called bosons. Particles with wave functions antisymmetric under exchange are called fermions.

For a system of N particles, with the i -th particle having space and spin coordinates $i = (r_i, \sigma_i)$, $r_i \in \mathbb{R}^3$, the wave function $\psi(1, 2, \dots, N)$ is determined by solving the time independent Schrödinger equation,

$$H\psi = E\psi. \quad (3)$$

The eigenvalues of H correspond to the possible values of the energy.

Since H is linear, the set of solutions is a vector space. A consequence is that that Ω^{BE} and Ω^{FD} can be viewed, respectively, as the dimensions of antisymmetric and symmetric subspaces. If the particles are non interacting, the Hamiltonian splits,

$$H = \sum_{i=1}^N h_i$$

where h_i is the Hamiltonian for the i 'th particle. Since H is linear, an eigenfunction of the Schrödinger equation corresponding to an energy eigenvalue E , is a product:

$$\psi(1, 2, \dots, N) = \phi_{j_1}(1) \cdots \phi_{j_N}(N)$$

where the ϕ_{j_i} , are the single particle wave functions. If ϵ_{j_i} is the energy eigenvalue corresponding to ϕ_{j_i} then $h\phi_{j_i} = \epsilon_{j_i}\phi_{j_i}$ and it follows that

$$E = \epsilon_{j_1} + \epsilon_{j_2} + \dots + \epsilon_{j_N}$$

To take degeneracy into account, one particle quantum states and energies can be relabeled

$$v^1, v^2, \dots, v^{g_1}, w^1, w^2, \dots, w^{g_2}, \dots$$

where $v^1, v^2, \dots, v^{g_1}$ have energy ϵ_1 , $w^1, w^2, \dots, w^{g_2}$ have energy ϵ_2 , etc., and $\epsilon_i < \epsilon_j$ for $i < j$. It is assumed that these states are linearly independent and normalized.

²Recall that every permutation can be realized as a product of transpositions

Let n_i be the number of particles with energy ϵ_i so that

$$\sum_{i=1}^n n_i = N \quad \text{and} \quad \sum_{i=1}^n n_i \epsilon_i = E. \quad (4)$$

Let W be the vector space of solutions of (3) and W_E the subspace of the N -fold tensor product spanned by all products of single particle states that realise the given occupation numbers n_i so that the constraints (4) be satisfied. In particular, each product must have n_1 terms taken from $v^1, v^2 \dots v^{g_1}$, n_2 taken from $w^1, w^2 \dots w^{g_2}$, etc.

1. Fermi-Dirac Case

If the particles are fermions, the requirement that the wave function be antisymmetric with respect to particle interchange means that physically acceptable solutions of (3) must also lie in the vector subspace W_E^{FD} of W_E consisting of antisymmetric functions. The number of microstates Ω^{FD} is precisely the dimension of W_E^{FD} . By analogy with the definition of the determinant (which is easily shown to have the required antisymmetry) define $\mathcal{A} : W_E \rightarrow W_E^{FD}$ by

$$\mathcal{A}\psi = \frac{1}{N!} \sum_{\sigma \in S_N} \epsilon(\sigma) \hat{\sigma} \circ \psi$$

where S_N is the set of permutations of $\{1, 2, \dots, N\}$, and $\epsilon(\sigma)$ is the sign of permutation σ and

$$\hat{\sigma} \circ \psi(x_1, x_2, \dots, x_N) = \psi(x_{\sigma(1)}, x_{\sigma(2)}, \dots, x_{\sigma(N)}).$$

The map $\mathcal{A}$, called the *antisymmetrizer*, is a surjective linear map onto the subspace of antisymmetric wave functions. In the case under discussion where the quantum state is a product of single particle states, the antisymmetrizer is actually a determinant, in fact a multiple of the well known Slater determinant.

$$\mathcal{A}\phi_{j_1}(1) \cdots \phi_{j_N}(N) = \frac{1}{N!} \begin{vmatrix} \phi_{j_1}(1) & \phi_{j_1}(2) & \cdots & \phi_{j_1}(N) \\ \phi_{j_2}(1) & \phi_{j_2}(2) & \cdots & \phi_{j_2}(N) \\ \vdots & \vdots & \cdots & \vdots \\ \phi_{j_N}(1) & \phi_{j_N}(2) & \cdots & \phi_{j_N}(N) \end{vmatrix}.$$

It follows that $\Omega^{FD} = \dim(\text{Im } \mathcal{A})$, the dimension of the image of W_E under $\mathcal{A}$. The combinatorial problem of counting microstates is thus reduced to the algebraic one of finding the rank of a linear map. In the special case of two fermions each

admitting two degenerate eigenstates v^1 and v^2 (cf. spins), W_E is spanned by the set of products $v^1v^1, v^1v^2, v^2v^1, v^2v^2$.

Since $A\psi(1, 2) = 0 \iff \psi(1, 2) - \psi(2, 1) = 0$, the kernel of $\mathcal{A}$ is the set

$$K = \{\alpha v^1v^1 + \beta(v^1v^2 + v^2v^1) + \gamma v^2v^2 : \alpha, \beta, \gamma \in \mathbb{R}\},$$

a three dimensional subspace of W_E . Since $\mathcal{A} : W_E \rightarrow W_E^{\text{FD}}$ is a linear map, the rank-nullity theorem gives

$$\dim(W_E) = \dim \ker(\mathcal{A}) + \dim(\text{Im } \mathcal{A}).$$

It follows that $\text{Im}(\mathcal{A})$ is a one dimension subspace and that any vector not in K will constitute a basis for W_E^{FD} . Hence, the mixed state $v^1v^2 - v^2v^1$ is a basis for $\text{Im } \mathcal{A}$. In order to obtain a formula for $\dim(\text{Im } \mathcal{A})$ in the case of N particles, recall, by the first isomorphism theorem that the quotient space $W_E / \ker \mathcal{A}$ is isomorphic to $\text{Im } \mathcal{A}$. Let $K = \ker \mathcal{A}$. By definition W_E / K consists of the equivalence classes of the relation on W_E given by

$$\phi \sim \psi \iff \psi - \phi \in K \iff \mathcal{A}(\psi - \phi) = 0).$$

By definition, the equivalence class of $\phi \in W_E$, denoted $[\phi]$ is the set

$$[\phi] = \{\psi : \phi \sim \psi\} = \phi + K.$$

A student of Linear Algebra should recognize this as a coset of the kernel and recall that two equivalence classes $[a], [b]$ are equal if and only if $a \in [b]$.

The vector space structure of W_E / K is induced by the one W_E by defining

$$(a + K) + (b + K) = (a + b) + K.$$

The zero of this space is the kernel K . Since a surjective linear map a basis onto a spanning set, to construct a basis for W_E / K it suffices to list all non zero equivalence classes of members of our basis for W_E eliminating those which fall within the span the remaining vectors.

For example in the case of the two fermions discussed previously, under the assumption that the pure states $v^1v^1, v^1v^2, v^2v^1, v^2v^2$ comprise a basis for W_E then the set of equivalence classes

$$\{[v^1v^1], [v^1v^2], [v^2v^1], [v^2v^2]\}$$

will span W_E / K and hence contain a basis. The dimension of this basis will yield the number of microstates Ω^{FD} . Since a basis is a minimal spanning set, a basis can be obtained in the usual manner by eliminating classes (vectors) which are contained in

the span of the remaining classes. In particular, the zero class K must be eliminated. In the simple case under consideration,

$$[v^1 v^1] = [v^2 v^2] = K = 0$$

and so we eliminate these classes. Moreover,

$$\begin{aligned} v^1 v^2 + v^2 v^1 \in K &\implies v^1 v^2 \in -v^2 v^1 + K \\ &\implies [v^1 v^2] = [-v^2 v^1] \\ &\implies [v^1 v^2] = -[v^2 v^1]. \end{aligned}$$

Since $[v^2 v^1]$ lies in the span of $[v^1 v^2]$ it may also be eliminated. Hence, as already mentioned, the singleton $\{[v^1 v^2]\}$ is a basis for the one dimensional space W_E/K . again confirming that $\Omega^{FD} = 1$.

The general case is handled in a similar manner. Notice that the set of all classes of the form

$$[v^{a_1} v^{a_2} \dots v^{a_{n_1}} w^{b_1} w^{b_2} \dots w^{b_{n_2}} \dots] \quad (5)$$

where $a_1, a_2, \dots, a_{n_1}$ are n_1 integers chosen from $\{1, 2, \dots, g_1\}$, $b_1, b_2, \dots, b_{n_2}$ are n_2 integers chosen from $\{1, 2, \dots, g_2\}$, etc., is a spanning set for $W_E/\ker \mathcal{A}$. Since a determinant with two equal columns is zero, all classes with a repetition, say $[\dots v^i \dots v^i \dots]$, are equal to the zero class and must be deleted.

Next, suppose that $[\psi]$ is a class of the form (5) and τ a transposition. Then

$$\begin{aligned} \mathcal{A}(\hat{\tau} \circ \psi) &= \frac{1}{N!} \sum_{\sigma \in S_N} \text{sgn}(\sigma) \hat{\sigma} \circ \hat{\tau} \circ \psi \\ &= -\frac{1}{N!} \sum_{\sigma \in S_N} \text{sgn}(\sigma \circ \tau) \hat{\sigma} \circ \hat{\tau} \circ \psi. \end{aligned}$$

As σ runs through S_N so does $\sigma \circ \tau$, and therefore

$$\mathcal{A}(\hat{\tau} \circ \psi) = -\mathcal{A}(\psi).$$

Hence

$$\hat{\tau} \circ \psi + \psi \in \ker \mathcal{A} \implies [\hat{\tau} \circ \psi] = -[\psi].$$

Since every permutation $\sigma \in S_N$ is a product of transpositions, iteration yields

$$[\hat{\sigma} \circ \psi] = \text{sgn}(\sigma) [\psi].$$

In particular, the two cosets differ at most by the non-zero scalar ± 1 and therefore span the same one-dimensional subspace of the quotient. Consequently it is enough to retain a single representative from each orbit under the action of S_N . We may

therefore impose the strict orderings

$$[v^{a_1} v^{a_2} \dots v^{a_{n_1}} w^{b_1} w^{b_2} \dots w^{b_{n_2}} \dots] \quad (6)$$

where

$$1 \leq a_1 < a_2 < \dots < a_{n_1} \leq g_1,$$

$$1 \leq b_1 < b_2 < \dots < b_{n_2} \leq g_2,$$

and likewise for every subsequent energy level.

It remains only to count the admissible sequences for a single energy level, say the v -level. Since, the number of strictly increasing sequences of length n_1 drawn from $\{1, \dots, g_1\}$ is just the number of subsets of n_1 elements in a set of size g_1 , that is $\binom{g_1}{n_1}$

An identical count holds for every energy level, and the choices for distinct levels are independent. Therefore, taking the product over all energy levels (i), the number of microstates in the Fermi-Dirac case is

$$\begin{aligned} \Omega^{FD} &= \dim(W_E / \ker \mathcal{A}) \\ &= \prod_i \binom{g_i}{n_i} \\ &= \prod_i \frac{g_i!}{(g_i - n_i)! n_i!}. \end{aligned}$$

In summary, we have shown that the anti-symmetrizer $\mathcal{A}$ is a surjective projection onto the antisymmetric subspace of the energy eigenspace W_E , the first-isomorphism theorem realises that subspace as the indicated quotient, and a basis for the quotient is obtained by retaining one representative from each orbit under the action of S_N . The classical formulae (1) is obtained by counting this basis.

2. Bose–Einstein case

Since Bosons have symmetric wave functions, the procedure used in the Fermi-Dirac case will work if the anti-symmetrizer is replaced by a surjective projection onto the symmetric subspace of the energy eigenspace W_E^{BE} .

Define the symmetrizer

$$\mathcal{S} = \frac{1}{N!} \sum_{\sigma \in S_N} \hat{\sigma}$$

(the orthogonal projection of W_E onto its totally symmetric subspace). Exactly as

in the Fermi–Dirac argument one has

$$\Omega^{\text{BE}} = \dim(W_E / \ker \mathcal{S}).$$

A spanning set for the quotient consists of the cosets of all product states that realise the given occupation numbers n_i :

$$[v^{a_1} \dots v^{a_{n_1}} w^{b_1} \dots w^{b_{n_2}} \dots],$$

where the indices a_k run through $\{1, \dots, g_1\}$, the indices b_ℓ run through $\{1, \dots, g_2\}$, etc. Because $\mathcal{S}$ is invariant under arbitrary permutations, two such products determine the same coset whenever one is a rearrangement of the other. Consequently it is enough to keep a single representative from each orbit; we may therefore impose the weak orderings

$$\begin{aligned} 1 &\leq a_1 \leq a_2 \leq \dots \leq a_{n_1} \leq g_1, \\ 1 &\leq b_1 \leq b_2 \leq \dots \leq b_{n_2} \leq g_2, \end{aligned}$$

and likewise for every subsequent energy level. (Repetitions are now permitted, as required by Bose statistics.)

It remains only to count the admissible sequences for a single energy level, say the v -level. The set of non-decreasing sequences of length n_1 drawn from $\{1, \dots, g_1\}$ is in bijection with the set of strictly increasing sequences of length n_1 drawn from $\{1, \dots, g_1 + n_1 - 1\}$ [4] The number of the latter sequences is the ordinary binomial coefficient

$$\binom{g_1 + n_1 - 1}{n_1}.$$

An identical count holds for every energy level, and the choices for distinct levels are independent. Therefore, taking the product over all energy levels (i),

$$\Omega^{\text{BE}} = \prod_i \binom{g_i + n_i - 1}{n_i} = \prod_i \frac{(g_i + n_i - 1)!}{(g_i - 1)! n_i!}.$$

In both the Fermi–Dirac and Bose–Einstein cases, the selected cosets are linearly independent: any linear relation among them would lift to a linear relation among the corresponding symmetrized products, contradicting the assumed linear independence of the underlying single-particle states.

3. Conclusion

We have presented proofs of (1) and (2) that use elementary linear algebra to count quantum states, rather than combinatorial models based on indistinguishable particles or the more advanced language of exterior and symmetric algebras. This intermediate approach has the advantage of highlighting the algebraic structure that underlies the two statistics while remaining accessible to students who have completed a first course in linear algebra and elementary quantum mechanics. In particular, it makes transparent how the Bose–Einstein and Fermi–Dirac formulae arise from the symmetry or antisymmetry of the solutions of the Schrödinger equation under particle interchange.

4. References

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