Problem Set 12: Density Matrices
Graduate Quantum I
Physics 6572

James Sethna

Due Friday Nov. 14

Last correction at September 25, 2014, 2:48 pm

Potentially useful reading

Sakurai and Napolitano, section 3.4 (density matrices)
Schumacher & Westmoreland 8.1-2, 8.5, 8.7 (density matrices)
Weinberg pp.68,69 (density matrices)
Sethna, section 7.1 (density matrices)
Kittel, *Introduction to Solid State Physics*, chapter 18, subsection "Two barriers in series – resonant tunneling", edition 8, by Paul McEuen (α-decay).

12.1 **Spin density matrix.**[1] (Quantum) ③

Density matrices are Hermitian $\rho^\dagger = \rho$ and have trace one.

(a) *Show that any* 2×2 *density matrix may be written in the form*

$$\boldsymbol{\rho} = \frac{1}{2}(\mathbf{1} + \mathbf{n} \cdot \boldsymbol{\sigma}). \tag{1}$$

where $\mathbf{n}$ *is a three-dimensional real vector.*

Let the Hamiltonian for a spin be

$$\mathcal{H} = -\frac{\hbar}{2}\mathbf{B} \cdot \vec{\sigma}, \tag{2}$$

where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the three Pauli spin matrices, and $\mathbf{B}$ may be interpreted as a magnetic field, in units where the gyromagnetic ratio is unity. Remember that $\sigma_i\sigma_j - \sigma_j\sigma_i = 2\mathrm{i}\epsilon_{ijk}\sigma_k$.

(b) *Show that the equations of motion for the density matrix* $\mathrm{i}\hbar\partial\boldsymbol{\rho}/\partial t = [\mathcal{H}, \boldsymbol{\rho}]$ *can be written as* $\mathrm{d}\mathbf{n}/\mathrm{d}t = -\mathbf{B} \times \mathbf{n}$.

12.2 **Pure state density matrix evolution.** (Sakurai and Napolitano, problem 3.11) ②

(a) Prove that the time evolution of the density operator ρ (in the Schrödinger picture) is given by

$$\rho(t) = U(t, t_0)\rho(t_0)U^\dagger(t, t_0).$$

(b) Suppose we have a pure ensemble at $t = 0$. Prove it cannot evolve into a mixed ensemble as long as the time evolution is governed by the Schrödinger equation.

[1] Adapted from exam question by Bert Halperin, Harvard University, 1976.

12.3 **Does entropy increase in quantum systems?.** (Mathematics, Quantum) ③

One can show (Exercise (5.7) in my text, 'Entropy, Order Parameters, and Complexity') that in classical Hamiltonian systems the non-equilibrium entropy $S_{\mathrm{nonequil}} = -k_B \int \rho \log \rho$ is constant in a classical mechanical Hamiltonian system. Here you will show that in the microscopic evolution of an isolated quantum system, the entropy is also time independent, even for general, time-dependent density matrices $\rho(t)$.

Using the evolution law $\partial\rho/\partial t = [\mathcal{H}, \rho]/(i\hbar)$, prove that $S = -\mathrm{Tr}\,(\boldsymbol{\rho} \log \boldsymbol{\rho})$ is time independent, where $\boldsymbol{\rho}$ is any density matrix. (Hint: Go to an orthonormal basis ψ_i which diagonalizes ρ. Show that $\psi_i(t)$ is also orthonormal, and take the trace in that basis. Use the cyclic invariance of the trace.)

12.4 **F-electrons and graphene.** (Quantum) ③

In this exercise, we shall explore how seven degenerate f-electron states of an atom split under a weak perturbation which breaks the rotational symmetry.

Atoms often sit atop surfaces with weak interactions without strong bonding; we describe them as *adsorbed.* Consider a light atom[2] in an electronic f-state (i.e., with $\ell = 3$), adsorbed on a monolayer of graphene (Fig. 1). Assume the atom is positioned above a point of hexagonal symmetry, so the symmetry group for the atom is broken from $SO(3)$ to C_{6v}.

How do we know this? Why is the symmetry group not just C_6? Why is our system not symmetric under D_{6h}, the symmetry group of graphene?

(a) *What symmetry is exhibited by our adsorbed atom that is not in C_6? What symmetry in D_{6h} is not a symmetry of our adsorbed atom?*

The character of a spin-ℓ representation for SO(3) for a rotation by angle θ is $\chi^{(\ell)}(\theta) = \sin[(\ell + 1/2)\theta]/\sin[1/2\theta]$. (Check this for the $\ell = 1$ representation, where you know $\chi^{(1)}$ in terms of $\cos[\theta]$. You'll need to use L'Hôpital's rule to evaluate $\chi^{(\ell)}(0)$.)

Six of the symmetry operations in C_{6v} (conjugacy classes σ_v and σ'_v) are reflections – in $O(3)$ but not in $SO(3)$. The characters for representations of $O(3)$ are not so commonly studied. Let's figure them out for the special case of reflections.

---

[2]The atom is light so that we may ignore the spins of the electrons. A heavy atom would have significant spin-orbit interactions.

C_{6v}	E	C_2	$2C_3$	$2C_6$	$3\sigma_v$	$3\sigma_v'$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_2	1	-1	1	-1	1	-1
B_1	1	-1	1	-1	-1	1
E_2	2	2	-1	-1	0	0
E_1	2	-2	-1	1	0	0

Table 1: Character table for C_{6v}

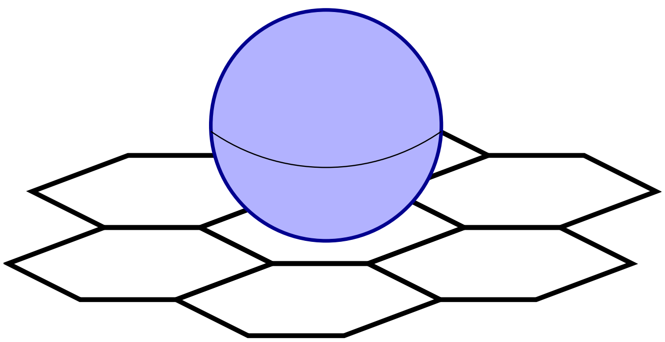

Fig. 1 ***Atom adsorbed on graphene***.

Every reflection $\Sigma(\hat{n})$ in $O(3)$ takes the mirror plane into itself, and the perpendicular $\hat{n}$ of the mirror plane to $-\hat{n}$. Thus $\Sigma(\hat{y})$ is a reflection in the $x-z$ mirror plane. Let $R_{\hat{n}}$ be a rotation that takes the coordinate axis $\hat{y}$ to $\hat{n}$.

(b) *Using $R_{\hat{n}}$, show that all reflections in $O(3)$ are conjugate to $\Sigma(\hat{y})$.*

Since the trace is invariant under rotations, and conjugacy in $SO(3)$ is a rotation, and the character is a trace, this means that all reflections will have the same character under representations of $O(3)$. Consider the angular momentum ℓ representation of $O(3)$ generated by the rotations of the spherical harmonics $Y_\ell^m(\theta, \phi)$. Remember that θ is the angle from the $\hat{z}$ axis, and ϕ is measured from the $\hat{x}$ axis.

(c) *How does Y_ℓ^m transform under the reflection $\Sigma(\hat{y})$ in the $x-z$ plane? In the $(2\ell+1)$-dimensional space of Y_ℓ^m for fixed ℓ, what are the elements of the $(2\ell+1) \times (2\ell+1)$ matrix $D_{mm'}$ representing $\Sigma(\hat{y})$? Show that the trace $\chi^{(\ell)}(\Sigma(\hat{y})) = 1$, and hence that the character for all reflections is one in all (integer) representations of $O(3)$, independent of ℓ.*

Table 1 gives the character table for C_{6v}.

(d) *When the f-electron eigenstates are split by the hexagonal crystal field from the graphene, what irreducible representations and degeneracies will be represented?* (Hint: Use the orthogonality of the representations to decompose the $\ell = 3$ representation. Also, check that the total number of states equals the number of f-states.) For example, your answer might be “Two non-degenerate eigenstates with reps A_1 and B_2, and three doublet eigenstates, two with reps E_2 and one with rep E_1.”)