EE201/MSE207 Lecture 18

Density matrix (density operator)

In this course we described a quantum state by a wavefunction. Wavefunction does not contain any randomness (entropy is zero, randomness only for measurement result). However, we often need to also describe a classical randomness (thermodynamics, decoherence, etc.)

A possible way: list of states with probabilities

State $|\psi_1\rangle$ with probability p_1, state $|\psi_2\rangle$ with prob. p_2, etc.

state $|\psi_i\rangle$ with probability p_i, $\sum_i p_i = 1$

However, this is a very lengthy description. Possible to use a shorter way.

Instead of this list, let us define an operator $\boxed{\hat{\rho} = \sum_i p_i\, |\psi_i\rangle\langle\psi_i|}$ (density matrix)

Somewhat surprisingly, this is a complete description of a quantum state (for different lists giving the same $\hat{\rho}$, all experimental predictions coincide).

Some properties of density operator $\hat{\rho}$

1. Hermitian (obvious, since a sum of projectors)
2. Positive semidefinite (all eigenvalues are non-negative)
3. $\mathrm{Tr}\,\hat{\rho} = 1$ (proof later)

Averages via density matrix

$\hat{\rho} = \sum_i p_i \, |\psi_i\rangle\langle\psi_i|$ for state $|\psi_i\rangle$ with probability p_i, $\sum_i p_i = 1$

Theorem

For any observable $\hat{A}$, its average (expectation) value is $\boxed{\langle\hat{A}\rangle = \mathrm{Tr}(\hat{\rho}\hat{A})}$

(this is why $\hat{\rho}$ is a complete description)

Proof

orthonormal basis

$$\langle\hat{A}\rangle = \sum_i p_i \, \langle\psi_i|\hat{A}|\psi_i\rangle \qquad \mathrm{Tr}(\hat{\rho}\hat{A}) = \sum_k \langle e_k|\hat{\rho}\hat{A}|e_k\rangle$$

$$\mathrm{Tr}(\hat{\rho}\hat{A}) = \sum_k \langle e_k|\hat{\rho}\hat{A}|e_k\rangle = \sum_{k,i} \langle e_k\underbrace{|\psi_i\rangle \, p_i \, \langle\psi_i|}_{\hat{\rho}}\hat{A}|e_k\rangle =$$

$$= \sum_i p_i \sum_k \langle\psi_i|\hat{A}\underbrace{|e_k\rangle\langle e_k|}_{\hat{1}}\psi_i\rangle = \sum_i p_i \, \langle\psi_i|\hat{A}|\psi_i\rangle = \langle\hat{A}\rangle$$

QED

Corollary

$\langle\hat{1}\rangle = \mathrm{Tr}(\hat{\rho}\hat{1}) = \mathrm{Tr}(\hat{\rho})$ Therefore $\mathrm{Tr}(\hat{\rho}) = 1$

Evolution of density matrix

$$\hat{\rho} = \sum_i p_i \, |\psi_i\rangle\langle\psi_i|$$

$$\frac{d}{dt}\hat{\rho} = \sum_i p_i \left(\frac{d|\psi_i\rangle}{dt} \langle\psi_i| + |\psi_i\rangle \frac{d\langle\psi_i|}{dt} \right) =$$

$$= -\frac{i}{\hbar} \sum_i p_i \left(\hat{H}|\psi_i\rangle\langle\psi_i| - |\psi_i\rangle\langle\psi_i|\hat{H} \right) = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right]$$

$$\boxed{\frac{d}{dt}\hat{\rho} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right]}$$

(Schrödinger equation
for density matrix)

Pure and mixed states

Pure state: a state, which can be represented by a wavefunction

$|\psi\rangle$ with probability $p = 1$, so $\hat{\rho} = |\psi\rangle\langle\psi|$

Then $\hat{\rho}^2 = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = \hat{\rho}$ $\boxed{\hat{\rho}^2 = \hat{\rho}}$ $\mathrm{Tr}(\hat{\rho}^2) = 1$

Mixed state: a state, which can not be represented by a wavefunction

Then $\hat{\rho}^2 \neq \hat{\rho}$ $\mathrm{Tr}(\hat{\rho}^2) < 1$ (proof via eigenbasis, $\sum p_i^2 < (\sum p_i)^2 = 1$)

Thermal distribution (equilibrium d.m.)

$\hat{\rho} = e^{-\hat{H}/T} / \mathrm{Tr}(e^{-\hat{H}/T})$ or $\hat{\rho} = e^{-(\hat{H}-\mu\hat{N})/T} / \mathrm{Tr}(e^{-(\hat{H}-\mu\hat{N})/T})$

Next subject: Schrödinger and Heisenberg pictures

What we considered in this course is called Schrödinger picture.

In this case Schrödinger equation for state: $\frac{d}{dt}|\Psi\rangle = -\frac{i}{\hbar}\widehat{H}|\Psi\rangle$

If $\widehat{H}$ is time-independent, then formally $|\Psi(t)\rangle = e^{-i\widehat{H}t/\hbar}|\Psi(0)\rangle$

Then expectation value of an observable $\hat{A}$ at time t is

$$\langle\hat{A}\rangle_t = \langle\Psi(t)|\hat{A}|\Psi(t)\rangle = \langle\Psi(0)|\, e^{i\widehat{H}t/\hbar}\hat{A}\, e^{-i\widehat{H}t/\hbar}|\Psi(0)\rangle$$

Heisenberg picture

We could get the same $\langle\hat{A}\rangle$ is we assume that the state $|\Psi\rangle$ does not evolve, but instead the observable $\hat{A}$ evolves with time t:

$$\hat{A}(t) = e^{i\widehat{H}t/\hbar}\hat{A}\, e^{-i\widehat{H}t/\hbar}$$

$$\boxed{\frac{d}{dt}\hat{A}(t) = \frac{i}{\hbar}\left[\widehat{H},\hat{A}(t)\right]}$$

Interaction picture (main practical approach)

Interaction picture is a combination of both Schrödinger and Heisenberg pictures.

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

simple (solvable); assume time-independent

Heisenberg-picture idea for $\hat{H}_0$. For any observable $\hat{A}$,

$$\hat{A}(t) \equiv e^{i\hat{H}_0 t/\hbar}\hat{A}\, e^{-i\hat{H}_0 t/\hbar}$$

$$\boxed{\frac{d}{dt}\hat{A}(t) = \frac{i}{\hbar}\left[\hat{H}_0, \hat{A}(t)\right]}$$

Also introduce $\left|\tilde{\Psi}(t)\right\rangle = e^{\frac{i\hat{H}_0 t}{\hbar}}|\Psi(t)\rangle$ (here usual Schrödinger $|\Psi(t)\rangle$)

So that $\langle\hat{A}\rangle_t = \langle\Psi(t)|\hat{A}|\Psi(t)\rangle = \langle\tilde{\Psi}(t)|\underbrace{e^{\frac{i\hat{H}_0 t}{\hbar}}\hat{A}\, e^{\frac{-i\hat{H}_0 t}{\hbar}}}_{\hat{A}(t)}|\tilde{\Psi}(t)\rangle$

Then evolution for $|\tilde{\Psi}(t)\rangle$ is

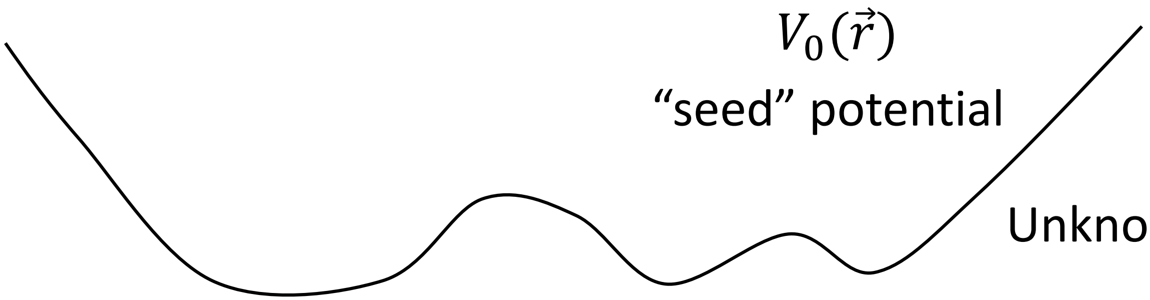
$$\frac{d}{dt}|\tilde{\Psi}\rangle = \frac{i\hat{H}_0}{\hbar}e^{\frac{i\hat{H}_0 t}{\hbar}}|\Psi\rangle + e^{\frac{i\hat{H}_0 t}{\hbar}}\underbrace{\frac{-i\hat{H}}{\hbar}|\Psi\rangle}_{\text{SE}} = e^{\frac{i\hat{H}_0 t}{\hbar}}\frac{-i\hat{H}_1}{\hbar}|\Psi\rangle =$$

$$= \underbrace{e^{\frac{i\hat{H}_0 t}{\hbar}}\frac{-i\hat{H}_1}{\hbar}e^{\frac{-i\hat{H}_0 t}{\hbar}}}_{\text{Heisenberg}}|\tilde{\Psi}\rangle$$

$$\boxed{\frac{d}{dt}|\tilde{\Psi}\rangle = -\frac{i}{\hbar}\hat{H}_1(t)\,|\tilde{\Psi}\rangle}$$

Next subject: Methods for interacting electrons

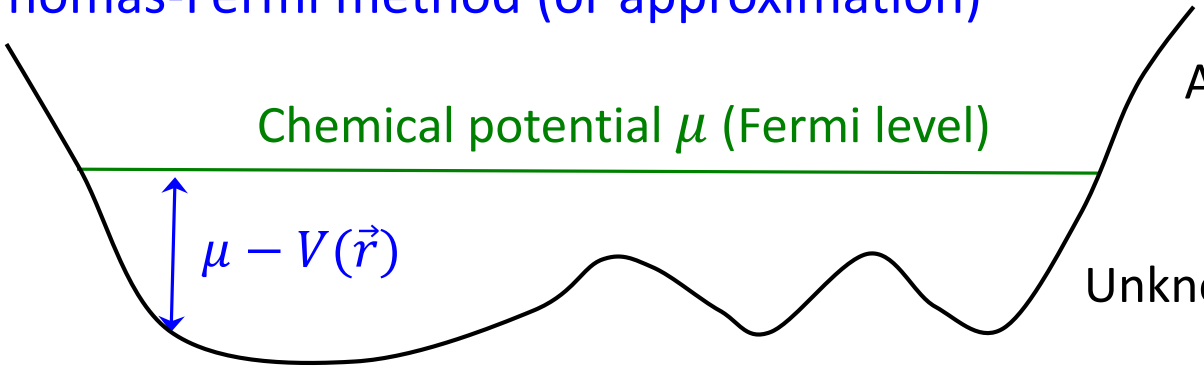
(terminology and ideas)



Unknown $V(\vec{r}) = V_0(\vec{r}) + \Delta V(\vec{r})$

Problem: $V(\vec{r})$ changes because of electron-electron interaction, so need some self-consistent approach.

Thomas-Fermi method (or approximation)



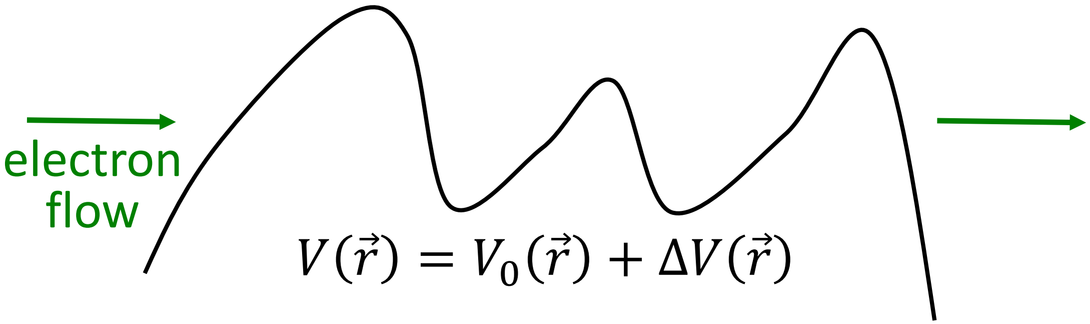
Assume equilibrium

Unknown $V(\vec{r}) = V_0(\vec{r}) + \Delta V(\vec{r})$

Idea: $\mu - V(\vec{r})$ determines density of electrons, $n(\vec{r}) = \frac{1}{3\pi^2}\left(\frac{2m\,(\mu - V)}{\hbar^2}\right)^{3/2}$,

then solve Poisson equation to find $\Delta V(\vec{r})$; self-consistency: $V \to n \to V$.

Hartree method (or approximation)



$V(\vec{r}) = V_0(\vec{r}) + \Delta V(\vec{r})$

Non-equilibrium,
but stationary case

no chemical potential

all electrons alike

Idea: solve Schrödinger equation $\hat{H}\psi = E\psi$ to find $\psi(\vec{r})$, then $n(\vec{r}) \propto |\psi(\vec{r})|^2$, then solve Poisson equation to find $\Delta V(\vec{r})$; self-consistency $V \to \psi \to n \to V$.

Hartree-Fock method (or approximation)

Idea: almost the same as Hartree, but excludes *e*-*e* interaction for an electron with itself, so that electron feels only field produced by other electrons

Density functional theory

Even better (more accurate), uses functionals of electron density $n(\vec{r})$

Next subject: Language of second quantization

This is a technique to describe states with variable number of particles. (Later it was found to be useful for a fixed number of particles as well.)

Occupation number representation

$|\vec{N}\rangle = |N_1, N_2, N_3, \dots\rangle$

State with N_1 particles on level 1, N_2 particles on level 2, etc. We do not distinguish which particle is where (indistinguishable).

This is now the basis, so that an arbitrary (pure) state is a superposition:

$|\psi\rangle = \sum_{\vec{N}} c(\vec{N})\, |\vec{N}\rangle$

$\left|c\left(\vec{N}\right)\right|^2$ is probability

This wavefunction lives in the occupation number space (Fock space)

Orthogonality: $\langle\vec{M}|\vec{N}\rangle = 0$ if $\vec{M} \neq \vec{N}$, $\langle\vec{N}|\vec{N}\rangle = 1$

Examples of (basis) states

$|0, 0, 0, \dots\rangle$ no particles, “vacuum”, $|\vec{0}\rangle$ or $|0\rangle$

$|0, 1, 0, \dots\rangle$ one particles in state 2

$|0, 2, 1, 0, \dots\rangle$ two particles in state 2, 1 particle in state 3

Second quantization (cont.)

Simple special case: one oscillator (main language in optics)

Basis: $|0\rangle$, $|1\rangle$, $|2\rangle$, $|3\rangle$, etc.
Instead of the level number, we think about number of photons

Wavefunction: $|\psi\rangle = \sum_n c(n)\,|n\rangle$ (Fock-space representation)

Creation and annihilation operators

$$\hat{a}_2^\dagger|0\rangle = |0,1,0,0,\ldots\rangle \qquad \hat{a}_3^\dagger|0\rangle = |0,0,1,0,\ldots\rangle$$

For <u>bosons</u> $\hat{a}_k^\dagger\,|\ldots N_k,\ldots\rangle = \sqrt{N_k+1}\ \,|\ldots N_k+1,\ldots\rangle$

creates extra particle on level k (factor $\sqrt{N+1}$ as for an oscillator)

For <u>bosons</u> $\hat{a}_k\,|\ldots N_k,\ldots\rangle = \sqrt{N_k}\ \,|\ldots N_k-1,\ldots\rangle$

annihilates (kills) one particle on level k (factor $\sqrt{N}$ as for an oscillator)

If $N_k = 0$, then $\hat{a}_k|\ldots 0_k,\ldots\rangle = 0$ (zero, not vacuum)

In particular, $\hat{a}_k^\dagger\hat{a}_k\,|\ldots N_k,\ldots\rangle = N_k\,|\ldots N_k,\ldots\rangle$, so $\hat{N}_k = \hat{a}_k^\dagger\hat{a}_k$

Commutation relations

$$\boxed{[\hat{a}_k,\hat{a}_l^\dagger] = \delta_{kl}\,, \quad [\hat{a}_k,\hat{a}_l] = [\hat{a}_k^\dagger,\hat{a}_l^\dagger] = 0}$$

Sufficient for the
whole theory

Second quantization (cont.)

Operators can often be expressed in terms of $\hat{a}^\dagger$ and $\hat{a}$

$$\widehat{\mathrm{H}} = \sum_k \varepsilon_k \, \hat{a}_k^\dagger \hat{a}_k$$ (non-interacting particles, basis of eigenstates)

If basis vectors are not eigenstates, then also terms $\sum_{kl} H_{kl} \, \hat{a}_k^\dagger \hat{a}_l$

Tight-binding model: $\widehat{H} = \sum_j \varepsilon_j \, a_j^\dagger a_j + \sum_j (T_j a_j^\dagger a_{j+1} + T_j^* a_{j+1}^\dagger a_j)$

Coulomb interaction: $\widehat{H} = \sum_{kl} H_{kl} \, \hat{a}_k^\dagger \hat{a}_k \, \hat{a}_l^\dagger \hat{a}_l$

For fermions similar, but commutation relations are

$$\boxed{\{\hat{a}_k, \hat{a}_l^\dagger\}_+ = \delta_{kl} \, , \; \{\hat{a}_k, \hat{a}_l\}_+ = \{\hat{a}_k^\dagger, \hat{a}_l^\dagger\}_+ = 0}$$

where

$$\{\hat{A}, \hat{B}\}_+ \equiv \hat{A}\hat{B} + \hat{B}\hat{A}$$

For example, this means that $\hat{a}_k^\dagger \hat{a}_k^\dagger |0\rangle = -\hat{a}_k^\dagger \hat{a}_k^\dagger |0\rangle$, so $\hat{a}_k^\dagger \hat{a}_k^\dagger |0\rangle = 0$

(Pauli exclusion principle)

For one particle it does not matter if it is fermion or boson, so boson rules are often used for electrons (in single-particle approaches)

Why called "second quantization"? $\psi(x) \rightarrow \hat{\psi} = \sum_k \psi_k \hat{a}_k$