Lecture 10

Finish stat mech from yesterday

Recall: \[ Q(N_1, N_2, \ldots) = \# \text{ of configurations for } N_n \text{ particles with energy } E_n \]

Assume system is usually close to configuration with largest possible \( Q \)

Use Lagrange multipliers to maximize \( Q \)

subject to constraints \( N = \sum N_n, E = \sum E_n \)

\[ N_n = \frac{dn}{e^{(\alpha + \beta E_n)} - 1} \]

For distinguishable particles in box, found

\[ \beta = \frac{3}{2} \frac{N}{E}, \quad e^{-\alpha} = \frac{N}{\nu} \left( \frac{2\pi k_B T}{m} \right)^{3/2} \]

Compare to thermodynamics of ideal gas:

\[ E = \frac{3}{2} N k_B T \]

\[ \Rightarrow \beta = \frac{1}{k_B T} \]
Also, \( \alpha = -\frac{\mu}{k_B T} \) chemical potential \( \mu \)

(less familiar thermodynamics)

This kind of counting argument connects microscopic QM to macroscopic thermodynamics

Surprisingly powerful!

What about identical particles?

Have \( N = \int \frac{1}{\exp[(\frac{\mathcal{E}}{k_B T} - \mu)/k_B T]^n + 1} \frac{V}{2\pi^2} k^2 dk \)

Can't do integral, have to solve numerically.

But in limit \( \mathcal{E} - \mu \gg k_B T \), \( \exp \) is large compared to 1

\( \Rightarrow \) looks like distinguishable particles again

Can get a good rule of thumb for when this happens:

For distinguishable particles, \( \mu = -\alpha k_B T \)

\[ = k_B T \ln \left[ \frac{N}{V} \left( \frac{2\pi m^2 k_B T}{\hbar^2} \right)^{3/2} \right] \]

Define \( \lambda = \sqrt{\frac{2\pi m}{\hbar}} \) "Thermal de Broglie wave length"

\[ = \text{typical wavelength for particles with } E \approx k_B T \]
So $\mu = k_B T \ln (\rho \Lambda^3)$

$\rho = \text{density} \frac{N}{V}$

where $\rho \Lambda^3 = \# \text{ of particles within one cubic wavelength}$

Suppose $\rho \Lambda^3 \ll 1$

Then $\ln \rho \Lambda^3 \ll 0$

$\Rightarrow \mu \ll k_B T$

Can ignore exchange effects if $E_k > \mu + k_B T$

but if $\mu \ll k_B T$, then $\mu + k_B T \ll 0$

Therefore just require $E_k > 0 \ \text{true for all states}$

Generally true:
Can ignore exchange effects if $\rho \Lambda^3 \ll 1$

Consistent with earlier argument that exchange only matters when wave functions of particles overlap.

"Size" of wave function $\approx$ de Broglie wavelength

Wraps up Ch 5
Next: Ch 6: Perturbation theory

Probably the most important thing we'll do

Basic idea: You've solved about all the QM problems that are exactly solvable

- square well / free particle
- harmonic oscillator
- hydrogen atom

But lots of other interesting & important problems!

One approach: solve Schrödinger numerically.
- gets very hard for complex systems
- don't get a lot of insight

Sometimes another possibility:
Say

$$H = H^{(0)} + H'$$

$$H^{(0)}$$ = "simple" Hamiltonian that we know how to solve

$$H'$$ = small deviation from $$H^{(0)}$$ = perturbation

Since $$H'$$ is small, can try to expand solutions in it as a sort of "power series"

To develop this idea, start with simple system that is exactly solvable, see how expansion works
Two-Level System

Suppose particle in a system with two accessible quantum states.

Obvious example: spin-\(\frac{1}{2}\) particle (comes up in other contexts too).

Label states \(|1\rangle, |2\rangle\).

Turns out we can solve system for any \(H\):

Express \(H\) in matrix form

\[
H \rightarrow \begin{bmatrix} \langle 1| H |1 \rangle & \langle 1| H |2 \rangle \\ \langle 2| H |1 \rangle & \langle 2| H |2 \rangle \end{bmatrix} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}
\]

with \(H_{21} = H_{12}^*\)

And \(|\psi\rangle = c_1 |1\rangle + c_2 |2\rangle\)

\[
\rightarrow \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}
\]

Then Schrödinger equation \(H|\psi\rangle = E|\psi\rangle\) becomes

\[
\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}
\]
Standard eigenvalue problem.

Solve by setting

\[
\begin{vmatrix}
H_{11} - E & H_{12} \\
H_{21} & H_{22} - E
\end{vmatrix} = 0
\]

\[
= H_{11}H_{22} - E(H_{11} + H_{22}) + E^2 - |H_{12}|^2
\]

Solve for \( E \):

\[
E = \frac{1}{2} \left[ \left( H_{11} + H_{22} \right) \pm \sqrt{(H_{11} + H_{22})^2 - 4(H_{11}H_{22} - |H_{12}|^2)} \right]
\]

\[
E = \frac{1}{2} \left[ H_{11} + H_{22} \pm \sqrt{(H_{22} - H_{11})^2 + 4|H_{12}|^2} \right]
\]

That's energies. Can get eigenstates too:

Solve

\[
\begin{bmatrix}
H_{11} & H_{12} \\
H_{21} & H_{22}
\end{bmatrix}
\begin{bmatrix}
c_1 \\
c_2
\end{bmatrix} = E \begin{bmatrix}
c_1 \\
c_2
\end{bmatrix}
\]

So

\[
H_{11}c_1 + H_{12}c_2 = Ec_1
\]

\[
c_2 = c_1 \frac{E - H_{11}}{H_{12}}
\]

Simplify notation, define

\[
\Delta = H_{22} - H_{11}
\]

\[
H_{12} = \frac{1}{2}Ve^{i\phi} \Rightarrow |H_{12}|^2 = \frac{V^2}{4}
\]

Then

\[
E \mp H_{11} = \frac{1}{2} \left( \Delta \pm \sqrt{\Delta^2 + 4|H_{12}|^2} \right)
\]
So \( c_2 = e^{-i\phi} \frac{\Delta + \sqrt{\Delta^2 + v^2}}{v} \)

Also need \( |c_1|^2 + |c_2|^2 = 1 \)

So \( |c_1|^2 \left[ 1 + \frac{(\Delta + \sqrt{\Delta^2 + v^2})}{v^2} \right] = 1 \)

Solve for \( |c_1|^2 = \frac{V^2}{2J\Delta \nu^2 (\sqrt{\Delta^2 + \nu^2} \pm \Delta)} \)

Put into nice form:

\[
|c_1|^2 = \frac{\nu^2 + \Delta^2 - \Delta^2}{2J\Delta \nu^2 (\sqrt{\Delta^2 + \nu^2} \pm \Delta)}
\]

\[
= \frac{(\nu^2 + \Delta^2 + \Delta)(\sqrt{\nu^2 + \Delta^2} - \Delta)}{2J\Delta \nu^2 (\sqrt{\Delta^2 + \nu^2} \pm \Delta)}
\]

\[
= \frac{\sqrt{\Delta^2 + \nu^2} + \Delta}{2J\Delta \nu^2}
\]

So \( c_1 = \frac{1}{\sqrt{2}} \left( 1 \pm \frac{\Delta}{\sqrt{\Delta^2 + \nu^2}} \right)^{1/2} \)

Use this to get \( c_2 = \pm e^{-i\phi} \frac{1}{\sqrt{2}} \left( 1 \pm \frac{\Delta}{\sqrt{\Delta^2 + \nu^2}} \right)^{1/2} \)

Complete solution for any \( \Delta \)

Next time, see what this implies for perturbations