PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 29:

Quantum effects in statistical mechanics

Reading: Chapter 7 (mostly 7.3)

1. **Summary of results concerning statistical mechanics of Fermi particles**
2. **Ideal Fermi gas of spin ½ particles; results at T=0 K and at T>0 K.**
3. **Other examples of Fermi particle systems**

21	Mon: 03/22/2021	Chap. 6.1 & 6.5	Microcanonical and canonical ensembles		
22	Wed: 03/24/2021	Chap. 6.1-6.2	Canonical distributions	#18	03/26/2021
23	Fri: 03/26/2021	Chap. 6.1-6.7	Canonical distributions	6.49	03/29/2021
24	Mon: 03/29/2021	Chap. 6.1-6.7	Canonical distributions	#20	03/31/2021
25	Wed: 03/31/2021	App. A & Chap. 7.1	Quantum mechanical effects	#21	04/02/2021
26	Fri: 04/02/2021	Chap. 7.1-7.2	Quantum mechanical effects		
27	Mon: 04/05/2021	Chap. 7.3	Bose and Fermi statistics	#22	04/09/2021
	Wed: 04/07/2021	No class	*Holiday*		
28	Fri: 04/09/2021	Chap. 7.3 & 7.4	Bose and Fermi statistics	#23	04/12/2021
29	Mon: 04/12/2021	Chap. 7.3	Fermi examples	#24	04/16/2021
30	Wed: 04/14/2021	Chap. 7.5	Bose examples and lattice vibrations		
31	Fri: 04/16/2021	Chap. 7.6	Bose condensation		
32	Mon: 04/19/2021	Chap. 8.1	Interacting particles		
33	Wed: 04/21/2021	Chap. 8.2	Spin magnetism		
34	Fri: 04/23/2021	Chap. 8.2	Spin magnetism		
35	Mon: 04/26/2021	Chap. 8.2	Spin magnetism		
36	Wed: 04/28/2021		Review		
37	Fri: 04/30/2021		Review		
37	Mon: 05/03/2021		Review		
38	Wed: 05/05/2021		Review		

PHY 341/641 -- Assignment #24

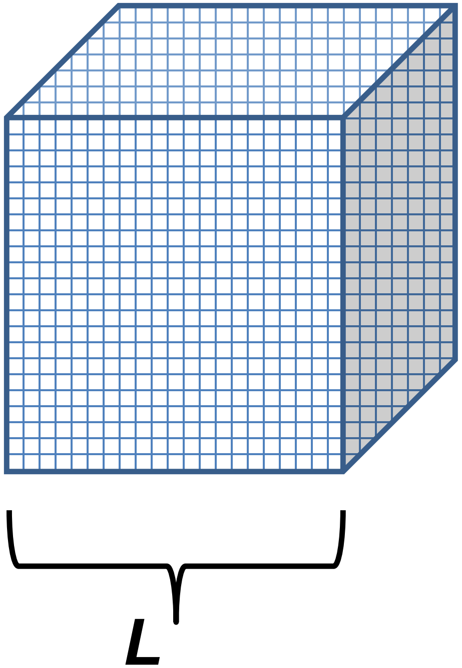
April 12, 2021

Continue reading Chapter 7 in **Schroeder** .

Consider an ideal Fermi gas of spin 1/2 particles confined in a two dimensional plane of length *L* and area *A*. Each particle has mass *m* and there are *N* particles. The spatial quantum states of the particles can be enumerated with the integers n_x and n_y for $-\infty \le n_{x,y} \le \infty$ according to

$$\varepsilon = h^2/(2mL^2)\,(n_x^2 + n_y^2).$$

1. *Find the density of states g(ε) for this system. Do not be surprised to find that it does not depend on ε.*
2. *Evaluate the chemical potential μ at T=0K.*
3. *Evaluate the Grand potential Ω at T=0K.*
4. *Evaluate the internal energy U at T=0K.*



L^3=V

Comment on evaluating density of states $g(\varepsilon)$ in 3 dimensions --

For: $-\infty \leq n_{x,y,z} \leq \infty$

Spatial energy for electron: $\epsilon_{n_x n_y n_z} = \frac{h^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

Summing over all modes $(n_x . n_y, n_z)$ in continuum limit:

Let $q \equiv \sqrt{n_x^2 + n_y^2 + n_z^2}$ $\quad \int dn_x \int dn_y \int dn_z = 4\pi \int q^2 dq$

$$g(\epsilon) = 2\, 4\pi \int q^2 dq\ \delta\left(\epsilon - \frac{h^2 q^2}{2mL^2}\right)$$

Spin degeneracy

Note that $\int dx\, f(x)\ \delta(a - x) = f(a)$

Let $x = \frac{h^2 q^2}{2mL^2}$ $\quad g(\epsilon) = 2\ 4\pi \left(\frac{2mL^2}{h^2}\right)^{3/2} \frac{1}{2} \int \sqrt{x} dx\ \delta(\epsilon - x)$

$$g(\epsilon) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \sqrt{\epsilon} \qquad V \equiv L^3$$

Important results from last time

Properties of the "Grand potential"

$$\Omega(T,V,\mu) = F - \mu N \qquad d\Omega = -SdT - PdV - Nd\mu$$

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \qquad P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \qquad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T}$$

Relationship of Grand potentials to other thermodynamic potentials

Internal: $U(S,V,N)$ $\qquad \Omega = U - ST - \mu N$

Enthalpy: $H(S,P,N) = U + PV$ $\qquad \Omega = H - PV - ST - \mu N$

Helmholtz: $F(T,V,N) = U - ST$ $\qquad \Omega = F - \mu N$

Gibbs: $G(T,P,N) = F + PV$ $\qquad \Omega = G - PV - \mu N = -PV$

Important results from last time

The grand canonical partition function $Z_{Grand}(T,V,\mu)$

is directly connected to the Grand potential

according to $\Omega(T,V,\mu) = -kT\ln\left(Z_{Grand}(T,V,\mu)\right)$

True for all indistinguishable quantum particles (Fermi or Bose).

For the case of Fermi particles --

$$\ln\left(Z_{GrandFermi}(T)\right) = \sum_s \ln\left(1+e^{-\beta(\epsilon_s-\mu)}\right)$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)}+1} = N$$

Constraint which defines μ.

True for all indistinguishable and non-interacting Fermi quantum particles.

Examples of (approximately) non-interacting Fermi particles

1. 3 dimensional spin ½ Fermi gas (approximated by ideal 3-dimensional metals.
2. 2 dimensional spin ½ Fermi gas (your homework problem)
3. Graphene (real 2 dimensional spin ½ Fermi gas; has a different density of states than your homework
4. Semi-conductors and insulating materials
5. Electronic states of atoms and molecules

Evaluation of integrals --

$$\ln\left(Z_{GrandFermi}(T)\right) = \sum_s \ln\left(1 + e^{-\beta(\epsilon_s - \mu)}\right)$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1} = N$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1} \rightarrow \int d\epsilon \; g(\epsilon) \frac{1}{e^{\beta(\epsilon - \mu)} + 1}$$

For 3 dimensional ideal Fermi gas

$$g(\epsilon) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \sqrt{\epsilon}$$

Evaluation of integrals for T=0 --

$$\int d\epsilon \; g(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)}+1} \approx \int_0^{\mu} d\epsilon \; g(\epsilon) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\mu} d\epsilon \; \sqrt{\epsilon}$$

$$\Rightarrow \; 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{2}{3} \mu^{3/2} = \mathrm{N}$$

$$\Rightarrow \mu(T=0) \equiv \epsilon_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}$$

Evaluation of the Grand potential:

$$\Omega(T,V,\mu) = -kT\ln\left(Z_{GrandFermi}(T)\right) = -kT\sum_s \ln\left(1+e^{-\beta(\epsilon_s-\mu)}\right)$$

$$= -kT\int d\epsilon\; g(\epsilon)\ln\left(1+e^{-\beta(\epsilon-\mu)}\right)$$

For $T\rightarrow 0,\ \beta\rightarrow\infty:$ $\quad \ln\left(1+e^{-\beta(\epsilon_s-\mu)}\right) \approx \begin{cases} \beta(\mu-\epsilon) & \text{for } \epsilon<\mu \\ 0 & \text{for } \epsilon>\mu \end{cases}$

$$\Omega(T\rightarrow 0,V,\mu) = -\int_0^\mu d\epsilon\; g(\epsilon)(\mu-\epsilon)$$

$$= -4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int_0^\mu d\epsilon\,\sqrt{\epsilon}\,(\mu-\epsilon)$$

$$= -4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\frac{4}{15}\,\mu^{5/2}$$

Summary of results for an ideal Fermi gas of s=1/2 particles in three dimensions evaluated in the limit that T→0 K

Evaluation of the Grand potential:

$$\Omega(T \to 0, V, \mu) = -\int_0^{\mu} d\epsilon \; g(\epsilon)(\mu - \epsilon)$$

$$= -4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\mu} d\epsilon \; \sqrt{\epsilon} \; (\mu - \epsilon)$$

$$= -4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{4}{15} \; \mu^{5/2}$$

$$\int d\epsilon \; g(\epsilon) \frac{1}{e^{\beta(\epsilon - \mu)} + 1} = N$$

$$\mu(T = 0) \equiv \epsilon_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}$$

Some approximate Fermi energies for metals (from Ashcroft and Mermin, Solid State Physics)

Metal	μ(T=0 K) (eV)
Na	3.24
Mg	7.08
Al	11.70
Cu	7.00
Ag	5.49
Au	5.53

Visualization of density of states for ideal 3-dimensional Fermi gas

Calculated density of states for Cu metal
G. Burdick, Phys. Rev. 129, 138 (1963)

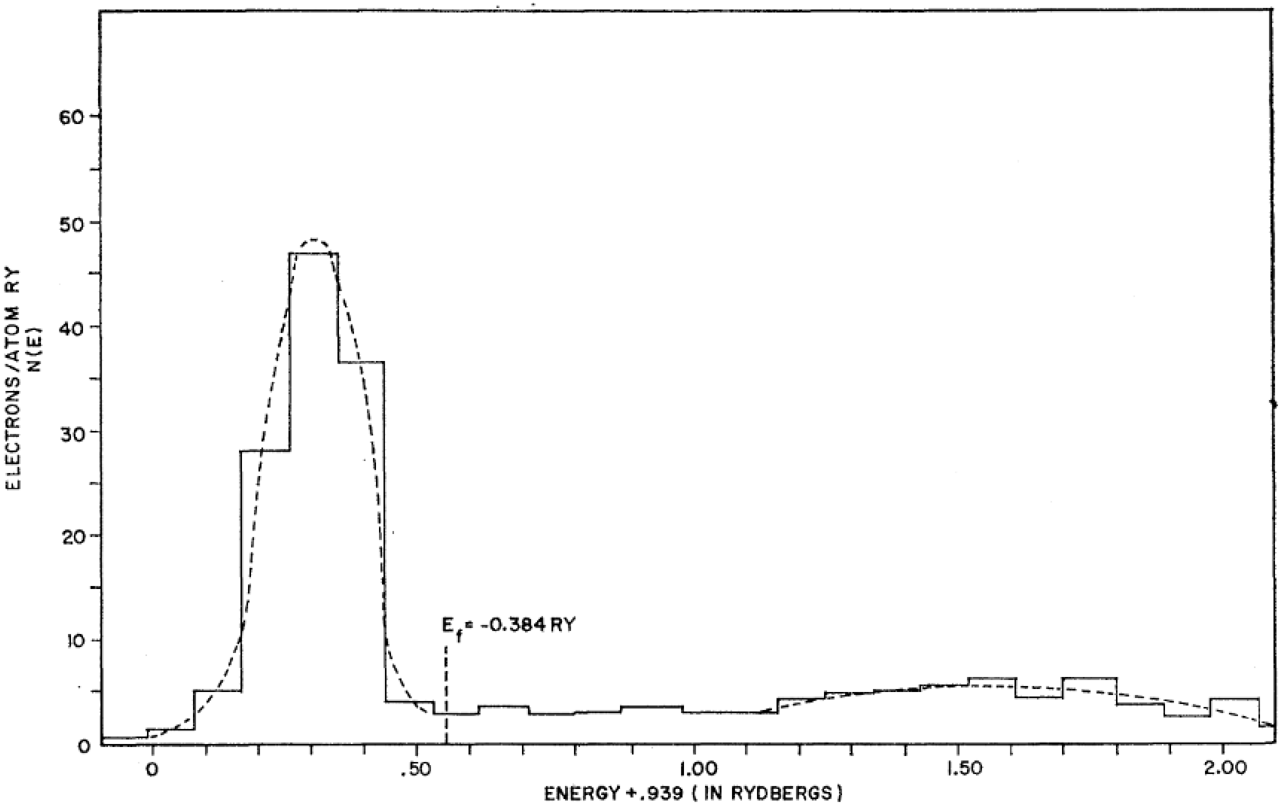


FIG. 5. Histogram for the density of states.

➔More modern theory takes into account modification to density of states due to more realistic quantum treatment

What about effects of T>0?

Evaluation of μ:

$$\int d\epsilon\ g(\epsilon)\frac{1}{e^{\beta(\epsilon-\mu)}+1}=N$$

Evaluation of the Grand potential:

$$\Omega(T,V,\mu)=-kT\int d\epsilon\ g(\epsilon)\ln\left(1+e^{-\beta(\epsilon-\mu)}\right)$$

For 3 dimensional ideal Fermi gas

$$g(\epsilon) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \sqrt{\epsilon}$$

Evaluation of the Grand potential:

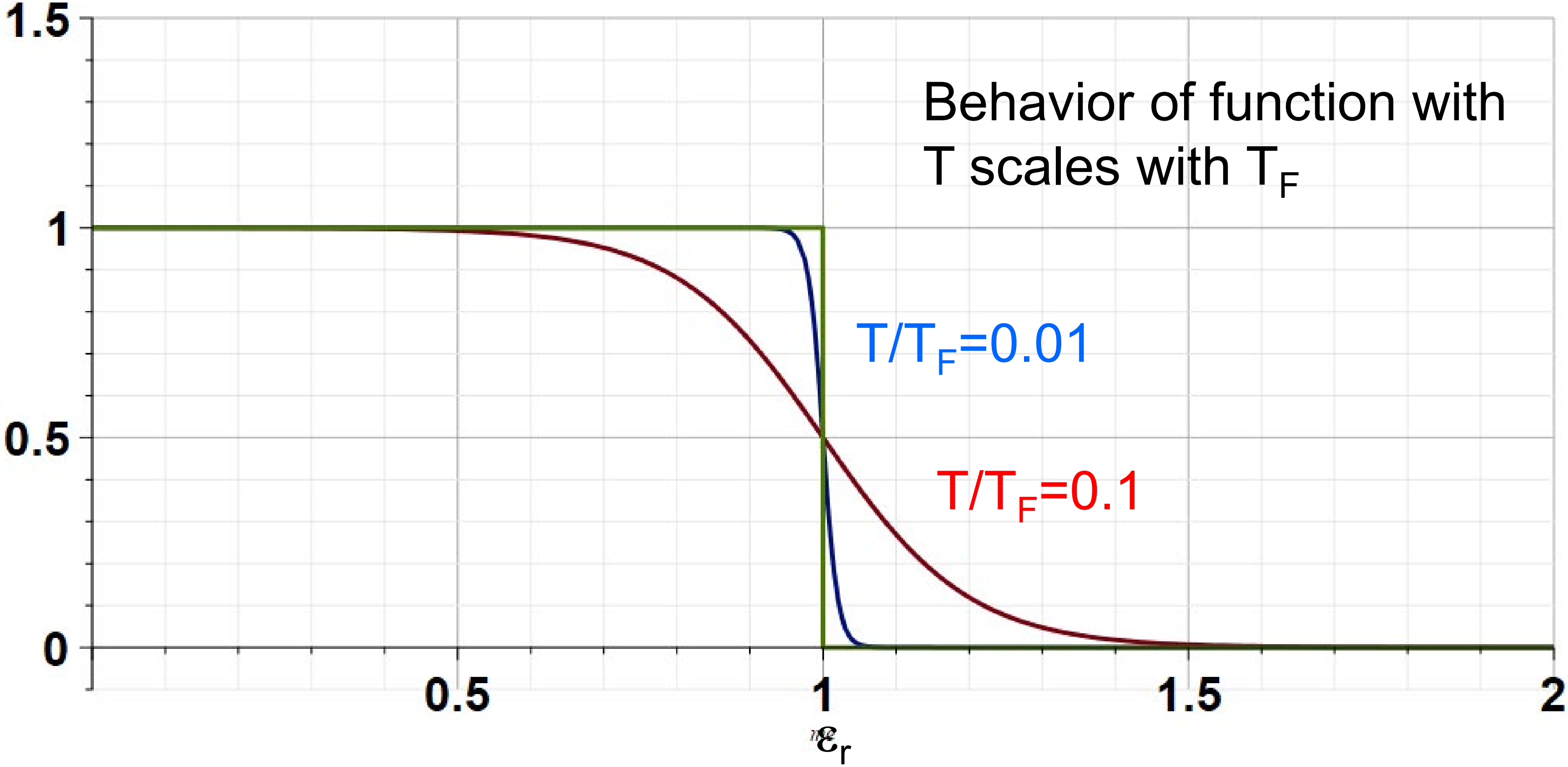
$$\Omega(T,V,\mu) = -kT \int d\epsilon \; g(\epsilon) \ln\left(1 + e^{-\beta(\epsilon-\mu)}\right)$$

For $g(\epsilon) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \sqrt{\epsilon}$ and integrating by parts --

$$\Omega(T,V,\mu) = -\frac{2}{3} 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)} + 1}$$

Fermi function $\mathcal{F}(\epsilon, T, \mu) \equiv \frac{1}{e^{\beta(\epsilon-\mu)}+1} = \frac{1}{e^{\frac{T_F}{T}(\epsilon_r-\mu_r)}+1}$

where $T_F \equiv \frac{\mu(T=0)}{k} = \frac{\epsilon_F}{k}$ $\quad \epsilon_r \equiv \frac{\epsilon}{\epsilon_F}$ $\quad \mu_r \equiv \frac{\mu}{\epsilon_F}$



Some approximate Fermi energies for metals (from Ashcroft and Mermin, Solid State Physics)

Metal	μ(T=0 K) (eV)	T_F (K)
Na	3.24	37700
Mg	7.08	82300
Al	11.70	136000
Cu	7.00	81600
Ag	5.49	63800
Au	5.53	64200

Evaluating integrals for T>0K --

Note that all integrals we need to evaluate have the form

$$\int d\epsilon \boldsymbol{\mathcal{F}}(\epsilon) H(\epsilon).$$

Suppose that $H(\epsilon) \equiv \int_0^{\epsilon} d\epsilon \; h(\epsilon)$

Then: $\int d\epsilon \boldsymbol{\mathcal{F}}(\epsilon) H(\epsilon) = \int d\epsilon \boldsymbol{\mathcal{F}}(\epsilon) \frac{dh(\epsilon)}{d\epsilon}.$

Some details --

$$\int_0^{\infty} d\epsilon \boldsymbol{\mathcal{F}}(\epsilon) \frac{dh(\epsilon)}{d\epsilon} \approx \left(\boldsymbol{\mathcal{F}}(\epsilon) h(\epsilon) \right)\Big|_0^{\infty} - \int_0^{\infty} d\epsilon \frac{d\boldsymbol{\mathcal{F}}(\epsilon)}{d\epsilon} h(\epsilon)$$

Highly peaked function for $\varepsilon \approx \mu$

Results given in Sec. 7.3 of your textbook --

$$\mu = \epsilon_F \left(1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 + ... \right)$$

$$U = \frac{3}{5} N \epsilon_F + \frac{\pi^2}{4} N \frac{(kT)^2}{\epsilon_F} ....$$

What about Fermi systems with different densities of states?

An example of an insulating material where the available electrons fill up the core and valence states of the material.

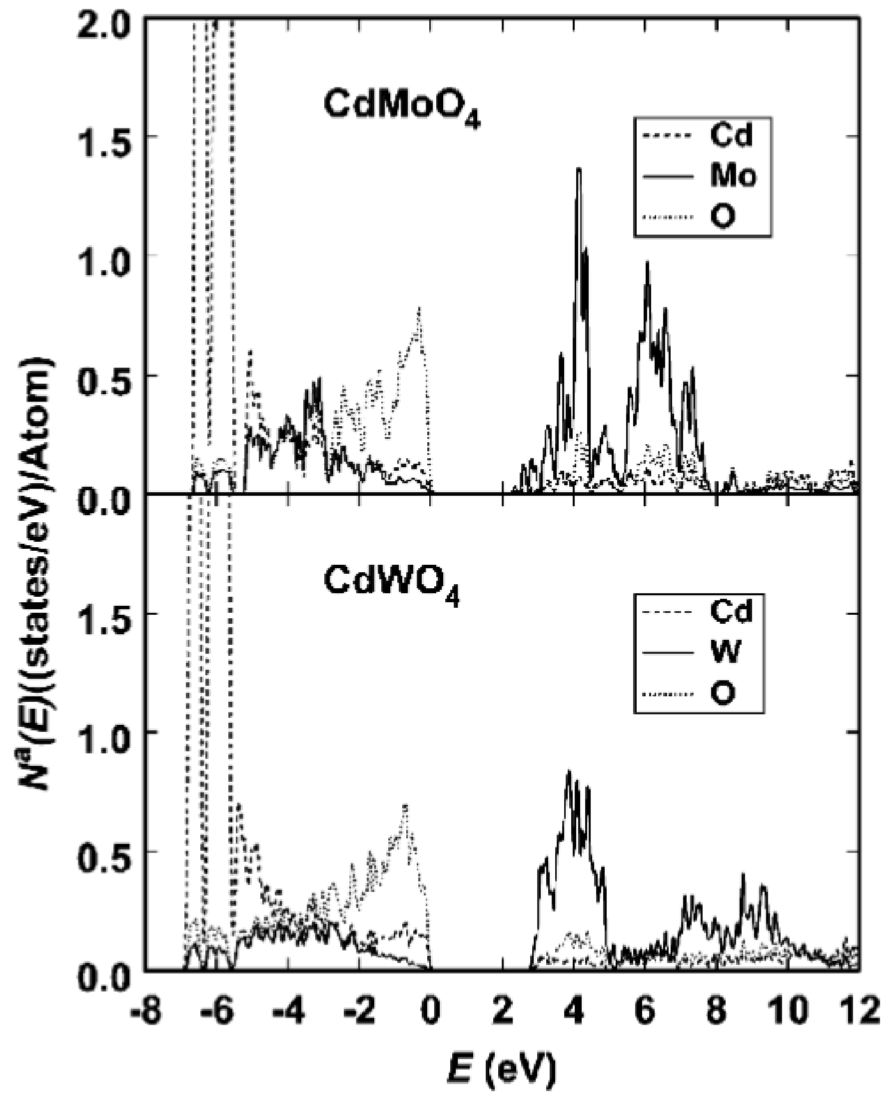


FIG. 2. Partial density-of-states for valence and conduction bands of $CdMoO_4$ and $CdWO_4$, indicating Cd, Mo or W, and O contributions with dashed, solid, and dotted lines, respectively.

Electronic structure of atoms and molecules

Each spatial state can accommodate up to 1 spin up state and 1 spin down state

Li atom