

ECE 162A  
Mat 162A

Lecture #15: Identical particles,  
multielectron atoms  
E/R: Chapter 9

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Lecture Today, Thursday, Friday (1 pm)

# Identical Particles

- In classical physics, particles can be followed, and hence labels can be attached to each.
- In quantum physics, measurable results obtained from calculations should not depend on the assignment of labels to identical particles.

# Example: Two identical particles in a box-no interaction between particles

$x_1$  The position of particle 1

$x_2$  The position of particle 2

$V(x_1, x_2) = 0$  for  $0 < x_1, x_2 < L$ ;  $\infty$  otherwise

$$\left[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right) + V(x_1, x_2) \right] \psi(x_1, x_2) = E \psi(x_1, x_2)$$

# Example: Two identical particles in a box-no interaction between particles

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$$\left[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right) + V(x_1, x_2) \right] \psi(x_1, x_2) = E \psi(x_1, x_2)$$

This is separable since  $V$  depends on only one particle at a time.

$$\psi(x_1, x_2) = \psi_{n_1}(x_1) \psi_{n_2}(x_2)$$

This can be substituted into SE, and the solution is

$$\psi_{n_1}(x_1) = A_1 \sin \frac{n_1 \pi x_1}{L}$$

$$\psi(x_1, x_2) = A_3 \sin \frac{n_1 \pi x_1}{L} \sin \frac{n_2 \pi x_2}{L}$$

But, this is not symmetric under exchange of  $1 \rightarrow 2$

# Example: Two identical particles in a box-no interaction between particles

$$\psi(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2)$$

This wavefunction is symmetric under exchange  $1 \rightarrow 2$

$$\psi_S(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_{n_1}(x_1)\psi_{n_2}(x_2) + \psi_{n_2}(x_1)\psi_{n_1}(x_2))$$

This wavefunction changes sign under exchange, so  $\psi^*\psi$  is the same under exchange.

$$\psi_A(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_2}(x_1)\psi_{n_1}(x_2))$$

# Pauli Exclusion Principle

- In a multielectron atom, there can never be more than one electron in the same quantum state.
- **Note that this is satisfied automatically by the antisymmetric state:**

$$\psi_{S_{n_1 n_1}}(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_{n_1}(x_1)\psi_{n_1}(x_2) + \psi_{n_1}(x_2)\psi_{n_1}(x_1)) = \sqrt{2}\psi_{n_1}(x_1)\psi_{n_1}(x_2)$$

$$\psi_{A_{n_1 n_1}}(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_{n_1}(x_1)\psi_{n_1}(x_2) - \psi_{n_1}(x_2)\psi_{n_1}(x_1)) = 0$$

- **A system containing several electrons must be described by an antisymmetric total eigenfunction.**

- Fermions: particles with half integral spin ( $1/2, 3/2, \dots$ ) such as electrons and protons. Fermions obey the Pauli exclusion principle and have antisymmetric wavefunctions.
- Bosons: particles with integral spin ( $0, 1, \dots$ ) such as photons, They need not obey the Pauli Exclusion Principle and have symmetric wavefunctions.

# Multi-Electron Wave-functions Independent Particle Approximation

For a system with two electrons:

Total Wave-function = (Spatial Component) X (Spin Component)

Independent electrons:

Spatial Component =  $\Psi_A(1) \times \Psi_B(2)$

- Separation of Variables can be applied to the two-particle Hamiltonian if electrons are independent
- Also a consequence of the fact that the joint distribution of two *independent* random variables is a product of their individual distributions



# Multi-Electron Wave-functions Independent Particle Approximation

For a system with two electrons:

Total Wave-function = (Spatial Component) X (Spin Component)

Independent electrons:

Spatial Component =  $\Psi_A(1) \times \Psi_B(2)$

- Labels (1) and (2) represent the two electrons
- A and B represent the energy levels they occupy respectively
- This state does not go into  $\pm$  itself on interchange of 1 and 2
- Problem: However, electrons are indistinguishable!
- $|\Psi|^2$  is physically measurable, must not depend on electron labeling

# Multi-Electron Wave-functions Independent Particle Approximation

Fix: Linear Combinations of Degenerate Solutions  
Spatial Component =  $(1/2)^{1/2} [\Psi_A(1) \Psi_B(2) \pm \Psi_B(1) \Psi_A(2) ]$

- Labels (1) and (2) represent the two electrons
- A and B represent the energy levels they occupy respectively
- This state goes into  $\pm$  itself on interchange of 1 and 2
- Both physically acceptable, one (+) symmetric and the other (-) anti-symmetric under exchange

# Multi-Electron Wave-functions Independent Particle Approximation

For a system with two electrons:

Total Wave-function = (Spatial Component) X (Spin Component)

## **Spin Component**

Terminology:  $|\frac{1}{2}, -\frac{1}{2}\rangle$

- Meaning: The first electron is spin-up, the second is spin-down
- Again there is lack of symmetry on exchange of particles 1 and 2

# Multi-Electron Wave-functions Independent Particle Approximation

Spin Component, Contd.

Problem: Lack of Exchange Symmetry

Fix:

- Spin-symmetric states – Triplet:

$$|\frac{1}{2}, \frac{1}{2} \rangle$$

$$|-\frac{1}{2}, -\frac{1}{2} \rangle$$

$$(1/2)^{1/2} [ |\frac{1}{2}, -\frac{1}{2} \rangle + |-\frac{1}{2}, \frac{1}{2} \rangle ]$$

- Spin-anti-symmetric state:  $(1/2)^{1/2} [ |\frac{1}{2}, -\frac{1}{2} \rangle - |-\frac{1}{2}, \frac{1}{2} \rangle ]$

# Hartree Theory

- Multielectron atomic theory
- First consider a nuclear attractive coulombic force:  $+Ze$
- Include the coulombic repulsion due to the average position of other electrons:  $-(Z-1)e$
- Assume each electron moves independently of each other.
- Schroedinger's equation becomes separable into  $Z$  separate equations for the motion of each electron:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V(r)\psi = E\psi$$

# What is $V(r)$ ?

- First guess:

- For  $r \rightarrow 0$ ,

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

- For  $r \rightarrow \text{infinity}$

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

- Then, solve SE and calculate  $V(r)$

# Hartree Solution

- Assume  $V(r)$  (previous slide)
- Calculate the solutions

$$\psi_\alpha(r, \theta, \phi), \psi_\beta(r, \theta, \phi), \psi_\gamma(r, \theta, \phi), \dots$$

with energies

$$E_\alpha, E_\beta, E_\gamma, \dots$$

- Put one electron in each state. Soln is the product of one electron states.

$$\psi = \psi_\alpha(r_1, \theta_1, \phi_1), \psi_\beta(r_2, \theta_2, \phi_2), \psi_\gamma(r_3, \theta_3, \phi_3), \dots$$

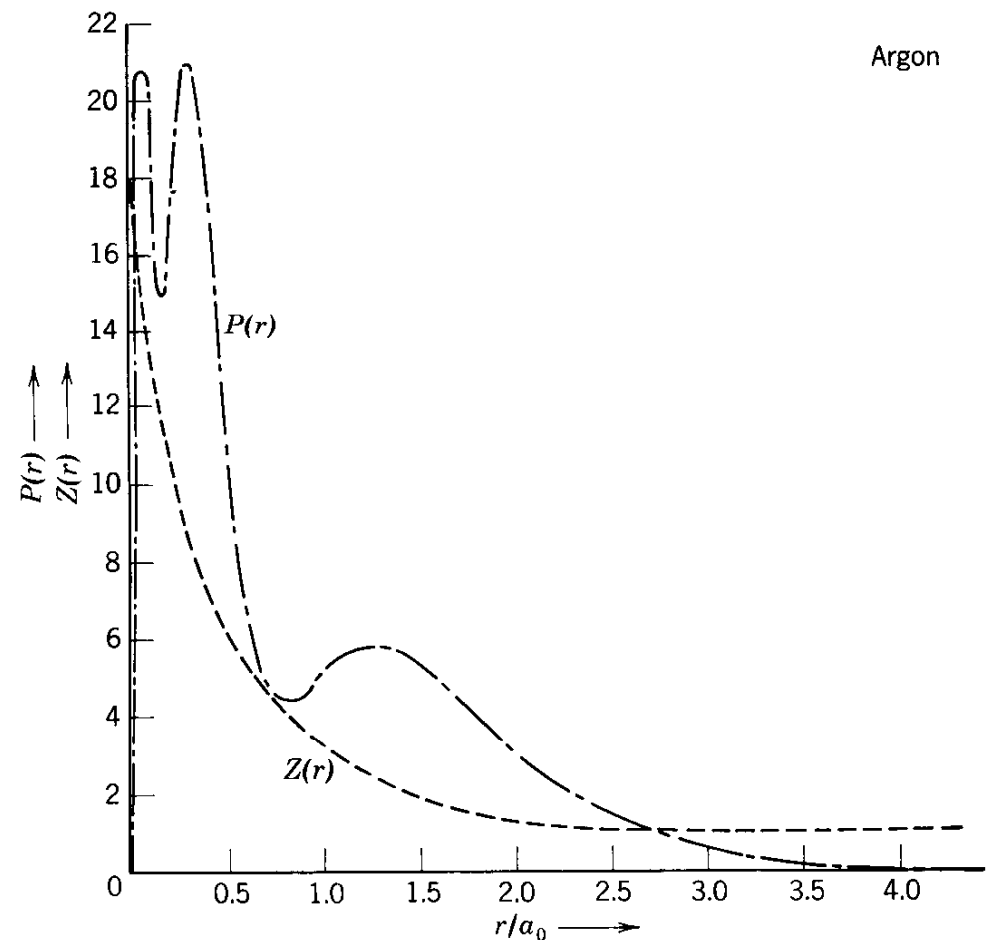
- Note:  $\alpha, \beta, \gamma$  includes space and spin

$$\alpha : |n = 1; l = 0; m_l = 0, \uparrow\rangle$$

$$\beta : |n = 1; l = 0; m_l = 0, \downarrow\rangle$$

# Hartree Solution (cont)

- Use  $\psi^*\psi$  to calculate  $V(r)$
- Iterate:
  - Soln SE using new  $V(r)$
  - Put one electron in each state to assemble  $\psi$
  - Calculate  $V(r)$





# Hartree Fock Theory

- Hartree theory ignores the requirement of antisymmetric wave functions.
- Fock included this.
- For a N electron atom, N! terms are added in the expression for  $\psi$  (It is an N dimensional Slater determinant).
- The effect is only significant for the valence electrons.

# $\Theta$ - $\phi$ Dependence

- The  $\Theta$ - $\phi$  dependence is the same as for the hydrogen atom since we didn't assume anything for the form of  $V(r)$ .

# Solution to SE in Spherical Coordinates

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

$$\text{If } V(r, \theta, \phi) = V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

*Then try separation of variables*

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

*Substitute and divide by  $R\Theta\Phi$*

$$-\frac{\hbar^2}{2mR} \left( \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) \right) + \frac{1}{\Theta r^2 \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi r^2 \sin^2 \theta} \frac{d^2\Phi}{d^2\phi} + V(r) = E$$

# Separate $\phi$ dependence

*Rearrange :*

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d^2 \phi} = -\frac{2mr^2 \sin^2 \theta}{\hbar^2} (E - V(r)) - \frac{\sin^2 \theta}{R} \left( \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) \right) - \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right)$$

*LHS is a function of  $\phi$  only.*

**No assumption on the form of  $V(r)$ !**

# Solution of $\Phi$

No assumption on the form of  $V(r)$ !

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d^2 \phi} = -m_l^2$$

$$\Phi = A e^{im_l \phi}$$

*Single valued means*

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

*Which means  $m$  is an integer.*

# Separation of $r$ and $\theta$

$$-m_l^2 = -\frac{2mr^2 \sin^2 \theta}{\hbar^2} (E - V(r)) - \frac{\sin^2 \theta}{R} \left( \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) \right) - \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right)$$

*Rearrange:*

$$-\frac{2mr^2}{\hbar^2} (E - V(r)) + \frac{1}{R} \left( \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) \right) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) \equiv l(l+1)$$

*LHS is a function of  $r$  only and RHS is a function of  $\theta$  only.*

**No assumption on the form of  $V(r)$ !**

# Solution of $\Theta$

$$\frac{m_l^2 \Theta}{\sin^2 \theta} - \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) = l(l+1)\Theta$$

The solution is in Appendix N.

Use a power series expansion in  $\cos \theta$ .

The series terminates for

$$l = |m_l|, |m_l + 1|, \dots$$

$$\Theta = \sin^{m_l} \theta F_{lm_l}(\cos \theta)$$

**No assumption on the form of  $V(r)$ !**

# Results of Hartree Theory

- Eigenfunctions labeled by  $n, l, m, m_l, m_s$
- ( $E$  will not be given by  $E_0/n^2$ )
- Important for solid state physics.
- Numerical calculation programs exist for Hartree and Hartree-Fock



# Labeling of energy levels (shells)

- $N=1, l=0$       1s      2 states (up, down) H, He

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- $N=2, l=1$       2p      6 states ( $2 \times (m_l = -1, 0, 1)$ )  
B, C, N, O, F, Ne

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- $N=3, l=0$       3s      2 states ( $2 \times (m_l = 0)$ )

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# Order and Labeling of energy levels (shells)

- $N=1, l=0$       1s      2 states (up, down) H,He
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- $N=3, l=1$       3p      6 states ( $2 \times (m_l = -1, 0, 1)$ )
- **$N=4, l=0$**       **4s**      **2 states ( $2 \times (m_l = 0)$ )**
- $N=3, l=2$       3d      10 states ( $2 \times (m_l = -2, -1, 0, 1, 2)$ )
- $N=4, l=1$       4p      6 states ( $2 \times (m_l = -1, 0, 1)$ )

# Order and Labeling of energy levels (shells)

- $N=1, l=0$       1s      2 states
- $N=2, l=0$       2s      2 states
- $N=2, l=1$       2p      6 states
- $N=3, l=0$       3s      2 states
- $N=3, l=1$       3p      6 states
- **$N=4, l=0$**       **4s**      **2 states**
- $N=3, l=2$       3d      10 states
- $N=4, l=1$       4p      6 states
- $N=5, l=0$       5s      2 states
- $N=5, l=1$       5p      6 states
- $N=6, l=0$       6s      2 states
- $N=4, l=3$       4f      14 states

# Chemistry

- Inner electrons affected by nucleus, not other atoms
- Outer electrons see a potential of  $+e$  or  $+2e$  and are affected by adjacent atoms.
- The outer electrons are called valence electrons and are involved in bonding to other atoms.
- Atoms with the same valence structure behave similarly chemically.

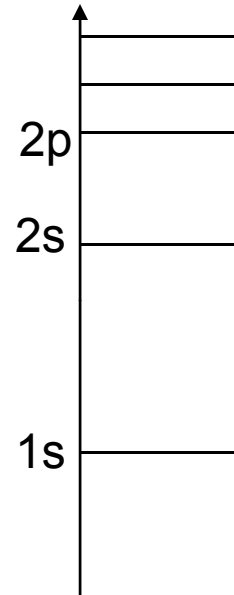


# Periodic Table (Mendeleev in 1869)

1s	1 H											2 He																					
2s	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne															
3s	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar															
4s	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr $4s^1 3d^5$	25 Mn	26 Fe	27 Co	28 Ni	29 Cu $4s^1 3d^{10}$	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr															
5s	37 Rb	38 Sr	39 Y	40 Zr	41 Nb $5s^1 4d^4$	42 Mo	43 Tc	44 Ru $5s^1 4d^7$	45 Rh $5s^1 4d^8$	46 Pd $5s^0 4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe															
6s	55 Cs	56 Ba	57 La Lanthanides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt $6s^1 5d^9$	79 Au $6s^1 5d^{10}$	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn															
7s	87 Fr	88 Ra	89 Ac Actinides																														
$s^1$	$s^2$											$p^1$	$p^2$	$p^3$	$p^4$	$p^5$	$p^6$																
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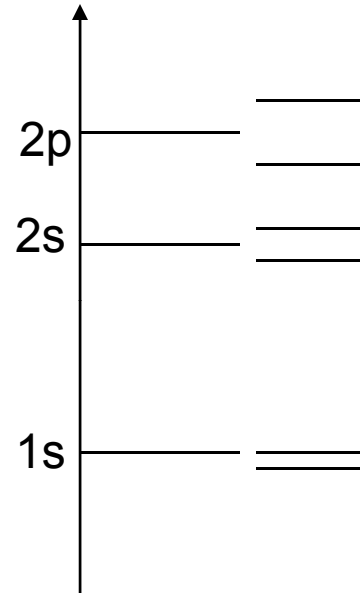
# Band Theory of Solids

- Isolated atom (B)



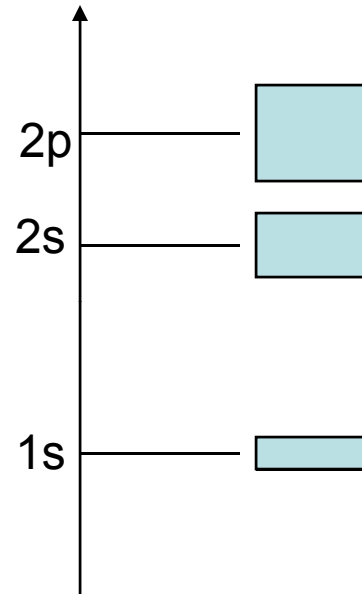
# Band Theory of Solids

- Isolated  $\rightarrow$  2 atoms



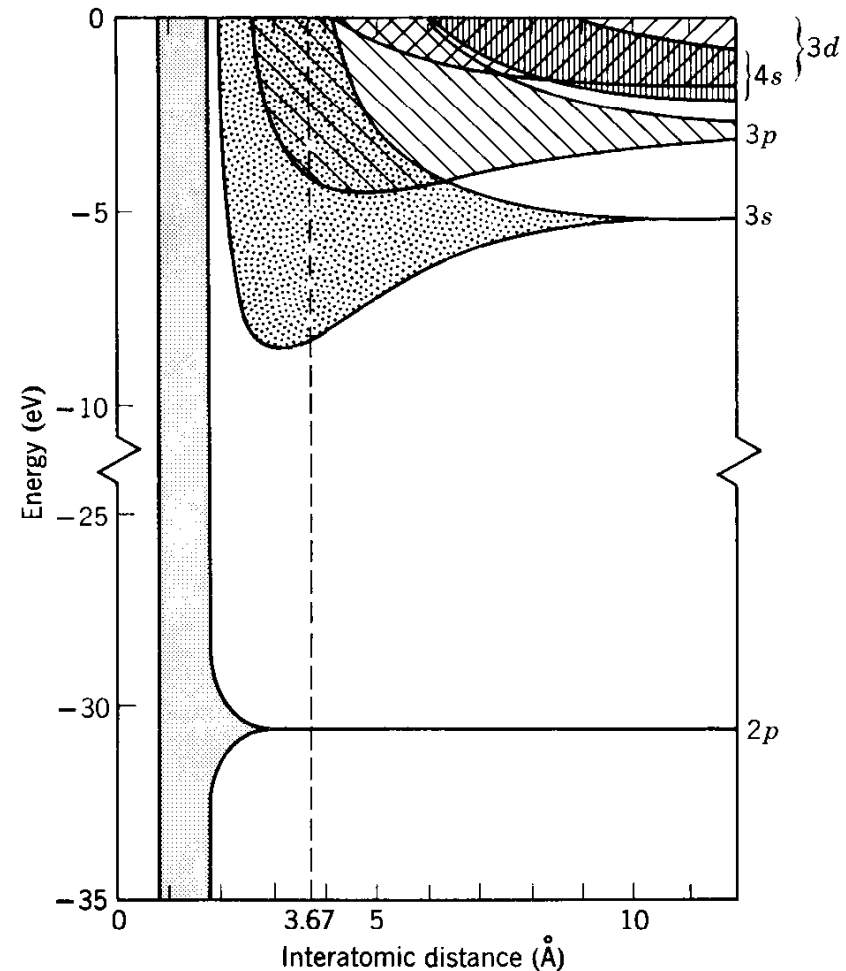
# Band Theory of Solids

- Isolated  $\rightarrow$  solid
- Splitting higher for outer electrons; more overlap.
- Splitting increases as the separation decreases.



# Energy Bands

- Bands that originate from closed shells (e.g. 1s, 2s for boron) have filled bands
- Shells that are partially filled result in bands that are partially filled.
- Filled bands give insulators
- Partially filled bands give metals.
- Filled bands with empty bands close by (0.1 to 3 eV) are called semiconductors.
- Materials with odd number of electrons/atom are always metals.



# Quantum Statistics

- How are electrons distributed versus energy?
- Classical answer: Maxwell Boltzman distribution

$$P(E) = Ae^{-E/kT}$$

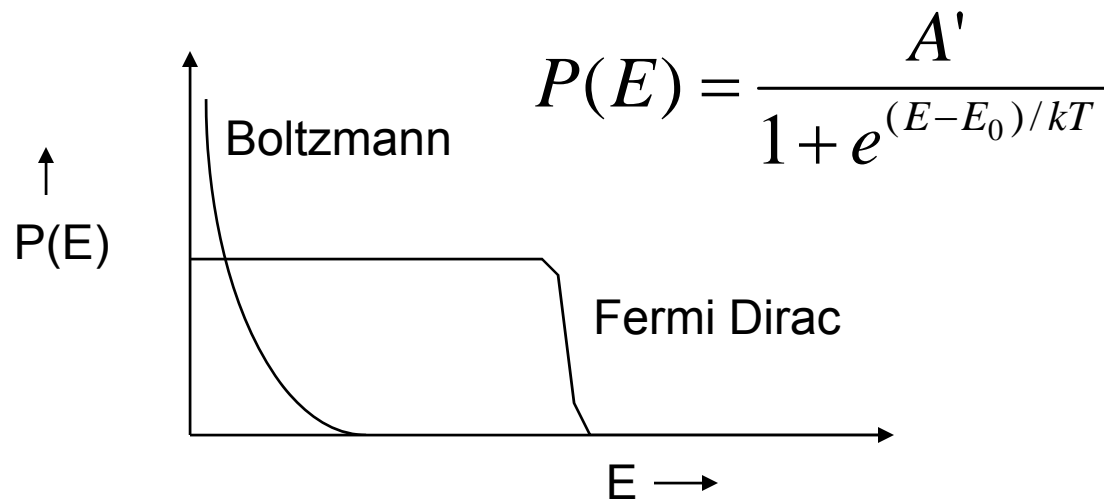
- However, this has most electrons at low energies, which violates the Pauli exclusion principle.

# Quantum Statistics

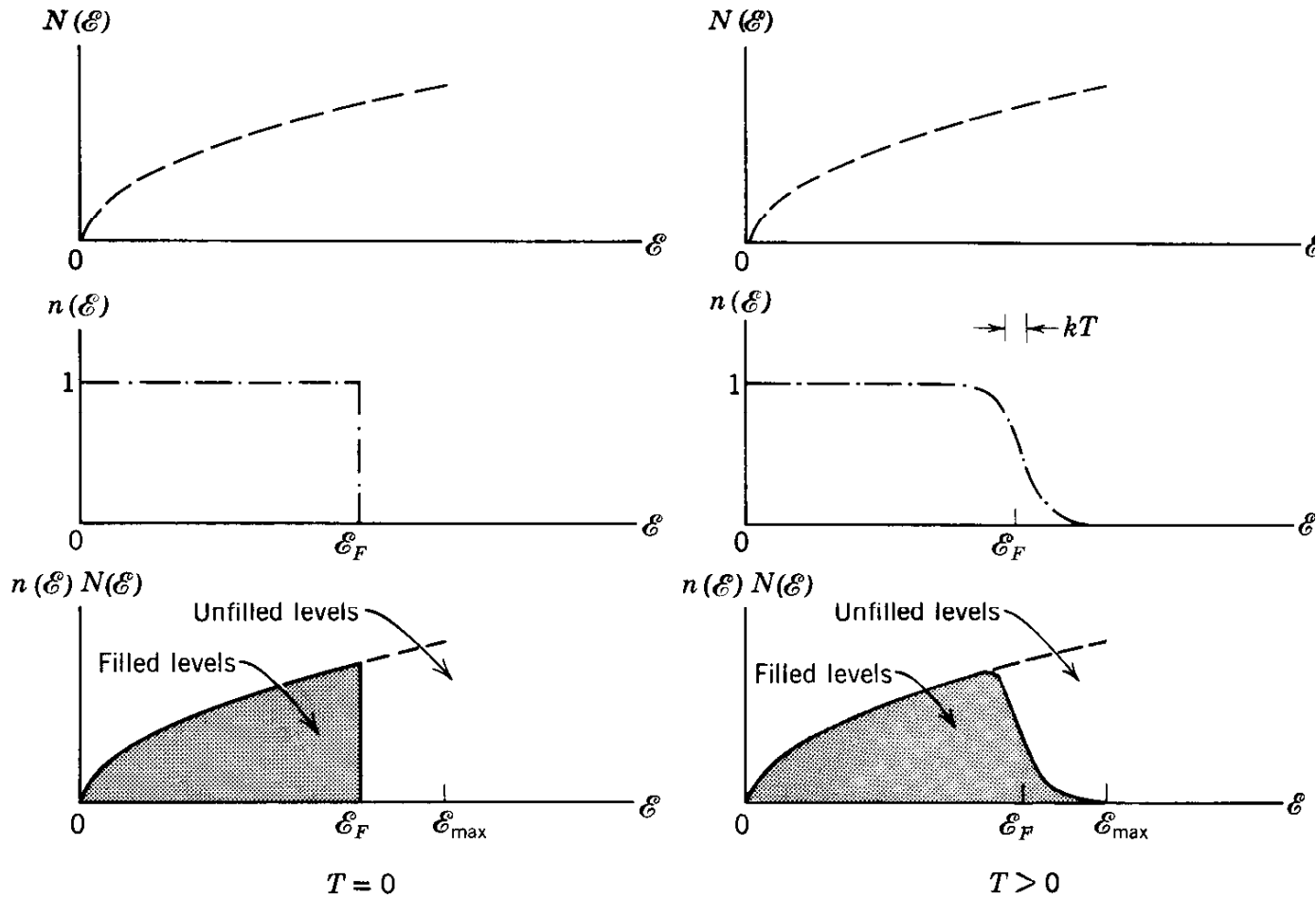
- How are electrons distributed versus energy?
- Classical answer: Maxwell Boltzman distribution

$$P(E) = Ae^{-E/kT}$$

- Quantum mechanical answer: Fermi Dirac distribution



# Electron distribution



$$n = \int_{-\infty}^{\infty} dE N(E) f(E)$$



# Conduction

- A filled band has no net current flow. For every electron going in one direction, there is an electron going in the opposite direction.
- In general (for electron conduction only),

$$n = \int_{-\infty}^{\infty} dE N(E) f(E)$$

$$j = env$$