Quantum mechanics

School of Physics and Information Technology

Shaanxi Normal University

Chapter 5

IDENTICAL PARTICLES

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5.1 Two-Particle System

For a single particle, is a function of the spatial coordinates **r** and the time *t* (here now we ignore the spin). The wave function for a *two*-particle system is a function of the coordinates of particle one ($\mathbf{r}_1$), the coordinates of particle two ($\mathbf{r}_2$), and the time:

Its time evolution is determined by the Schrodinger equation:

where *H* is the Hamiltonian for the whole system:

the subscript on ∇ indicates differentiation with respect to the coordinates of particle 1 or particle 2).

The statistical interpretation carries over in the obvious way:

is the probability of finding particle 1 in the volume $d^3\mathbf{r}_2$ and particle 2 in the volume $d^3\mathbf{r}_1$; evidently must be normalized in such a way that

For time-independent potentials, we obtain a complete set of solutions by separation of variables:

where the spatial wave function satisfies the time-independent Schrodinger equation, with E the total energy of the system,

5.1.1 Bosons and Fermions

Suppose particle 1 is in the (single-particle) state , and particle 2 is in the state . In that case is a simple conduct

Of course, this assumes that we can tell the particles apart. In quantum mechanics, all we could say is that one of the particle is in the state and the other is in the state of . In classical mechanics, we can always discriminate them from each other. In microscopic world, the fact is , all the electrons are *utterly* identical, in a way that no two classical objects can ever be.

Quantum mechanics neatly accommodates the existence of particles that are *indistinguishable in principle*: We simply construct a wave function that is *noncommittal* as to which particle is in which state. There are actually *two* ways to do it:

Thus the theory admits two kinds of identical particles: **bosons**, for which we use the plus sign, and **fermions**, for which we use the minus sign. Photons and mesons are bosons; protons and electrons are fermions. It so happens that

- all particles with **integer spins** are bosons, and
- all particles with **half-integer spins** are fermions.

Further, bosons and fermions have quite different statistical properties. The connection between spin and "statistics" can be proved in relativistic quantum mechanics; in non-relativistic theory it must be taken as an axiom.

It follows, in particular, that two identical fermions (for example, two electrons) cannot occupy the same state. For if , then

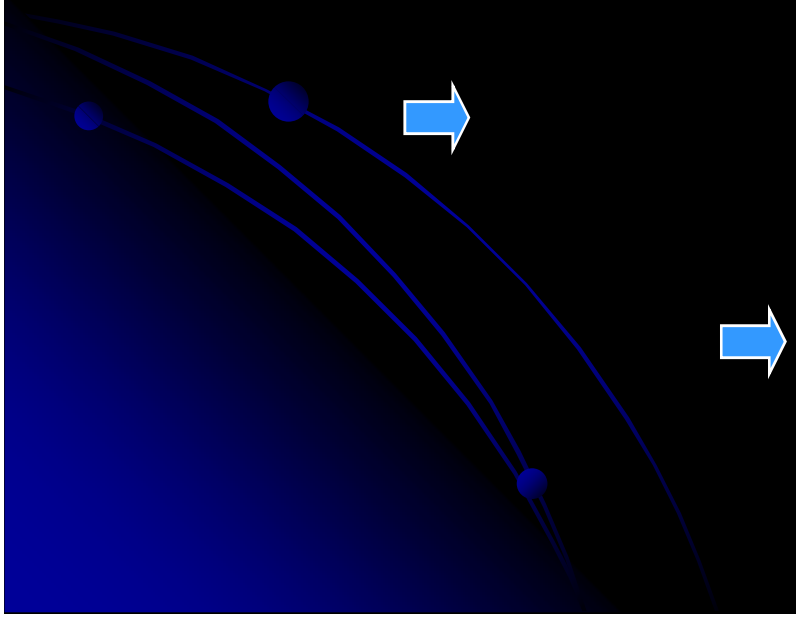
and we have left with no wave function at all. This is the famous ***Pauli exclusion principle.***

Another general way to formulate this problem: bosons and fermions

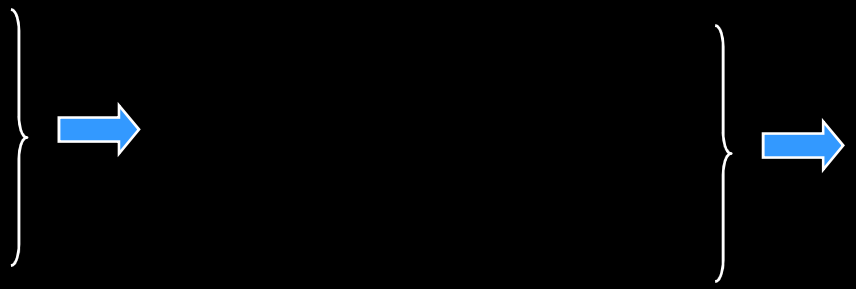
Let us define the exchange operator, P, which interchanges the two particles:

Clearly, $P^2=1$, and it follows that the eigenvalues of P are ± 1.

Now, if the two particles are identical, the Hamiltonian must treat tem the same:



Then we have, for any state



It follows that *P* and *H* are compatible observables,

and hence we can find a complete set of functions that are simultaneous eigenstates of both. That is to say, we can find solutions to the Schrodinger equation that are either symmetric or antisymmetric under exchange:

Moreover, if the system starts out in such a state, it will remain in such a state.

If for bosons

If for fermions

This is the symmetrization requirement of identical particles, and this is a general statement of bosons and fermions.

Example 5.1. On the book!

5.1.2 Exchange Forces

To give you some sense of what the symmetrization requirement actually does. Here we work out the simple one-dimensional example below. Suppose particle is in the (single-particle) state , and the other particle is in the state , and these two states are orthogonal and normalized. If the two particles are distinguishable, and number 1 is the one in state , then the combined wave function is

If they are identical **bosons**, the composite wave function is

and if they are identical **fermions**, it is

Let calculate the expectation value of the square of the separation distance between the two particles,

(1) Distinguishable particles.

For the wave function

Similarly,

and

In this case, then

If the states of two particles exchange, the answer will be the same.

(2) Identical particles (bosons and fermions).

For the wave function (Bosons + and fermions -)

$$|\psi_{\pm}(x_1, x_2)|^2 =$$

Similarly,

Naturally, , since we can’t tell them apart.

But

where

Evidently

Comparing the two cases, we see that the difference resides in the final term:

(Bosons - and fermions +)

(Bosons - and fermions +)

Discussion:

(1) Identical bosons tend to be somewhat closer together, and identical fermions somewhat father apart, than distinguishable particles in the same two states.

(2) Exchange force.

The system behaves as though there were a "force of attraction" between identical bosons, pulling them closer together, and a "force of repulsion" between identical fermions, pushing them apart (remember that we are for the moment ignoring spin). We call it an *exchange force*, although it's not really a force at all-----no physical agency is pushing on the particles; rather, it is a purely geometrical consequence of the symmetrization requirement. It is also a strictly quantum mechanical phenomenon, with no classical counterpart.

(Bosons + and fermions -)

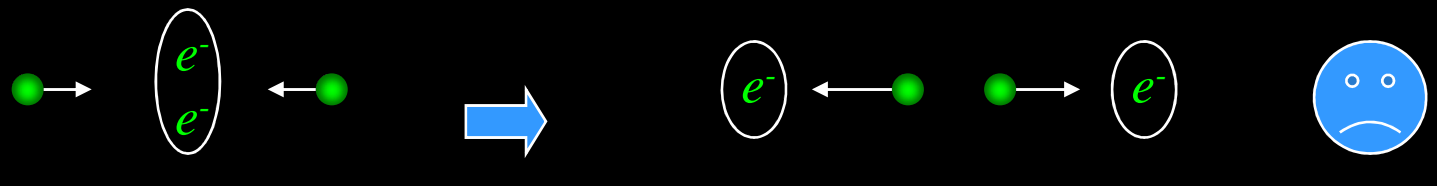
(3) Notice that $\langle x \rangle_{ab}$ vanishes unless the two wave functions overlap.

That is, if two particles are too far away, the difference between

, no matter bosons or fermions of the two particles is.

That is natural that, when two particles are very far away, the two particles become classical particles that can be distinguished.

(4) Effect: The symmetrization requirement on Hydrogen molecule (H_2)



bosons ⟶ fermions

?

Covalent bond 共价键

We have been ignoring spin. The complete state of the electron includes not only its position wave function, but also a spinor, describing the orientation of its spin:

antisymmetric

Triplet states: symmetric spin state

Antisymmetric spatial state

} antibonding

Singlet state: antisymmetric spin state

Symmetric spatial state

} *bonding*

5.2 Atoms

A neutral atom, of atomic number Z, consists of a heavy nucleus, with electric charge Ze, surrounded by Z electrons (mass m and charge $-e$). The Hamiltonian for this system is

[5.24]

The term in curly brackets represents the kinetic plus potential energy of the jth electron, in the electric field of the nucleus; the second sum (which runs over all values of j and k except $j=k$) is the potential energy associated with the mutual repulsion of the electrons (the factor of 1/2 in front corrects for the fact that summation counts each pair twice).

The problem is to solve Schrödinger's equation,

for the wave function .

Because the electrons are identical fermions, however, not all solutions are acceptable: only those for which the complete state (position and spin),

is *antisymmetric* with respect to interchange of any two electrons. In particular, no two electrons can occupy the *same* state.

Unfortunately, the Schrodinger equation with Hamiltonian in Equation 5.24 cannot be solved exactly (at any rate, it *hasn't* been), except for the very simplest case, $Z=1$ (hydrogen). In practice, one must resort to elaborate approximation methods. Some of these we shall explore in Part II. Now we plan only to sketch some qualitative features of the solutions, obtained by neglecting the electron repulsion term altogether.

In section 5.2.1 we study the ground state and excited states of helium.

In section 5.2.2 we will examine the ground states of higher atoms.

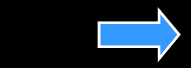
5.2.1 Helium

After hydrogen, the simplest atom is helium ($Z=1$). The Hamiltonian,

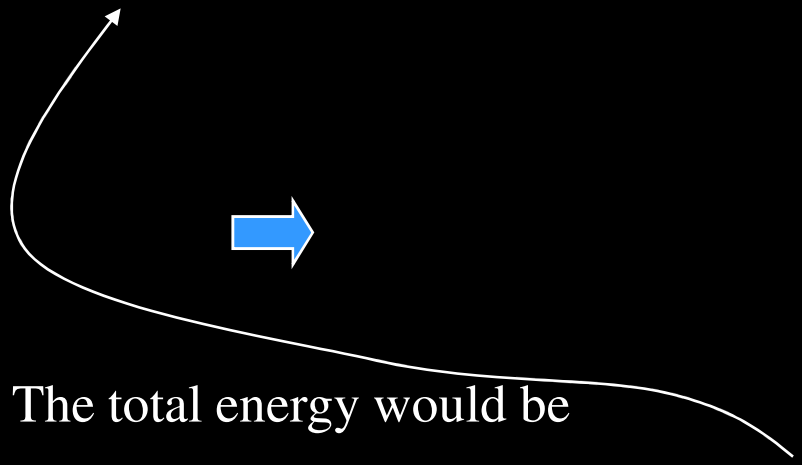
consists of two hydrogenic Hamiltonians (with nuclear charge $2e$), one for electron 1 and one for electron 2, together with a final term describing the repulsion of the two electrons. It is the last term that causes the trouble. If we simply ignore it, the Schrodinger equation separates, and the solutions can be written as products of hydrogen wave functions:

with half the Bohr radius,

$$a = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$



and four times the Bohr energies



The total energy would be

(1) In particular, the ground state would be

and its energy would be

Because the ground state is a symmetric function, the spin state has to be *antisymmetric*, so the ground state of helium should be a *singlet* configuration, which the spins "oppositely aligned". The actual ground state of helium is indeed a singlet, but the experimentally determined energy is –78.975 *eV*, so the agreement is not very good.

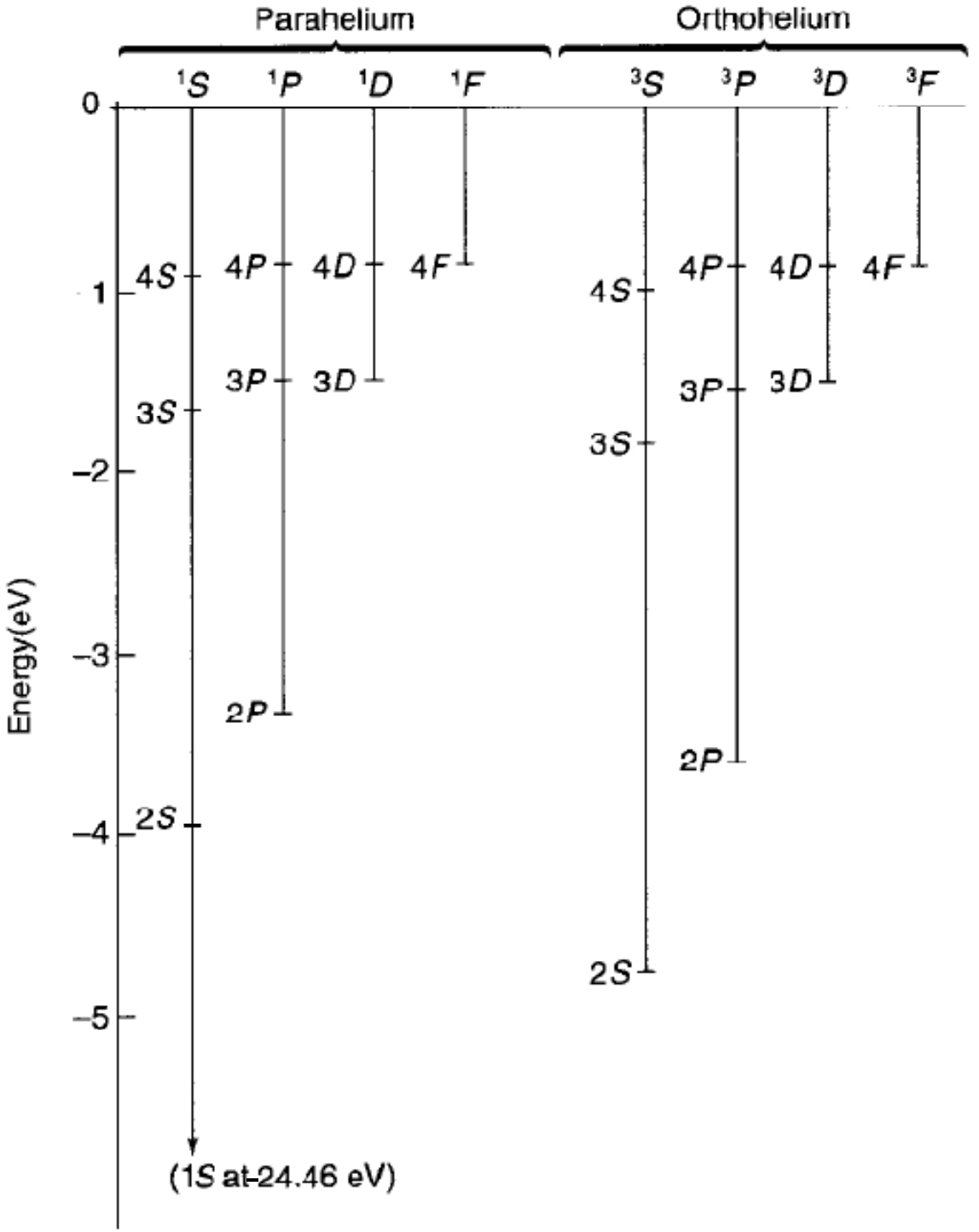
(2) The excited state

The excited states of helium consist of one electron in the hydrogenic ground state, and the other in an excited state:

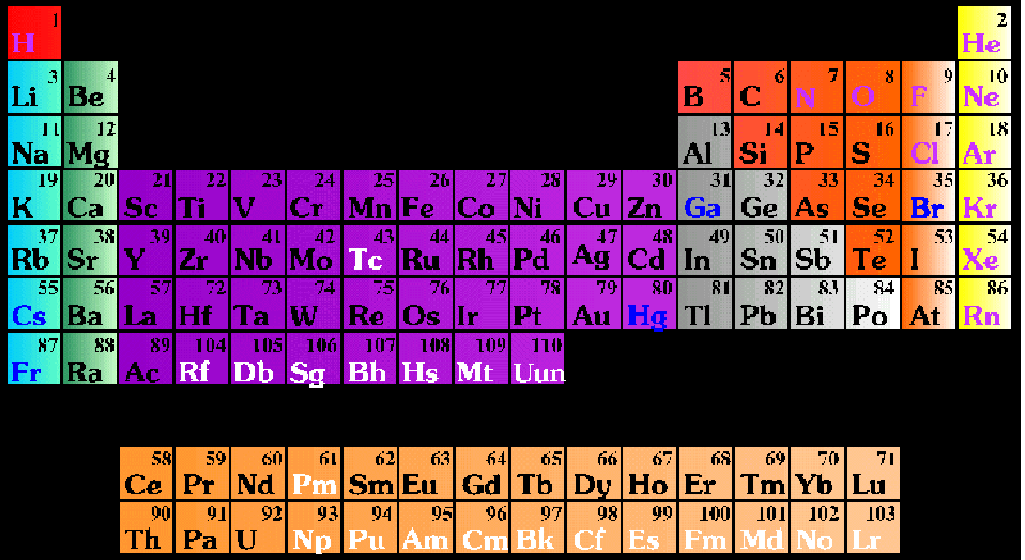
In this case, we can construct both symmetric and antisymmetric combinations, in the usual way;

The former go with the antisymmetric spin configuration (the singlet), and they are called *parahelium*, while the latter require a symmetric spin configuration (the triplet), and they are known as *orthohelium*.

The ground state is necessarily parahelium; the excited states come in both forms. Because the symmetric spatial state brings the electrons closer together, we expect a higher interaction energy in parahelium, and indeed, it is experimentally confirmed that the parahelium states have somewhat higher energy than their orthohelium counterparts.



5.2.2 The Periodic Table



The heavier atom: $Z > 2$

Ignoring the mutual repulsion between electrons.

The individual electrons occupy one-particle hydrogenic state—orbitals

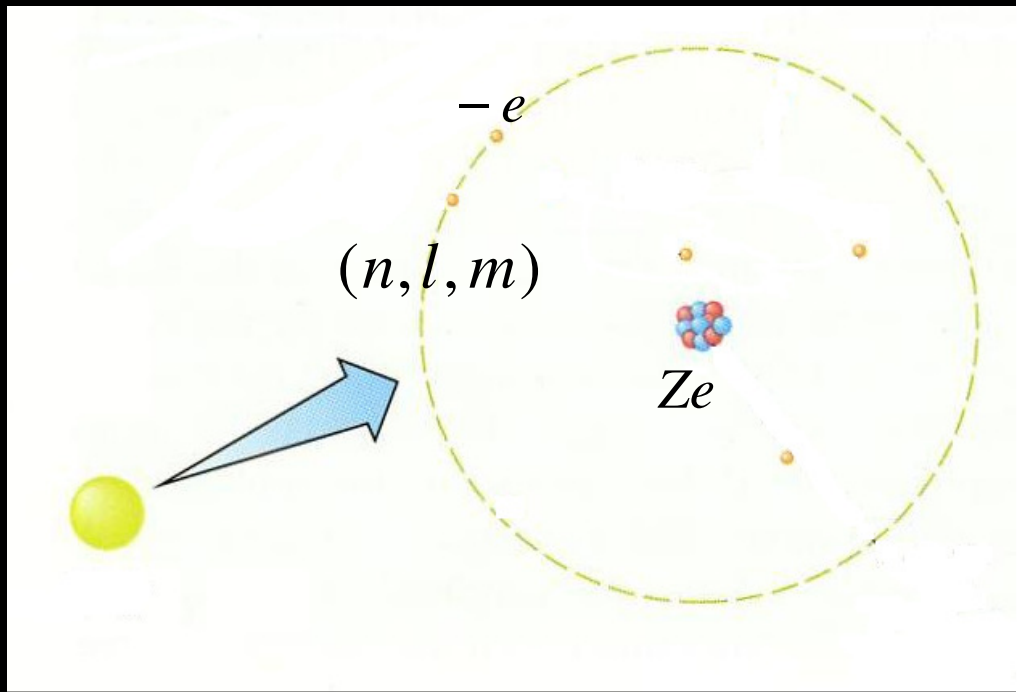
⟶

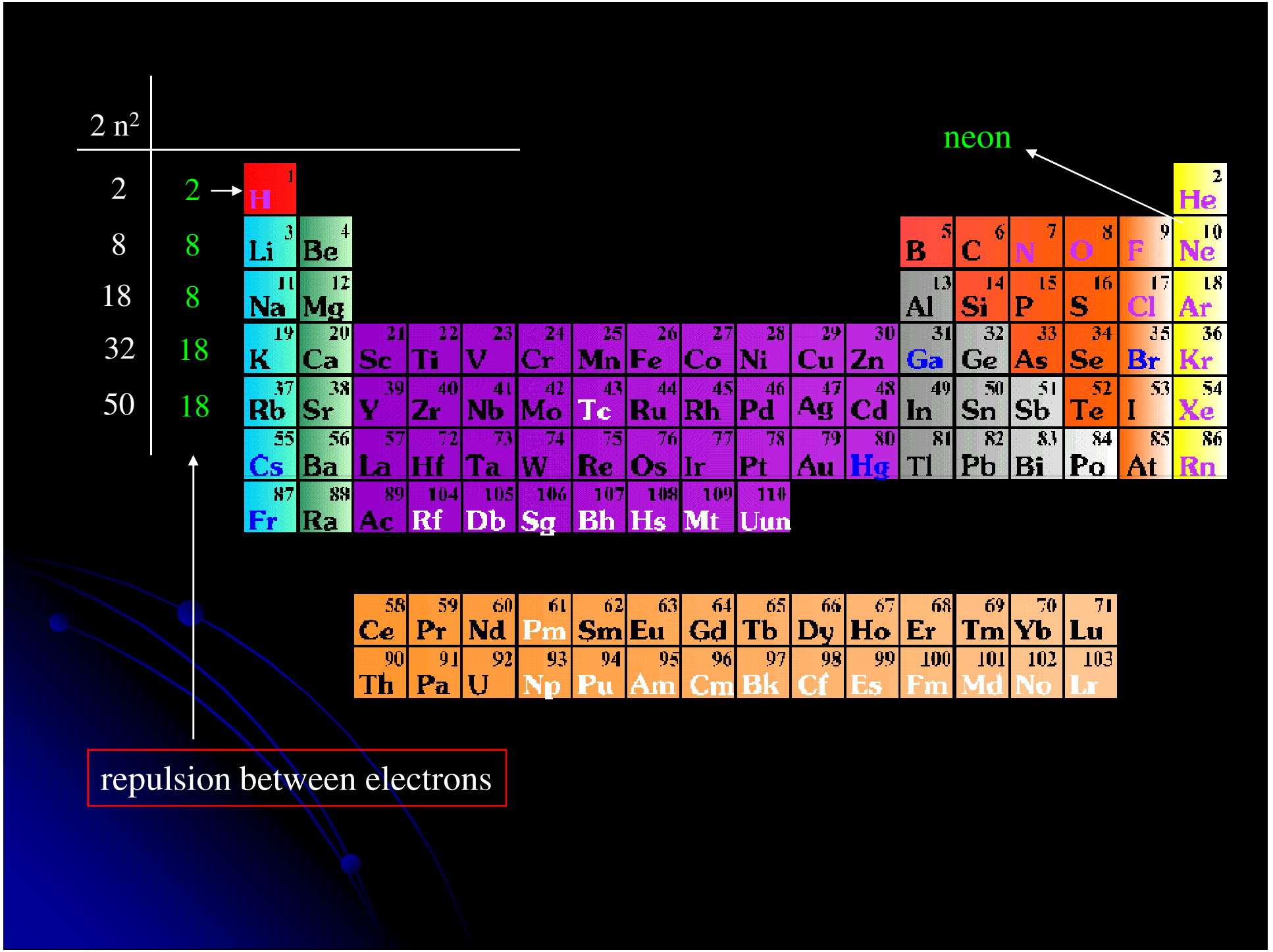
Pauli exclusion principle:

Only two electron can occupy one orbital

(P152 4.85)

*n*th *shell* ⇨




2 n²
2
8
18
32
50
2
8
8
18
18
neon
H 1
He 2
Li 3
Be 4
B 5
C 6
N 7
O 8
F 9
Ne 10
Na 11
Mg 12
Al 13
Si 14
P 15
S 16
Cl 17
Ar 18
K 19
Ca 20
Sc 21
Ti 22
V 23
Cr 24
Mn 25
Fe 26
Co 27
Ni 28
Cu 29
Zn 30
Ga 31
Ge 32
As 33
Se 34
Br 35
Kr 36
Rb 37
Sr 38
Y 39
Zr 40
Nb 41
Mo 42
Tc 43
Ru 44
Rh 45
Pd 46
Ag 47
Cd 48
In 49
Sn 50
Sb 51
Te 52
I 53
Xe 54
Cs 55
Ba 56
La 57
Hf 72
Ta 73
W 74
Re 75
Os 76
Ir 77
Pt 78
Au 79
Hg 80
Tl 81
Pb 82
Bi 83
Po 84
At 85
Rn 86
Fr 87
Ra 88
Ac 89
Rf 104
Db 105
Sg 106
Bh 107
Hs 108
Mt 109
Uun 110
Ce 58
Pr 59
Nd 60
Pm 61
Sm 62
Eu 63
Gd 64
Tb 65
Dy 66
Ho 67
Er 68
Tm 69
Yb 70
Lu 71
Th 90
Pa 91
U 92
Np 93
Pu 94
Am 95
Cm 96
Bk 97
Cf 98
Es 99
Fm 100
Md 101
No 102
Lr 103
repulsion between electrons

Occupation-filling rules:

(1) Helium, $Z=2$: two electrons ⇨ the $n=1$ shell is filled.

(2) Lithium, $Z=3$:

three electrons ⇨ The $n=1$ shell is filled with two, the other electron must be put into the $n=2$ shell.

$n=2$ ⇨ $l=1$, or $l=0$. ? electron repulsion ⇨ $l=0$

Within a given shell, the state with lowest energy is $l=0$, and the energy increases with increasing l.

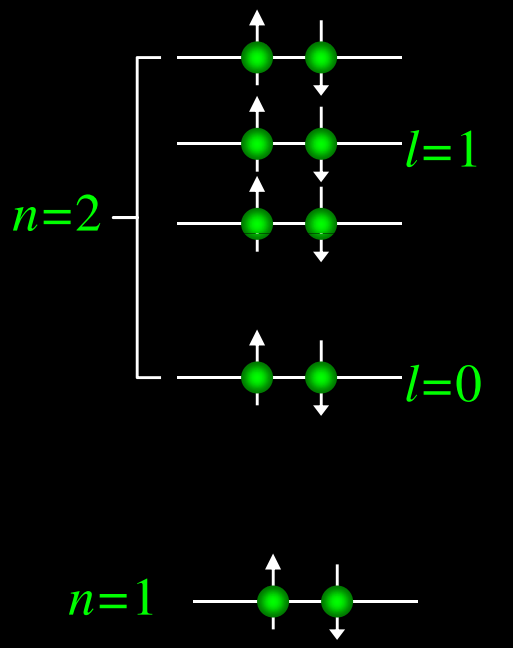
The third electron ⇨

(3) Beryllium, $Z=4$:

The third electron ⇨ Spin up

The fourth electron ⇨ Spin down

(4) Boron, $Z=5$: The fifth electron ⇨ $l=1$



(5) Neon, $Z=10$: $n=1$and $n=2$ shells are all filled.

(6) Sodium and magnesium: $Z=11,12$

Sodium

magnesium

Aluminum $Z=13$— Argon $Z=18$

Potassium $Z=19$

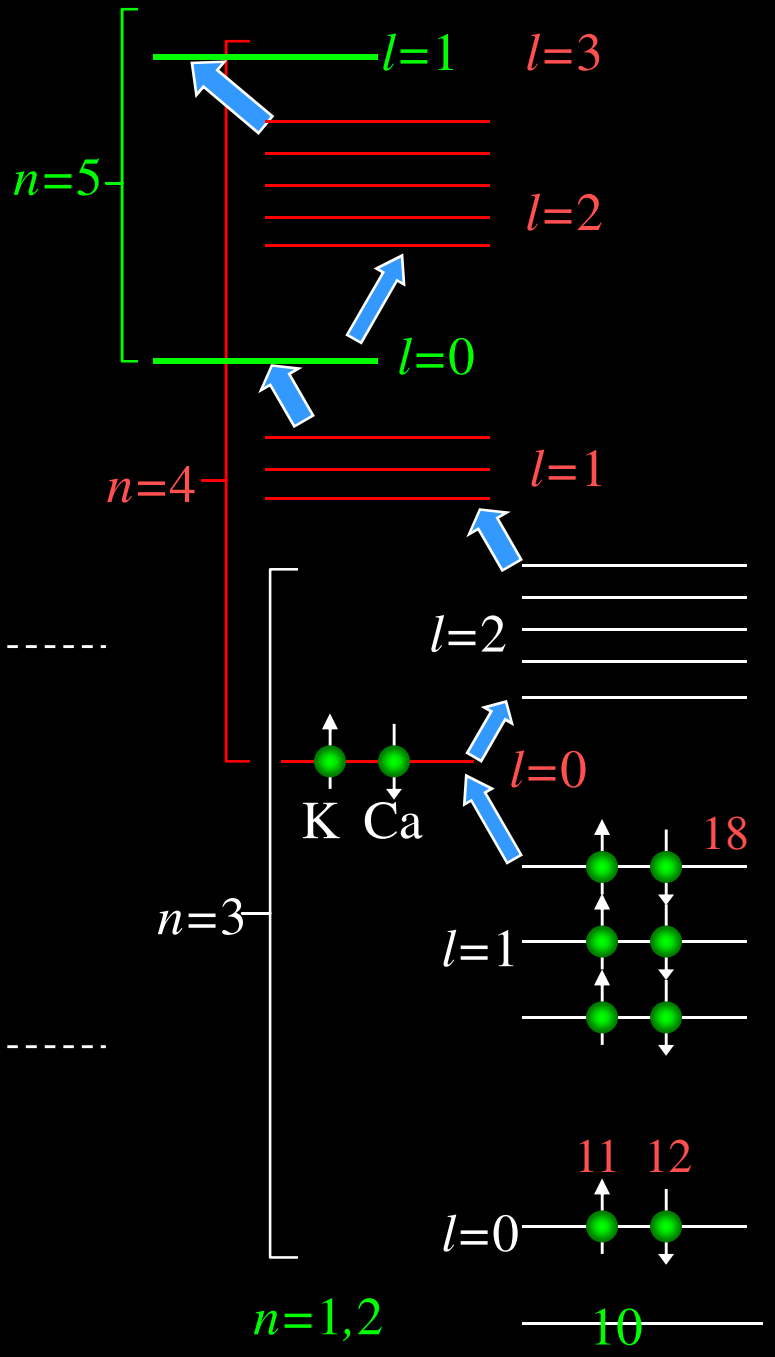
Calcium $Z=20$

Scandium $Z=21$— Zinc $Z=30$

Gallium $Z=31$— Krypton $Z=36$

Rubidium $Z=37$

Strontium $Z=38$



Nomenclature for atomic states:

shell	angular	magnetic
$n=1$ shell is called K	$l=0$ is called s (for "sharp")	not listed
$n=2$ shell is called L	$l=1$ is called p (for "principle")	
$n=3$ shell is called M	$l=2$ is called d (for "diffuse")	
$n=4$ shell is called N	$l=3$ is called f (for "fundamental")	
	$l=4$ is called g (out of imagination)	
	$l=5$ is called h	
	$l=6$ is called i	
	$l=7$ is called k	

The state of a particular electron is represented by the pair n,l, with n (the number) giving the shell and l (the letter) specifying the orbital angular momentum; the magnetic quantum number m is not listed, but an *exponent* is used to indicate the number of electrons that occupy the state in question.

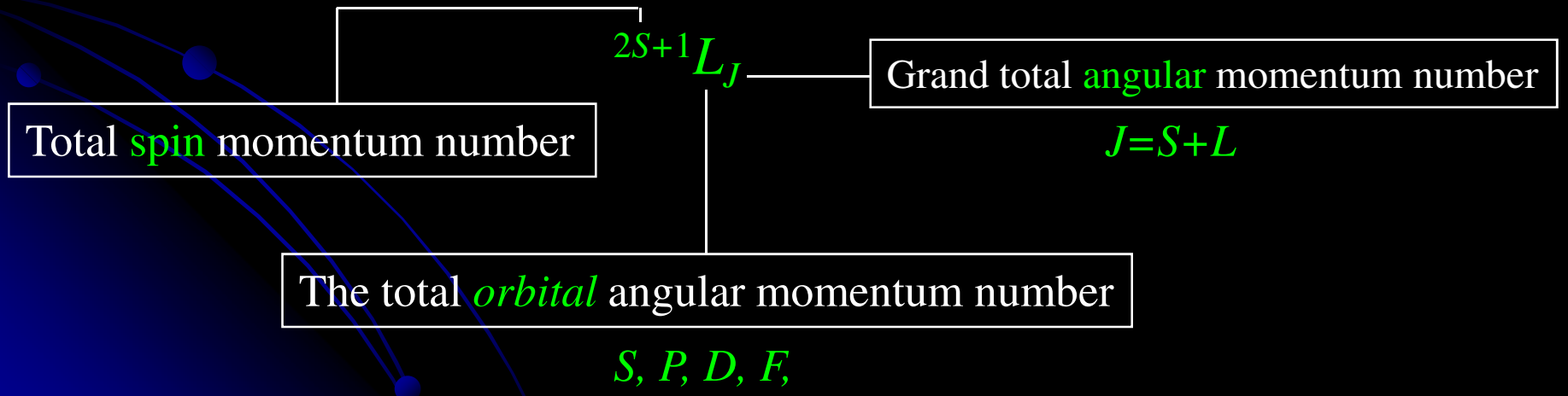
for example $(3d)^2$

The configuration, for example, for the ground state of *carbon*,

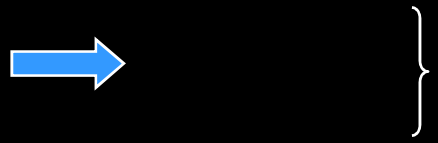
Tells us that there are two electrons in the orbital (1,0,0), two in the orbital (2,0,0), and two in some *combination* of the orbitals (2,1,1), (2,1,0) and (2,1,-1).

For total atom:

The total atom state can be presented by a the following label



For the ground state of ***carbon***

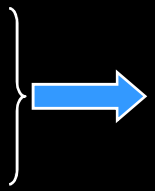


?

How to determine these total quantum number *L,S,J* ?

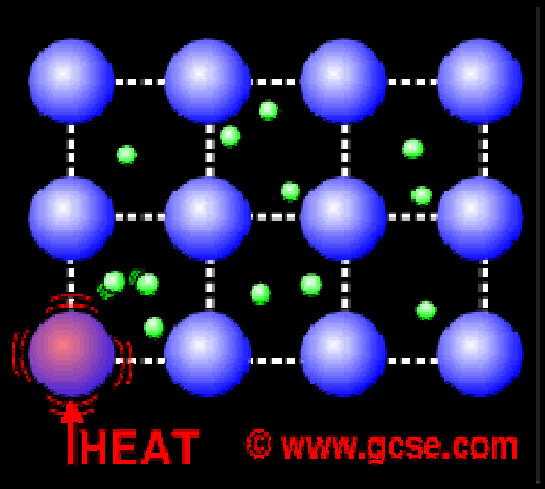
Hund's Rules: See book problem 5.13. homework

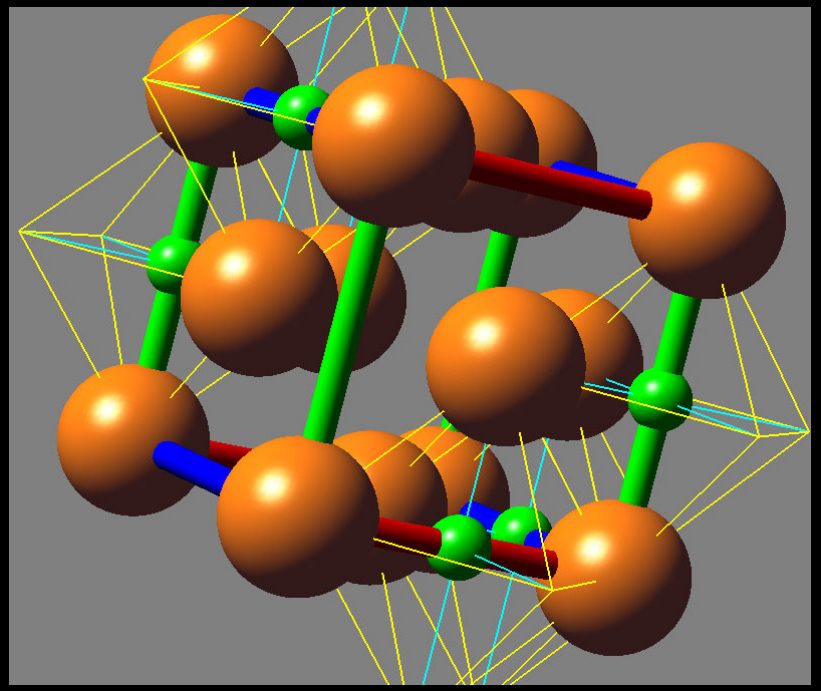
Ground state of carbon



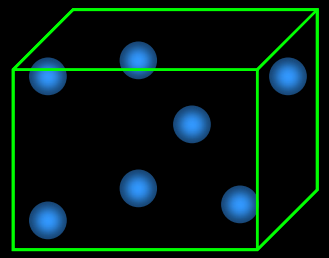
See book, the Table 5.1

5.3 Solids





In the solid state, outermost valence electron become detached, and roam throughout the material. Two primitive models:

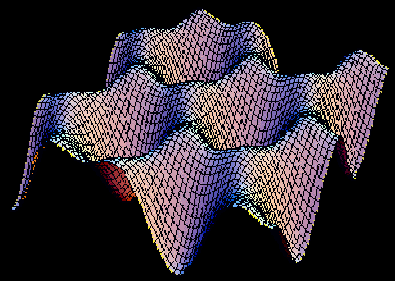


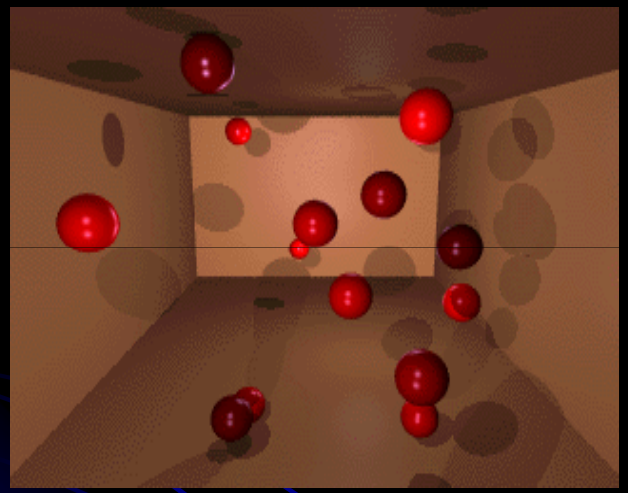
(1) The electron gas theory: 松模费德(Sommerfeld)

Which ignores *all* forces ⟶ Free particles in a box.

(2) Bloch's theory: Periodic potential Band

Which introduces a regularly spaced periodic potential.





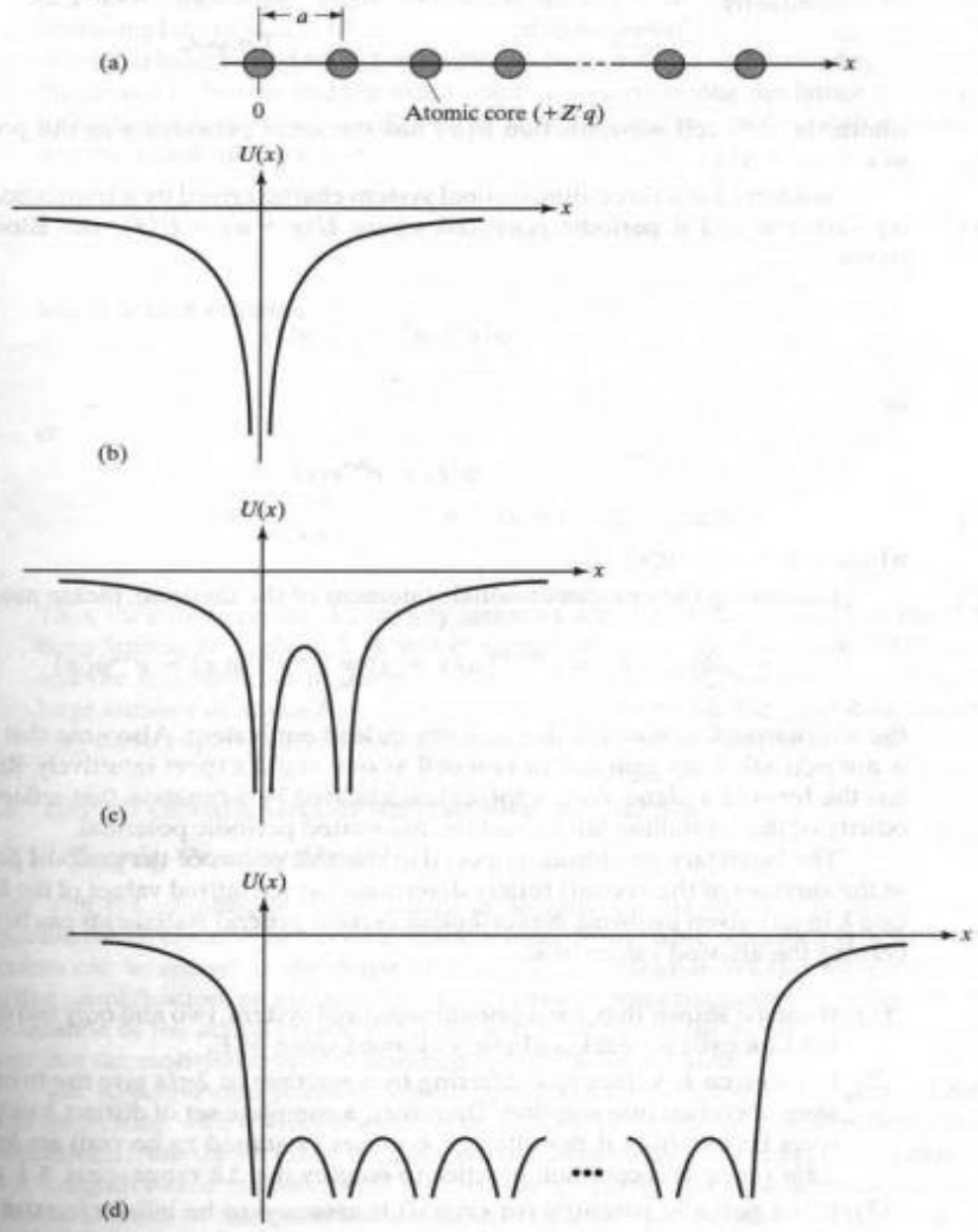
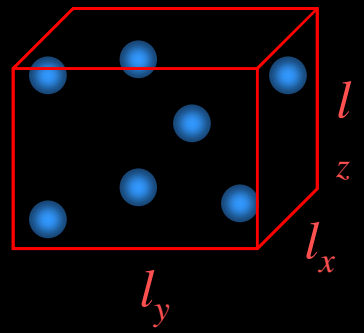


Figure 3.1 (a) One-dimensional crystalline lattice. (b–d) Potential energy of an electron inside the lattice considering (b) only the atomic core at $x = 0$, (c) the atomic cores at both $x = 0$ and $x = a$, and (d) the entire lattice chain.

5.3.1 The Free Electron Gas Theory

Suppose the object in question is a *rectangular* solid, with dimensions l_x, l_y, l_z, and imagine that an electron inside experiences no forces at all, except at the impenetrable walls:



The Schrodinger equation,

separates, in cartesian coordinates: with

$$-\frac{\hbar^2}{2m}$$

and Letting

we obtain the general solutions

The boundary conditions require that $X(0)=Y(0)=Z(0)=0$, so $B_x=B_y=B_z=0$, and $X(l_x)=Y(l_y)=Z(l_z)=0$, so that

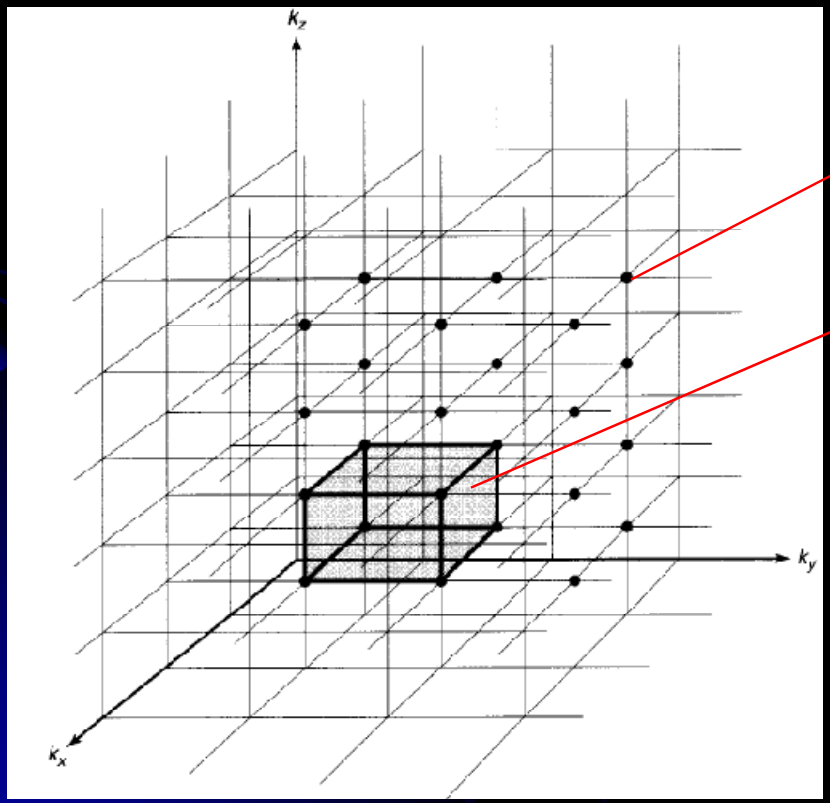
where each n is a positive integer:

The normalized wave functions are

and the allowed energies are

where k is the magnitude of the wave vector, $\boldsymbol{k}=(k_x,k_y,k_z)$.

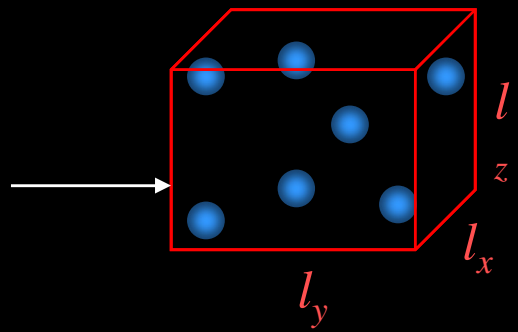
If you imagine a three-dimensional space, with axes k_x, k_y, k_z, and planes drawn in at



(k_x, k_y, k_z) One stationary state

Block: one state for every block

Each block in this grid, and hence each state, occupies a volume in k-space:

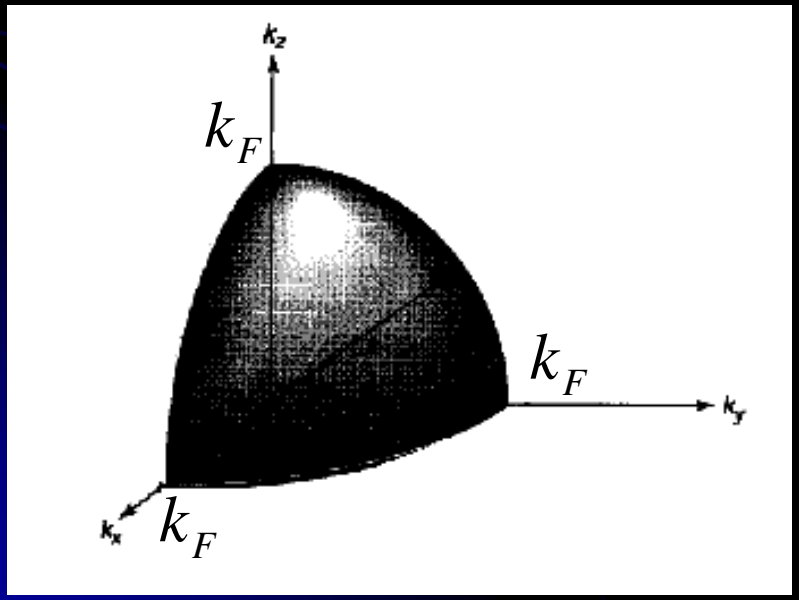


Suppose our sample contains N atoms, and each atom contributes q free electrons.

Avogadro's Constant = 6.0221415×10^{23} mol^{-1}

q is small number: 1 or 2

If electrons were bosons (or distinguishable particles), they would all settle down to the ground state, . But electrons are in fact identical fermions, subject to the Pauli exclusion principle, so only two of them can occupy any given state. They will fill up one octant of a sphere in k-space, whose radius, k_F, is determined by the fact that each pair of electrons requires a volume :



Volume

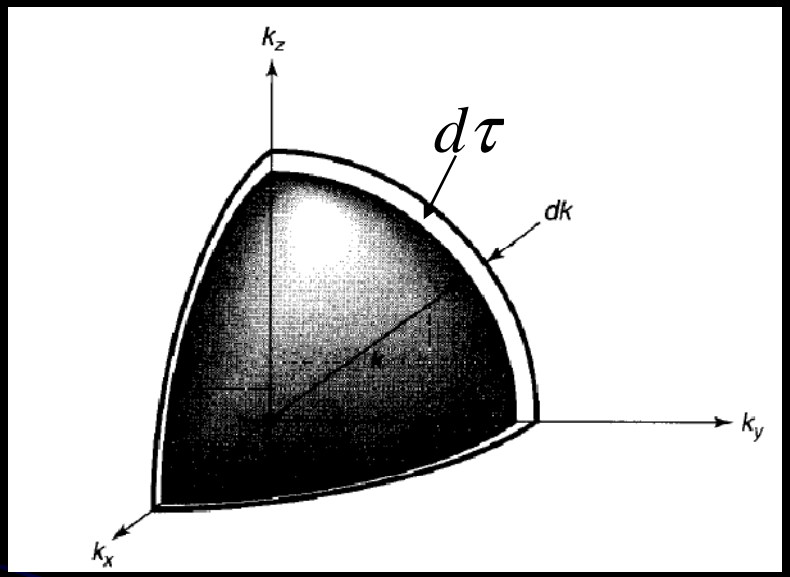
Thus

where

is the *free electron density* (the number of free electrons per unit volume).

The boundary separating occupied and unoccupied states, in k-space, is called the **Fermi surface** (hence the subscript F). The corresponding energy is called the **Fermi energy**, E_F; for a free electron gas,

The total energy of the electron gas can be calculated as follows: A shell of thickness *dk* contains a volume



so the number of electron states in the shell is

Each of these states carries an energy

so the energy of the shell is

and hence the total energy is

This quantum mechanical energy plays a role rather analogous to the internal thermal energy (U) of an ordinary gas. In particular, it exerts a *pressure* on the walls, for if the box expands by an amount dV, the total energy decreases:

and this shows up as work done on the outside ($dW=PdV$) by the quantum pressure P. Evidently

Quantum pressure *P*:

Collapse:

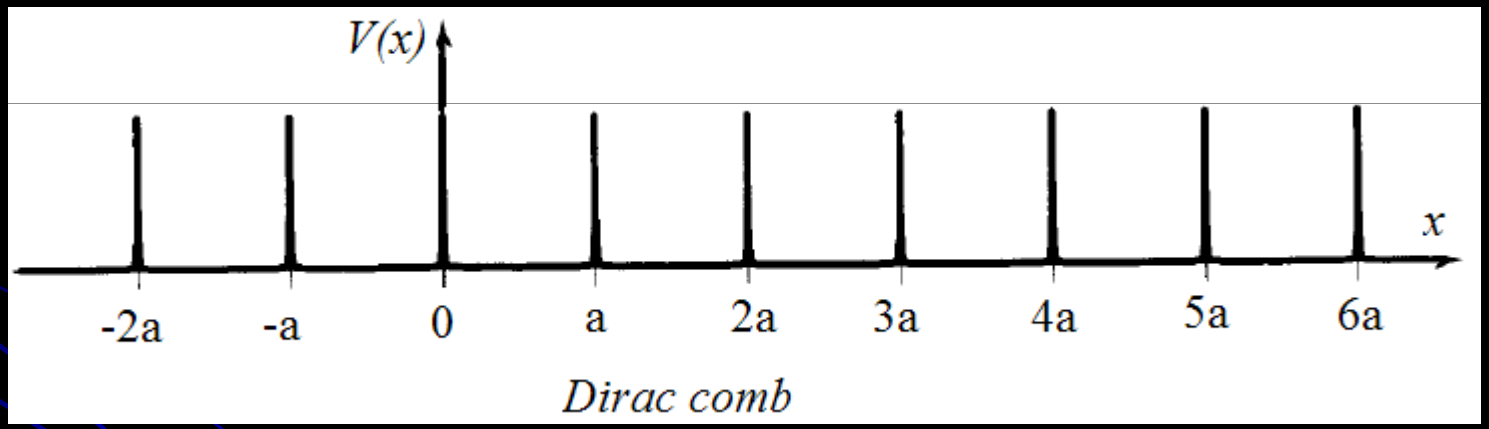
Quantum reason: internal quantum pressure

Quantum essential reason: antisymmetrization requirement of the wave function of identical fermions.

Degeneracy pressure *Exclusion pressure*

5.3.2 The Bloch's theory: Band Structure

We are now going to improve on the free electron model by including the forces exerted on the electrons by the regularly spaced, positively charged, essentially stationary nuclei. The periodic potential here determines the qualitative behavior of solids. Now we develop the simplest possible model: a one-dimensional *Dirac comb*, consisting of evenly spaced delta function spikes.



1. Theorem of periodic potential: Bloch theorem

A periodic potential is one that repeats itself after some fixed distance *a*:

Bloch theorem tells us that for such a potential the solutions to the Schrodinger equation,

can be taken to satisfy the condition

for some constant K, which is independent on x.

Proof: Let D be the "displacement" operator:

Then, for a periodic potential, we have

Therefore D commutes with the Hamiltonian H :

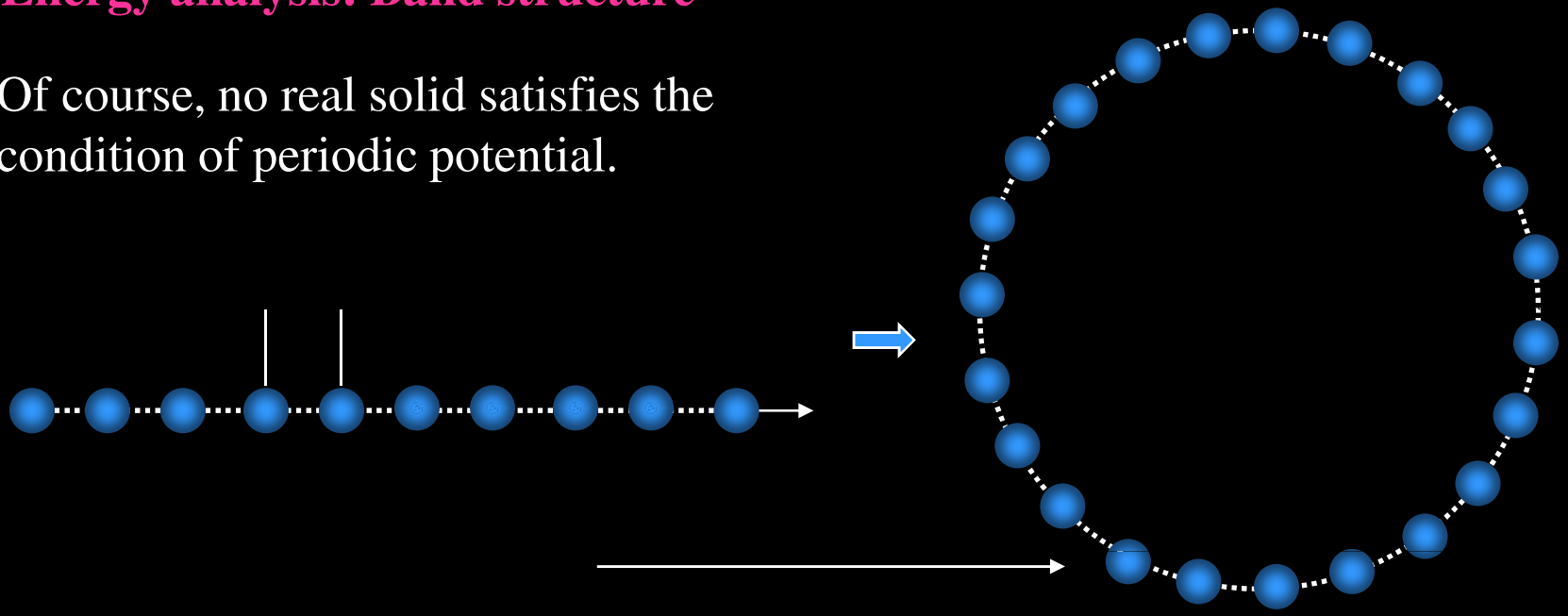
and hence we are free to choose eigenfunctions of H that are simultaneously eigenfunctions of D:

As

Now, λ is a nonzero constant complex number, and can be expressed as an exponential:

2. Energy analysis: Band structure

Of course, no real solid satisfies the condition of periodic potential.

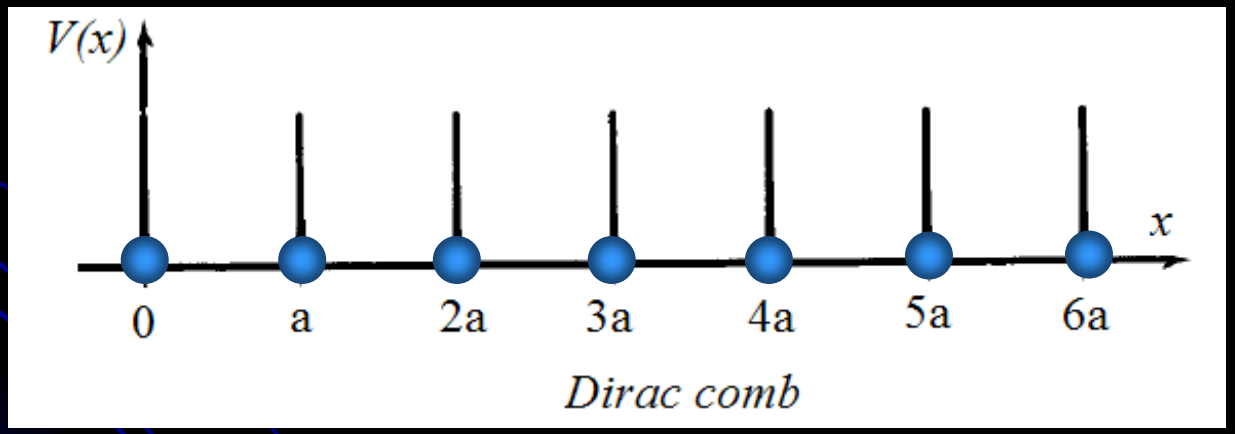


However, for large number of atoms containing in the solid, we can wrap the x-axis around a circle to meet the periodic condition and, finally, we impose the following boundary condition

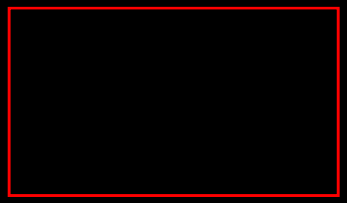
It follows that

so or and hence

Now, suppose the potential consists of a long string of delta-function spikes:



In region $0<x<a$ the potential is zero, so

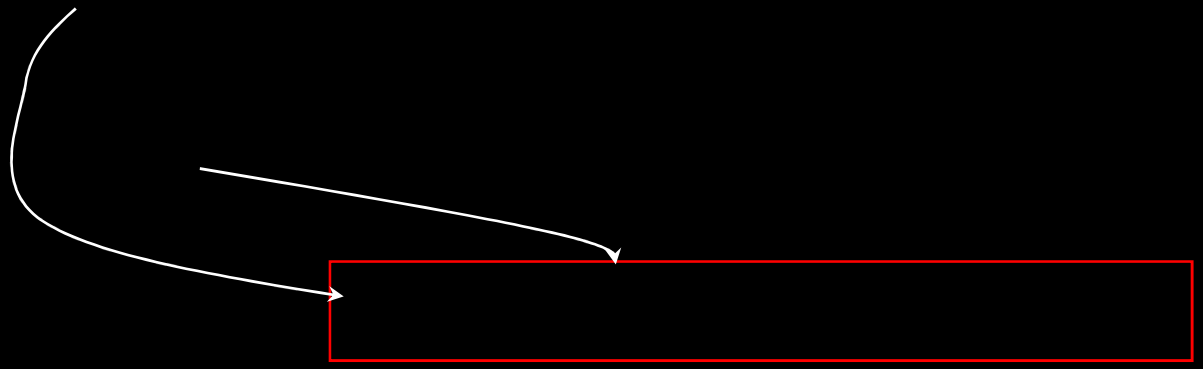


The general solution is

According to Bloch's theorem, the wave function in the cell immediately to the left of the origin is

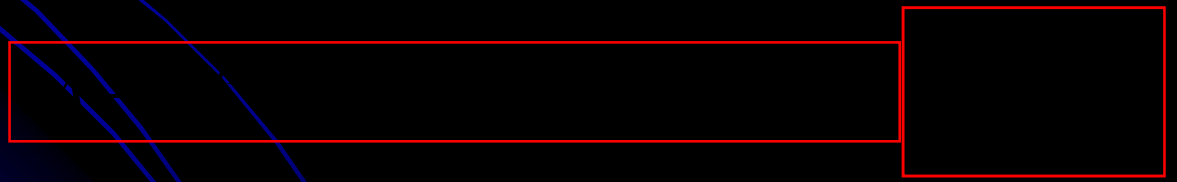
$$\psi(x') = e^{-ik\cdot x}$$

At $x=0$, ψ must be continuous, so



(Equation 5.61)

At $x=0$, ψ' (its derivative) is not continuous, satisfying [2.125]



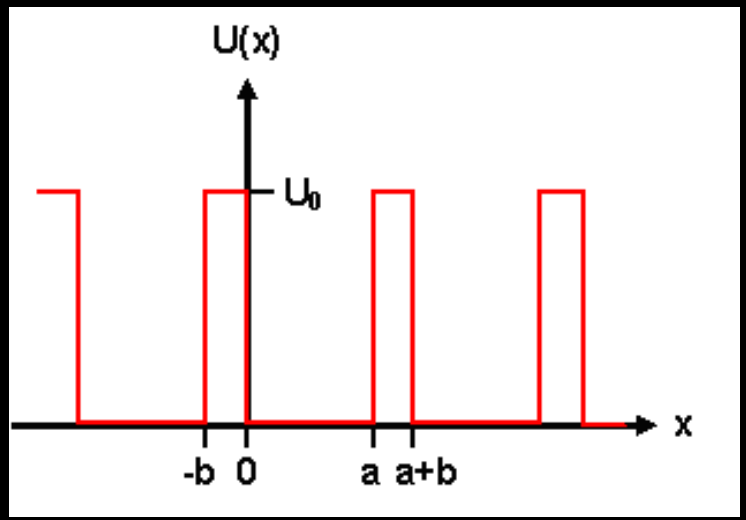
(Equation 5.62)

Solving Equation 5.61 for $Asin(ka)$ yields

Substituting this into Equation 5.62, and cancelling *kB*, we find

which simplifies to

This is the fundamental result, from which all else follows. For any other potential, *Kronig-Penney* for example, the above formula is more complicated, but is shares the qualitative features we are about to explore.



Discussion:

5.64

(1) Above equation determines the possible values of k, and hence the allowed energies.

(2) The allowed energy and energy band.

To simplify the notation, let

so the right set of equation 5.64 can be written as

The constant β is a dimensionless measure of the "strength" of the delta function.

Graph of $f(z)$:

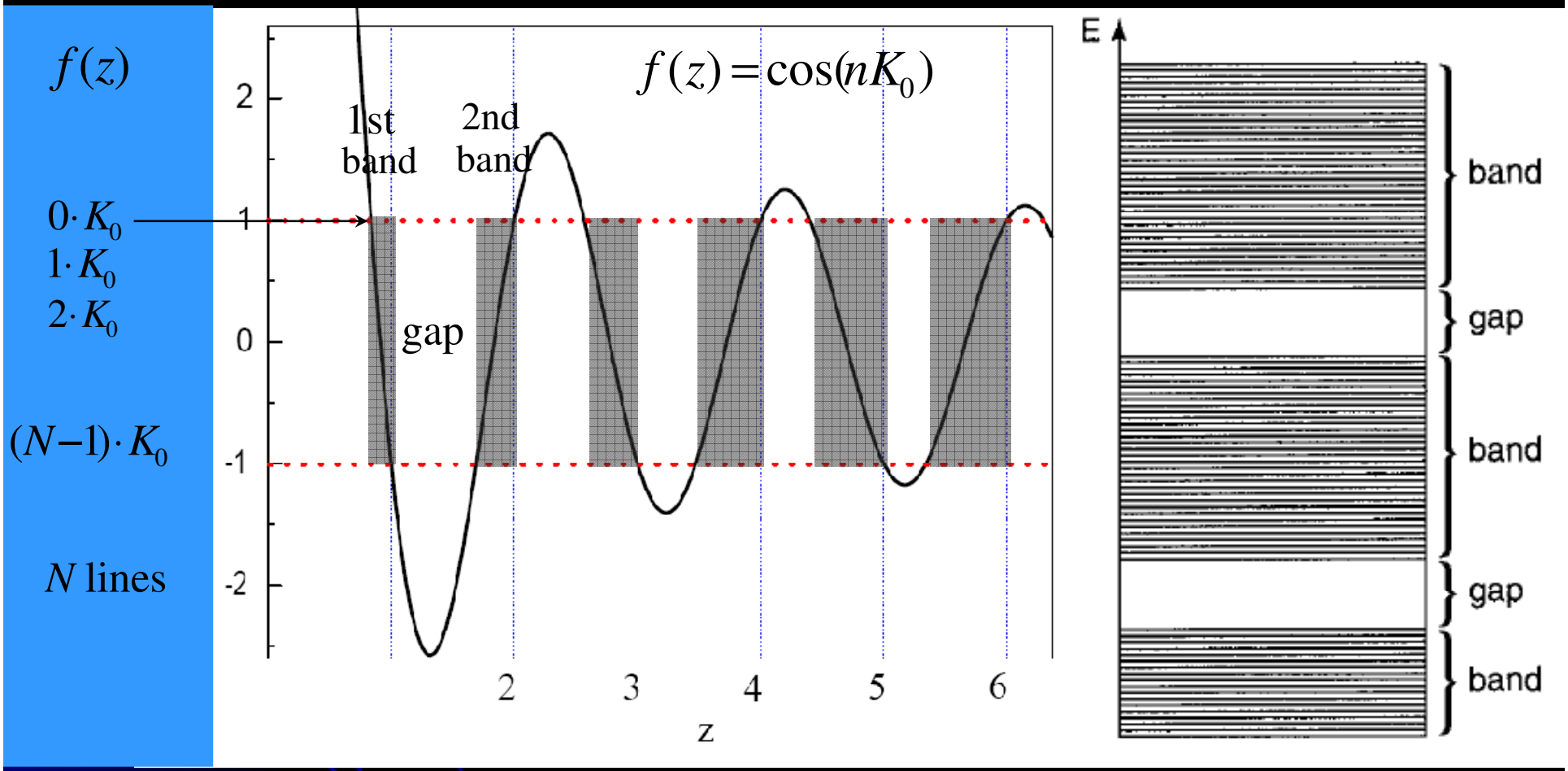


Figure 5.6 Graph of $f(z)$ for β=10, showing allowed bands (shaded) separated by forbidden gaps (where $|f(z)|>1$).

(1) Electrons occupation of the band:

In practice there will be Nq of them, where q is again the number of "free" electrons per atom. Because of Pauli exclusion principle, only two electrons can occupy a given spatial state, so if $q=1$, they will half fill the first band, if $q=2$ they will completely fill the first band, if $q=3$ they half fill the second band, and so on——in the ground state.

(2) Conductors, insulators and semiconductors

Band structure is the signature of periodic potential.

If a band is entirely filled, it takes a relatively large energy to excite an electron, since it has to jump across the forbidden zone. Such materials will be electrical insulators. On the other hand, if a band is only partly filled, it takes very little energy to excite an electron, and such materials are typically conductors. If you dope an insulator with a few atoms of larger or smaller q, this puts some "extra" electrons into the next higher band, or creates some holes in the previously filled one, allowing in either case for weak electric currents to flow; such materials are called semiconductors.

5.4 Quantum Statistical Mechanics

If we have a large number of N particles, in thermal equilibrium at temperature T, what is the probability that a particle would be found to have the specific energy, E_j?

The fundamental assumption of statistical mechanics is that in *thermal equilibrium* every distinct state with the same total energy, E, is equally probable.

The temperature, T, is a measure of the total energy of a system in *thermal equilibrium* in classical mechanics. *What is the new in quantum mechanics?* How to count the distinct states!

Why? Give a example to demonstrate!