## Soft Material <br> by Takehiko Mori

Electronic structure of solids. Band structure of solids, and the practical applications. I am ready to lecture the following items, from which some will be selected.
(1) Fundamentals of quantum mechanics
(2) Atomic orbitals to molecular orbitals
(3) Extension of molecular orbitals to solids
(4) Free electron model
(5) Fermi Dirac statistics
(6) Tight-binding model
(7) Energy band
(8) Symmetry of crystals
(9) Transport properties of solids
(10) Physics of semiconductor devices
(11) Magnetism
(12) Electron correlation
(13) Organic electronics

General representation of waves: $\phi(x, t)=\phi_{0} e^{2 \pi i\left(\frac{x}{\lambda}-v t\right)}$
where, $e^{i \theta}=\cos \theta+i \sin \theta$
For example, ac current is real part of $I(x, t)=I_{0} e^{2 \pi\left(\frac{1}{\lambda}-\right.}$
Real part at $t=0$ is:

$$
\begin{array}{r}
I(x)=\left(I_{0} \cos 2 \pi \frac{x}{\lambda}\right) \\
\text { Wave form: }
\end{array}
$$

Real part at $x=0$ is:

$$
I(t)=\left(I_{0} \cos 2 \pi \nu t\right)
$$

Phase = const. moves with the velocity (from the exponent $=0$ )

$\frac{\Delta x}{\Delta t}=C \nu \lambda$
moves to the right. Wave number $k=2 \pi / \lambda$
Angular frequency $\omega=2 \pi \nu \rightarrow$

$$
\phi(x, t)=\left[\phi_{0} e^{i(k x-\omega t)}\right)
$$

Quantum mechanics is derived from the following two theorems, which represent duality of wave and particle.
(1) A wave with frequency $\nu$ acts as a particle with energy $E=h \nu(=\hbar \omega)$.
(1) Planck's photon $\rightarrow$ Black body
(2) Photoelectron
(2) A particle with momentum $p$ acts as a wave with wavelength $\lambda=h / p$ (de Broglie wave).
(1) Electron diffraction
(2) Line spectra of hydrogen atoms

This leads to the correspondence:
Particle(Energy, Momentum) Wave (Frequency, Wavelength)

## Back body

Light with frequency $\nu$ has energy with integer times of $E=h \nu$. $\rightarrow \quad$ Photon with energy $E=h \nu$ or $E=h c / \lambda$.



Photoelectron $\quad h \nu=$ B.E.+K.E.

work function (of metal) or ionization energy

de Broglie wave

For light: | $\lambda \nu=c$ (wavelength) $\times($ frequency $)=($ velocity $)$ |
| :--- |
|  |
| $E=m c^{2}$ |
| $E=h \nu$ |$\quad$ Relativistic energy $\quad$ Planck's equation

These relations lead to $m c^{2}=h \nu=h c / \lambda$, so that

$$
m c=(h / \lambda)
$$

For particles, $p=$ mv, so we assume $\mathrm{mc} \rightarrow p$

Or

$$
\begin{aligned}
& p=(h / \lambda] \\
& \lambda=h / p \quad \text { de Broglie equation }
\end{aligned}
$$



Electron diffraction
Electron diffraction
Kinetic energy $=e V=\frac{p^{2}}{2 m}=\frac{1}{2 m}\left(\frac{h}{\lambda}\right)^{2}$ gives

$$
\lambda=\frac{h}{\sqrt{(2 m e V})}=\frac{1.2265 \mathrm{~nm}}{\sqrt{V}(\mathrm{~V})} \quad \begin{aligned}
& 0.1 \mathrm{~nm} \text { at } \\
& V=150 \mathrm{~V}
\end{aligned}
$$

Hydrogen atom
Coulomb

$$
\frac{e^{2}}{4 \pi \varepsilon_{0} r^{2}}=\frac{m v^{2}}{r}=\frac{p^{2}}{m r}
$$

Circle is integer times of wavelength
$2 \pi r=n \lambda$, and $\lambda=h / p$ leads to

$$
\begin{aligned}
r= & \left.\frac{\varepsilon_{0} h^{2}}{\pi m e^{2}}\right) n^{2}=a_{0} n^{2} \\
& a_{0}: \text { Bohr radius } 0.529 \AA
\end{aligned}
$$

Thus

$$
\begin{array}{r}
E=\frac{p^{2}}{2 m}-\frac{e^{2}}{4 \pi \varepsilon_{0} r}=-\frac{m e^{4}}{8 \varepsilon_{0} h^{2}} \frac{1}{n^{2}} \\
R h c=-13.6 \mathrm{eV}
\end{array}
$$

Rydberg constant


9


Line spectra of hydrogen atoms

$E=-\frac{R h c}{n^{2}}$
transition from $m$ to $n$ $\Delta E=R h c\left(\frac{1}{m^{2}}-\frac{1}{n^{2}}\right)$
or
$\frac{1}{\lambda}=\frac{\Delta E}{h c}=\left(R\left(\frac{1}{m^{2}}-\frac{1}{n^{2}}\right)\right)$

General wave $\phi(x, t)=\phi_{0} e^{2 \pi i\left(\frac{X}{\lambda}-v t\right)}$ is differentiated by $x$ ， to give

$$
\begin{equation*}
\frac{\partial \phi}{\partial x}=\frac{2 \pi i}{\lambda} \phi \stackrel{\downarrow}{\lambda} \stackrel{\hbar}{=} \frac{i}{\hbar} p \phi \quad \therefore p \phi=\left(\frac{\hbar}{i} \frac{\partial \phi}{\partial x}\right) \tag{1}
\end{equation*}
$$

Similarly differentiated by $t$ ，to give

$$
\begin{equation*}
\frac{\partial \phi}{\partial}=-2 \pi i v \phi \stackrel{E=h \nu}{=}-\frac{i}{\hbar} p \phi \quad \therefore E \phi=\left(i \hbar \frac{\partial \phi}{\partial t}\right) \tag{2}
\end{equation*}
$$

We can obtain $p$ and $E$ by differentiating $\phi$ by $x$ and $t$ ，and multiplying $h / i$（or ih）．
We can replace $p, E$ to differential operators：

$$
p \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} \quad E \rightarrow i \hbar \frac{\partial}{\partial}
$$

$E=\frac{p^{2}}{2 m}+V$ is inserted in Eq．（2），to give， $-\quad i \hbar \frac{\partial \phi}{\partial}=\left(\frac{p^{2}}{2 m}+V\right) \phi=\left(-\frac{\hbar^{2}}{2 m} \frac{\partial^{2}}{\partial x^{2}}+V\right) \phi$

When $E$ is independent of time，$\phi(x, t)=\phi(x) e^{-i \frac{E}{\hbar} t}$ is inserted in Eq．（3），to give，

$$
\left(-\frac{\hbar^{2}}{2 m} \frac{\partial^{2}}{\partial x^{2}}+V\right) \phi=(E \phi) \begin{gathered}
\text { Schrödinger equation }
\end{gathered}
$$

Eqs．（1），（2），（4）have a form of［Differential operator M］$\phi=m \phi$ and are differential equations as for $\phi$ ，which have solutions $\phi$ corresponding to particular $m$ ．
Thus the eigenvalue $m$（固有値）corresponds to the eigenfunction $\phi$（固有関数）．

Free electron for $V=0$
Schrödinger eq．$-\frac{\hbar^{2}}{2 m} \frac{\partial^{2}}{\partial x^{2}} \phi=E \phi$ has an eigenfunction $\phi(x)=e^{i k x}$ ．
The corresponding eigenvalue is $E=\left(\frac{\hbar^{2} k^{2}}{2 m}\right)$ ．
$\phi(x)=e^{i k x}$ is an eigenfunction of $\frac{\hbar}{i} \frac{\partial \phi}{\partial x}=p \phi \quad$ at the same time．
The corresponding eigenvalue is $[\hbar k]$ ．
The plane wave $\phi(x)=e^{i k x}$ has momentum $p=(\hbar k)$ and energy $E=\left(\frac{\hbar^{2} k^{2}}{2 m}\right)$ ，and is an eigenstate．
$\phi(x)=e^{-i k x}$ has momentum $p=(-\hbar k)$ and energy $E=\left(\frac{\hbar^{2} k^{2}}{2 m}\right)$
which proceeds in the opposite（negative $k$ ）direction，
which proceeds in the opposite（negative $k$ ）direction，
but has the same（absolute value of）momentum and energy．


Wave number $k=2 \pi / \lambda$ is inverse of the wavelength．
The number of waves in unit $\times 2 \pi$ length．

Hydrogen-like atom
Schrödinger equation
$\left[-\frac{\hbar^{2}}{2 m}\left(\frac{\partial^{2}}{\partial x^{2}}+\frac{\partial^{2}}{\partial y^{2}}+\frac{\partial^{2}}{\partial z^{2}}\right)+V\right] \phi=E \phi$


Put Coulomb force as $V=-\frac{Z e^{2}}{4 \pi \varepsilon_{0} r}$

$$
[\cdots]=H=-\frac{\hbar^{2}}{2 m} \nabla^{2}-\frac{Z e^{2}}{4 \pi \varepsilon_{0} r}
$$

Go to polar coordinates $(x, y, z) \rightarrow(r, \theta, \phi)$

$$
\phi=R_{n l}(r) Y_{l m}(\theta, \phi)=R_{n l}(r) \Theta_{l m}(\theta) \Phi_{m}(\phi)
$$

Radial part Angular part
The radial part follows the differential equation:

$$
\frac{d^{2} R}{d r^{2}}+\frac{2}{r} \frac{d R}{d r}+\left[\frac{2 m}{\hbar^{2}}\left(E+\frac{Z e^{2}}{4 \pi \varepsilon_{0} r}\right)-\frac{l(l+1)}{r^{2}}\right] R=0
$$

Problem
When $l=0$, show $R(r)=e^{-\zeta r}$ is a solution of $\frac{d^{2} R}{d r^{2}}+\frac{2}{r} \frac{d R}{d r}+\left[\frac{2 m}{\hbar^{2}}\left(E+\frac{Z e^{2}}{4 \pi \varepsilon_{0} r}\right)-\frac{l(l+1)}{r^{2}}\right] R=0$
and obtain $\zeta$ and $E$.
Solution Put $R(r)=e^{-\zeta r}$ into the above equation, to give,

$$
\zeta^{2}-\frac{2 \zeta}{r}+\left[\frac{2 m}{\hbar^{2}}\left(E+\frac{Z e^{2}}{4 \pi \varepsilon_{0} r}\right)\right]=0
$$

The term of $1 / r$ is 0 , leading to $\zeta=\frac{Z m e^{2}}{4 \pi \hbar^{2} \varepsilon_{0}}=\frac{Z}{a_{0}}$ Bohr radius
so

$$
E=-\frac{\bar{\hbar}^{2}}{2 m} \zeta^{2}=-\frac{Z^{2} m e^{4}}{32 \pi^{2} \varepsilon_{0}^{2} \hbar^{2}}=-Z^{2} R h c
$$

Rydberg constant
$R(r)=r^{l} e^{-\zeta r}$ is another solution at nonzero $l$.

Other solutions at $l=0: \quad \rho=2 \zeta r=\frac{2 Z}{n a_{0}} r$

$\notin$| 1 s | $R(r) \propto e^{-\rho / 2}$ |
| :--- | :--- |
| 2s | $R(r) \propto(2-\rho) e^{-\rho / 2}$ |
| 3s | $R(r) \propto\left(6-6 \rho+\rho^{2}\right) e^{-\rho / 2}$ |

> Associated Laguerre polynomials works to be 1s, 2s, 3s.. orthogonal


$1 \mathrm{~s}, 2 \mathrm{~s}, 3 \mathrm{~s}$ orbitals have

nodes in the radial direction, and the shape is (sphere).

Laguerre polynomials guarantees orthogonality of 1s, 2s, 3s orbitals, but complicates molecular orbital calculations.
They are not important in the usual distances of chemical bonds, so that we neglect them to

$$
\phi \propto e^{-\overleftarrow{\zeta} r} Y_{l m}(\theta, \phi) \quad \text { Slater orbital }
$$

$\zeta=\frac{Z}{a_{0}}$ increases as $Z$ increases (and the orbital size decreases).
The "outer most electron" is screened by other " $Z-1$ " electrons from the $Z+$ nuclear charge.
If the screening is complete, it feels $Z=1$ charge, but the screening is incomplete, because the focused electron is not always out of other electrons, so that the effective $Z^{*}$ is $1<Z^{*}<Z$.
Accordingly $\zeta$ changes as shown in the next page.
$\mathrm{C}(<) \mathrm{N}(<) \mathrm{O}$

Slater orbitals


Due to the imperfect screening, going right leads to (small) atomic orbitals.
Covalent and ionic radii also become (small).

Angular part $\quad \phi=R_{n l}(r) Y_{l m}(\theta, \phi)=R_{n l}(r) \underline{\Theta_{l m}(\theta) \Phi_{m}(\phi)}$
$\Phi$ part : $\quad-i \pi \frac{\partial \Phi}{\partial \phi}=\mu \Phi$ has soln: $\Phi_{m}(\phi) \propto e^{i m \phi} \quad m=0, \pm 1, \pm 2,, "$

$$
\mu=\hbar m \quad \text { Angular momentum }
$$

$\Theta$ part: $\quad \frac{1}{\sin \theta} \frac{d}{d \theta}\left(\sin \theta \frac{d \Theta}{d \theta}\right)+\left[l(l+1)-\frac{m^{2}}{\sin ^{2} \theta}\right] \Theta=0$
Problem: Show $\Theta_{10}(\theta)=\cos \theta$
is a solution of the above equation.
Put $l=1, m=0$, and

$$
\begin{gathered}
-\frac{1}{\sin \theta} \frac{d}{d \theta}(\sin \theta \sin \theta)+2 \cos \theta=0 \\
-\frac{2 \sin \theta \cos \theta}{\sin \theta}+2 \cos \theta=0
\end{gathered}
$$

This leads to $\quad \phi=R_{n l}(r) \Theta_{l m}(\theta) \Phi_{m}(\phi) \propto r e^{-r / a_{0}} \cos \theta \propto z e^{-r / a_{0}}$







Molecular orbital theory
（1）One－electron Schrödinger equation
$\left[-\frac{\hbar^{2}}{2 m} \nabla^{2}-\frac{e^{2}}{4 \pi \varepsilon_{0}} \sum_{n} \frac{Z_{n}}{r_{n}}\right] \phi=E \phi$
Put one electron in the arranged nuclei．
（2）LCAO－MO（Linear Combination of Atomic Orbitals）
$\phi=\sum^{N} c_{i} \chi_{i} \quad N$ ：total number of atomic orbitals

（4）Secular equation $N \times N$ Non diagonal：resonance integrals

（5）$N$－order equation of $E$
（6）$N$ energy levels of $E$（固有値）
1．Simultaneous equation for $c_{\mathrm{i}}$
（7）$N$－set of $c_{\mathrm{i}}$（固有関数）$=$ Molecular orbital（分子軌道）

Hydrogen Molecule
（2）LCAO－MO $\quad \phi=c_{\mathrm{A}} \chi_{\mathrm{A}}+c_{\mathrm{B}} \chi_{\mathrm{B}}$

Polar bond
（2）LCAO－MO $\quad \phi=c_{\mathrm{A}} \chi_{\mathrm{A}}+c_{\mathrm{B}} \chi_{\mathrm{B}}$
（4）Secular Eq．$\left|\begin{array}{cc}\alpha_{\mathrm{A}}-E & \beta \\ \beta & \alpha_{\mathrm{B}}-E\end{array}\right|=0$

$\rightarrow$ Electronically negative atom

Energy of Atomic Orbital $\alpha_{\mathrm{A}}=$ Ionization energy


Due to the imperfect screening, going right leads to
(large )ionization energy, and (deep) atomic orbital.
Going right leads to electronically negative.
$E \propto-\zeta^{2}$

Diatomic molecule like $\mathrm{N}_{2}$

$$
\mathrm{N} 1 \mathrm{~s}+2 \mathrm{~s}+2 \mathrm{p} \times 3 \rightarrow 5 \mathrm{AO} \times 2=10 \mathrm{AO}
$$



$$
\phi=c_{1} \chi_{1 \mathrm{~s}}^{\mathrm{A}}+c_{2} \chi_{1 \mathrm{~s}}^{\mathrm{B}}+c_{3} \chi_{2 \mathrm{~s}}^{\mathrm{A}}+c_{4} \chi_{2 \mathrm{~s}}^{\mathrm{B}}+c_{5} \chi_{2 \mathrm{pz}}^{\mathrm{A}}+c_{6} \chi_{2 \mathrm{pz}}^{\mathrm{B}}+c_{7} \chi_{2 \mathrm{py}}^{\mathrm{A}}+c_{8} \chi_{2 \mathrm{py}}^{\mathrm{B}}+c_{9} \chi_{2 \mathrm{px}}^{\mathrm{A}}+c_{10} \chi_{2 \mathrm{px}}^{\mathrm{B}}
$$



Electron configuration


Bond order $=[(\# B o n d i n g ~ o r b i t a l) —(\# A n t i b o n d i n g ~ o r b i t a l)] / 2$
$\pi$-Electron System Hückel Method
(1) $\sigma$ and $\pi$-orbitals are orthogonal.

$$
\left.\left\lvert\, \begin{array}{c|c|}
\sigma & 0 \\
\hline 0 & \pi
\end{array}\right.\right)=0
$$

(2) $\beta$ for nearby $\mathrm{C}=\mathrm{C}$ is nonzero. Others are zero.
(3) All overlap integrals are $S=0$.

Example ethylene
Bonding energy is
${\underset{H}{\mathrm{C}}={ }_{\mathrm{C}}^{\mathrm{H}_{2}^{\mathrm{H}}}}_{\mathrm{H}}^{\mathrm{H}} \quad\left|\begin{array}{cc}\alpha-E & \beta \\ \beta & \alpha-E\end{array}\right|=0 \quad 2(\alpha+\beta)-2 \alpha=(2 \beta$
$\alpha-\beta=\phi=\chi_{\mathrm{A}}-\chi_{\mathrm{B}}$
$\alpha+\beta \uparrow \phi=\chi_{\mathrm{A}}+\chi_{\mathrm{B}}$


Hückel Method for Complicated $\pi$-Electron Sytems
(1) Number carbon atoms with $\pi$, the total is $N$.
(2) Wright a $N \times N$ secular equation, with all diagonal terms $\alpha-E$.
(3) Nondiagonal terms are $\beta$ for bonded $i$-th and $j$-th carbons, and zero for non bonded carbons.
(4) $\mid$ determinant $\mid=0$ leads to $N$-th equation of $E$, which is solved to obtain $N$ energy levels.
(5) Put electrons from the bottom. (\#Electron)=(\#Carbon)

Wright the secular equation of cyclobutadiene.


The solution is
$\alpha-2 \beta=$
$\alpha \ddagger$

$$
\begin{gathered}
\alpha+2 \beta \nmid \quad \text { Bonding energy is } \\
2(\alpha+2 \beta)+2 \alpha-4 \alpha=(4 \beta
\end{gathered}
$$

There is no energy gain compared with two double bonds

$$
2 \times 2 \beta=4 \beta
$$

Wright the secular equation of benzene.


The solution
Bonding energy is

$$
\alpha-2 \beta-\quad 2(\alpha+2 \beta)+4(\alpha+\beta)-6 \alpha=(8 \beta
$$

$\alpha-\beta=$ Compared with three doublebonds
$\alpha+\beta \xlongequal{\text { 垂州 }}$
$\alpha+2 \beta$
$3 \times 2 \beta=6 \beta$, there is $2 \beta$ energy gain
(delocalization energy).
$4 n+2$ membered ring delocalization aromatic
$4 n$ membered ring no delocalization

