#### No. I

# **Condensed Matter Physics II**

#### Code: 35603-0098, GSC-PH5C30L2

#### Schedule of Lectures

#### 13:00-14:30

Ι.	Sep.	29	8. Nov.	24
2.	0ct.	6	9. Dec.	
3.	0ct.	13	IO.Dec.	8
4.	0ct.	20	II.Dec.	15
5.	0ct.	27	12.Dec.	22
6.	Nov.	10	13. Jan.	5
7.	Nov.	17	I4. Jan.	12

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## Overview of the lectures

We discuss electronic structures and cohesive mechanism of materials in isolated phases and condensed phases, and extend our discussion to understand optical, dielectric, magnetic, and transport properties.

Density functional theories and linear response theories giving a framework for a comprehensive understanding of the issues we cover will be introduced in a concise way.

We also cover how the theories and simulations can be compared to various experimental data together with introduction of experimental techniques and its applications.

# Topics we will discuss

- Structures and cohesive mechanism
- Density functional theories
- Linear response theories
- Optical and dielectric properties of materials
- Magnetic order and magnetic properties of solids
- Transport phenomena in materials
- Relativistic effects in materials

# Evaluation

- In most of classes, exercise problems will be given to promote your understanding.
- The evaluation will be made based on the reports for the exercise problems you will submit.
- In the beginning of the next class, you are requested to submit your report that I gave you in the last class.

# Lecture style

If you have a question, please post your question to "chat" on Zoon. We will have a time for discussion occasionally.

I may ask you some question during lecture randomly.

If you have a further question, please post your question to slack.

https://app.slack.com/client/T01B4G2L1RD/C01BKEKJHNX

# **References #I**

Electronic Structure: Basic Theory and Practical Methods, Richard M. Martin, Cambridge University Press. 日本語訳あり

固体 - 構造と物性、金森順次郎、米沢富美子、川村清、寺倉清之、 岩波書店.

多体問題特論 - 第一原理からの多電子問題、高田康民、朝倉書店. 量子化学入門(上・下)、米澤貞次郎等、化学同人. 遷移金属のバンド理論、小口多美夫、内田老鶴圃.

Density-Functional Theory of Atoms and Molecules, Robert G. Parr, Weitao Yang, Oxford University Press USA. 日本語訳あり

Bonding and Structure of Molecules and Solids, David G. Pettifor, Oxford University Press. 日本語訳あり

# References #2

Quantum Theory of Many-Particle Systems, Alexander L. Fetter, John Dirk Walecka, Dover Publications. 日本語訳あり

Solid State Physics, Giuseppe Grosso, Giuseppe Pastori Parravicini, Academic Press. 日本語訳あり

Band Theory and Electronic Properties of Solids, John Singleton, Oxford Master Series in Physics. 日本語訳あり

Magnetism in Condensed Matter, Stephen Blundell, Oxford Master Series in Physics.

Optical Properties of Solids, Mark Fox, Oxford Master Series in Physic.

# **Related information**

# WEB

https://t-ozaki.issp.u-tokyo.ac.jp/lecture.html

# Slack

https://app.slack.com/client/TOIB4G2LIRD/COIBKEKJHNX

# Email

t-ozaki@issp.u-tokyo.ac.jp

# Lecture I

- Experiments and theories
- Density functional theory
- Virial theorem
- Bonding in a H<sub>2</sub> molecule
- Electronic structures of simple molecules

# Atomic unit

	a.u.	Expression	SI unit	
Mass of electron	1	m	9.109384 × 10 <sup>-31</sup> kg	
Elementary charge1e1.602177×		1.602177 × 10 <sup>-19</sup> C		
Reduced Plank's constant	1	$\hbar = h / 2\pi$	1.054572×10 <sup>-34</sup> J ∙ s	
Length	1	$a_0 = 4\pi\varepsilon_0\hbar^2 / (me^2)$	$5.291772 \times 10^{-11} \text{ m}$	
Energy	1	$E_{\rm h} = m e^4 / \left(4\pi \varepsilon_0 \hbar\right)^2$	4.359745 × 10 <sup>-18</sup> J	
Magnetic flux density	1	$\hbar/(ea_0^2)$	$2.350518 \times 10^5 \mathrm{T}$	
Velocity	1	$\alpha c = \left( e^2 / (4\pi \varepsilon_0 \hbar c) \right) c$	$2.187691 \times 10^{6} \text{ m} \cdot \text{s}^{-1}$	
Coulomb force constant	1	$k_e = 1/4\pi\varepsilon_0$	8.987552 × 10 <sup>9</sup> kg • m <sup>3</sup> • s <sup>-2</sup> • C <sup>-2</sup>	
Magnetic dipole moment	1	$e\hbar/m = 2e\hbar/(2m) = 2\mu_B$	$B = 18.5480202 \times 10^{-24} \text{ J T}^{-1}$	

#### Cooperative collaboration between experiments and theories

- Size of ellipse reflects activities of current status.
- In the near future, the exploration of new materials are expected.

# Analysis of Materials

Vibration, UV, IR, NMR Geometry, Stability

Proposal of novel functionalities

Engineering of band structures Spin current, topological insulators Exploration of new materials

Prediction of new crystals, reverse engineering from functions to structures

## Targets in Condensed Matter Physics

- I. To understand chemical and physical properties of molecules and solids by solving Schrödinger/Dirac eqs. as accurate as possible.
- 2. To design materials which may have desired properties before actual experiments.
- 3. To propose a way of synthesis for designed materials from a theoretical point of views.

## Governing equation for physics of solids



Conditions that wave functions must satisfy

(1) Indistinctiveness of electrons

(2) anticommutation (Pauli's exclusion principle)

(3) Orthonormalization of wave functions

### **Classification of electronic structure methods**

Wave function theory	Computational complexity	Features	
e.g., configuration interaction (CI) method			
$\Psi = \sum_{I=1}^{N} C_{I} \left  \phi_{I1} \left( x_{1} \right) \phi_{I2} \left( x_{2} \right) \cdots \phi_{IN_{e}} \left( x_{N_{e}} \right) \right $	<b>U(e</b> ™)	High accurary High cost	
Density functional theory	1		
$E[\rho] \qquad \rho(\mathbf{r}) = \sum_{i=1}^{N_{e}} f(\varepsilon_{i}) \phi_{i}^{*}(\mathbf{r}) \phi_{i}(\mathbf{r})$	<b>O(N</b> <sup>3</sup> )	Medium accuracy Low cost	
Quantum Monte Carlo method			
$_{F}$ $_{-}\left\langle \Psi _{lpha }\left  \hat{H} \right  \Psi _{lpha } ight angle$	0(N <sup>3~</sup> )	High accuray High cost	
$E = \frac{\left\langle \Psi_{\alpha} \middle  \Psi_{\alpha} \right\rangle}{\left\langle \Psi_{\alpha} \middle  \Psi_{\alpha} \right\rangle}$		Easy to parallel	
Many body Green's function metho	d		
	<b>O</b> (N <sup>3</sup> ~)	Medium accuray	

 $G = G_0 + G_0 \Delta G_0 + G_0 \Delta G_0 \Delta G_0 + \cdots$ 

Medium accuray Excited states

# Density functional theory

• The total energy can be expressed by a functional of  $\rho$ . Hohenberg-Kohn theorem

$$E[\rho] = \int dr^3 \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + T[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

 By taking account of quantum many body interaction into the exchange-correlation energy, one can formulate an one-body problem as the Kohn-Sham equation.
 Kohn-Sham Ansatz

$$\hat{H}_{\rm KS}\phi_i = \varepsilon_i\phi_i \qquad \hat{H}_{\rm KS} = -\frac{1}{2}\nabla^2 + v_{\rm eff}$$
$$v_{\rm eff}(\mathbf{r}) = v_{\rm ext}(\mathbf{r}) + v_{\rm Hartree}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}$$

### Summit in ORNL: 200 Peta flops machine

Summit - IBM Power System AC922, IBM POWER9 22C 3.07GHz, NVIDIA Volta GV100, Dual-rail Mellanox EDR Infiniband , IBM DOE/SC/Oak Ridge National Laboratory, United States

Cores: 2,414,592+NVIDIA Tesla V100 GPUs Rmax: 148,600 (TFLOP/sec.) Pmax: 200,795 (TFLOPS/sec.)



### According to Moore's law …



 $\rm H_2$  is the simplest molecule which has two nuclei and two electrons.

The bonding mechanism is understood by the virial theorem.

Derivation of virial theorem
 DFT calc. of H<sub>2</sub>

### Virial theorem #1

We consider a system consisting of N-electrons and M-nuclei defined by

$$\hat{H} = \hat{T} + \hat{U} \qquad \hat{T} = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_{i}^{2} \right)$$
$$\hat{U} = \sum_{i>j}^{N} \frac{1}{\left| \mathbf{r}_{i} - \mathbf{r}_{j} \right|} + \sum_{n>n'}^{M} \frac{Z_{n} Z_{n'}}{\left| \mathbf{R}_{n} - \mathbf{R}_{n'} \right|} + \sum_{i,n}^{N,M} \frac{1}{\left| \mathbf{r}_{i} - \mathbf{R}_{n'} \right|}$$

We introduce scaled variables and a scaled wave function of the ground state:

$$\mathbf{r}_{i} = s^{-1} \left( s \mathbf{r}_{i} \right) = s^{-1} \left( \overline{\mathbf{r}}_{i} \right)$$
$$\Psi_{s} = s^{3N/2} \Psi \left( \overline{\mathbf{r}}_{1}, \overline{\mathbf{r}}_{2}, \cdots, \overline{\mathbf{r}}_{N} \right)$$

The ground state energy of E can be written by a s-dependent form as:

$$E(s) = s^2 T(s) + s \ U(s)$$

Per-Olov Loewdin, J. Mol. Spect. 3, 46 (1959).

### Virial theorem #2

Since the total energy is minimized at s=l, we have

$$\frac{\partial E}{\partial s} = 2s T(s) + U(s) + \sum_{n,p} \left( s^2 \frac{\partial T(s)}{\partial \overline{R}_{np}} + s \frac{\partial U(s)}{\partial \overline{R}_{np}} \right) R_{np} = 0$$
(A)

Noting that the atomic force is given by

$$F_{np} = -\frac{\partial E}{\partial R_{np}} = s^{-1} \frac{\partial T}{\partial \overline{R}_{np}} + \frac{\partial U}{\partial \overline{R}_{np}}$$

and inserting the expression of forces to Eq. (A), we have the virial theorem.

$$2T + U = \sum_{n} \mathbf{R}_{n} \cdot \mathbf{F}_{n}$$

## Virial theorem #3

In a large bulk, the atomic forces are non-zero around surface.

$$\sum_{\{d\mathbf{S}\}} \mathbf{R}_n \cdot \mathbf{F}_n \simeq \mathbf{R} \cdot \left(\sum_{\{d\mathbf{S}\}} \mathbf{F}_n\right) = \mathbf{R} \cdot (pd\mathbf{S})$$

Using the Gauss theorem, one can rewrite as

$$\sum_{\{\mathbf{S}\}} \mathbf{R}_n \cdot \mathbf{F}_n \simeq p \int_{S} \mathbf{R} \cdot d\mathbf{S} = p \int (\nabla \cdot \mathbf{R}) dr^3 = 3 p V$$

Thus, the virial theorem is now given by

$$2T + U = 3pV$$

### Analysis of cohesive energy by the virial theorem



The cohesive energy is

given by

At the equilibrium and the well separated atomic state, forces acting on atoms become zero. Thus, from the virial theorem we have

$$2T_{eq} + U_{eq} = 0 \qquad 2T_{at} + U_{at} = 0$$

The total energy is given by

$$E_{eq} = T_{eq} + U_{eq} = -T_{eq} = 1/2U_{eq}$$
$$E_{at} = T_{at} + U_{at} = -T_{at} = 1/2U_{at}$$

$$E_{coh} = -\left(E_{eq} - E_{at}\right) = T_{eq} - T_{at} = \frac{1}{2}\left(U_{at} - U_{eq}\right)$$

 $E_{coh}$  should be positive. Thus, we have an important general consequence:

$$T_{eq} > T_{at}, \quad U_{eq} < U_{at}$$

## A simple example: $H_2$ molecule

 $H_2$  is the simplest molecule which has two nuclei and two electrons. According to the virial theorem, the bonding energy can be understood by the mechanism (a).

### How can we confirm this by DFT ?

	Kinetic energy	
(a)	destabilization	

- (b) stabilization
- (c) stabilization

Potential energy stabilization destabilization stabilization

Total energy  $E(R_{\infty}) = T(R_{\infty}) + V(R_{\infty})$  $E(R_{eq}) = T(R_{eq}) + V(R_{eq})$  Virial theorem  $2T(R_{\infty}) + V(R_{\infty}) = 0$  $2T(R_{eq}) + V(R_{eq}) = 0$ 

From the four eqs. above, the cohesive energy  $\rm D_{eq}$  is given by

$$D_{\rm eq} = -\left(E\left(R_{\rm eq}\right) - E\left(R_{\infty}\right)\right)$$
$$= T\left(R_{\rm eq}\right) - T\left(R_{\infty}\right)$$

The kinetic energy must increase by the bond formation.

# Energy curve of $H_2$



# Binding energy of H<sub>2</sub> #1

		Total energy	
<b>State</b>		(Hartree)	
$H_2$		-1.16581	
H (non-spin polari:	zation)	-0.45781	
H (spin polarizatio	on)	-0.49914	
Spin polarization of	energy	0.04133	
Binding energy =	2 H - H <sub>2</sub>		
=	$2 \times (-0.499)$	4) - (-1.16581)	
=	0.1675 (Har	tree)	
=	4.56 (eV)		
Expt.	4.75 (eV)		

The calculated value is underestimated by 0.19 eV.

# Binding energy of $H_2$ #2

### Kinetic energy

#### Potential energy



 $\Delta E_{kin} = 1.11582-0.98309 = 0.13273 \text{ (Hartree)} = 3.612 \text{ (eV)}$   $\Delta E_{pot} = -2.28163 \text{-}(-1.98139) = -0.30024 \text{ (Hartree)} = -8.170 \text{ (eV)}$  $\Delta E_{tot} = -4.56 \text{ (eV)}$ 

In fact, one can see that the energy gain follows the virial theorem.

Strictly speaking, the discussion should be corrected in GGA, since the correlation energy includes a part of the kinetic energy. But the effect is not so large.

## Shrinking of Kohn-Sham orbital in H<sub>2</sub>



The KS orbital shrinks, and localized around the bond center, resulting in the increase of kinetic energy.

The superposition of nucleus potentials at the bond center provides a deeper potential, resulting in the lowering of potential energy.

⇒ The energy gain is obtained.

# Difference electron density



Red:increaseBlue:decrease

The increase of electron density can be seen between nuclei.

The electrons obtain energy gain due to localization at the place of the deeper potential.

Difference electron density = (electron density of H2) - (superposition of two H electron density)

### Why the FM state is stable when separated ?



# Eigenenergies of HOMO and LUMO



The HOMO-LUMO gap is getting smaller as increasing the bond distance.

At 5Å, it becomes almost zero.

According to a simple tight-binding model, Eigenvalues  $E = \mathcal{E}_0 \pm h$   $\varepsilon_0$  (+h) (-h)  $\varepsilon_0$  (+h)  $\phi_e = \frac{1}{\sqrt{2}} \chi_1 - \frac{1}{\sqrt{2}} \chi_2$   $\phi_g = \frac{1}{\sqrt{2}} \chi_1 + \frac{1}{\sqrt{2}} \chi_2$ 

### Density of states of $H_2$ at 3Å separation



In the non-magnetic state the up- and down states are degenerate.

In the magnetic state, we have a large exchange splitting between up and down spin state. Two electrons populate only in the up spin states.

Note: the chemical potential is set to zero.

### Competition between two energies

For  $H_2$  at 3Å separation, the energy contributions of the NM and FM states are given by

	NM	FM	
Ekin	0.8231	0.9634	
E <sub>pot</sub>	-1.7306	-1.9148	
	-0.9076	-0.9514	
			in Hartree

In the FM state, the increase of the kinetic energy is overly compensated by the decrease of the potential energy which is the sum of the Coulomb and exchange-correlation energies.

Why does this happen ?

### Molecular orbitals of HOMO and LUMO states

At the equilibrium bond length, isosurfaces of the HOMO and LUMO states are shown below:

HOMO

LUMO



LUMO has a node. Thus, the kinetic energy increase if an electron populates in LUMO.

### Reason why the FM state is favored when separated

When an electron is promoted from the HOMO to LUMO states, the kinetic energy increases, since the LUMO state has the nodal structure in the molecular orbital unlike the HOMO state.

On the other hand, the promoted electron can be resident in the different orbital.

This leads to the decrease of the potential energy (Coulomb+exchange-correlation energies).

Since the total energy is the sum of two energies, the energetics is determined by the competition between them. Around 2.0Å, there is the phase boundary.

A similar mechanism will be found in many materials such as the Stoner condition.



	NM	FM
E <sub>kin</sub>	0.8231	0.9634
E <sub>pot</sub>	-1.7306	-1.9148
Etot	-0.9076	-0.9514



To get familiar with analysis of electronic structure, we analyze simple molecules.

Methane
Benzene
H<sub>2</sub>0

### Hybridized orbitals and molecular structures

#### sp<sub>3</sub> hybridized orbitals

$$\phi_{1} = \frac{1}{2} \chi_{s} + \frac{\sqrt{3}}{2} \chi_{p_{x}}$$

$$\phi_{2} = \frac{1}{2} \chi_{s} - \frac{1}{2\sqrt{3}} \chi_{p_{x}} + \sqrt{\frac{2}{3}} \chi_{p_{y}}$$

$$\phi_{3} = \frac{1}{2} \chi_{s} - \frac{1}{2\sqrt{3}} \chi_{p_{x}} - \frac{1}{\sqrt{6}} \chi_{p_{y}} + \frac{1}{\sqrt{2}} \chi_{p_{z}}$$

$$\phi_{4} = \frac{1}{2} \chi_{s} - \frac{1}{2\sqrt{3}} \chi_{p_{x}} - \frac{1}{\sqrt{6}} \chi_{p_{y}} - \frac{1}{\sqrt{2}} \chi_{p_{z}}$$

sp<sub>2</sub> hybridized orbitals

$$\phi_{1} = \frac{1}{2} \chi_{s} + \sqrt{\frac{2}{3}} \chi_{p_{x}}$$

$$\phi_{2} = \frac{1}{\sqrt{3}} \chi_{s} - \frac{1}{\sqrt{6}} \chi_{p_{x}} + \frac{1}{\sqrt{2}} \chi_{py}$$

$$\phi_{3} = \frac{1}{\sqrt{3}} \chi_{s} - \frac{1}{\sqrt{6}} \chi_{p_{x}} - \frac{1}{\sqrt{2}} \chi_{py}$$

sp hybridized orbitals

$$\phi_1 = \frac{1}{\sqrt{2}} \chi_s + \frac{1}{\sqrt{2}} \chi_{p_x}$$
$$\phi_2 = \frac{1}{\sqrt{2}} \chi_s - \frac{1}{\sqrt{2}} \chi_{p_x}$$

Methane



Benzene

Acetylene



### Simple picture of hybridization



### Density of states of $CH_4$



DOS suggests  $sp_3$  hybrid orbitals may not be formed.

Instead, it is natural to consider that s,  $p_x$ ,  $p_y$ ,  $p_z$ orbitals form the bonding states with s-orbitals of H atoms.

#### A picture by DFT



### DOS of a benzene molecule





### DOS of a benzene molecule



### Bonding in a benzene molecule



### DOS and molecular orbitals of $H_2O$



# Summary

Understanding the cohesive mechanism is a starting point for materials science. The virial theorem provides us a firm basis in understanding the cohesion. Through the analysis of  $H_2$  molecule, we saw how the bonding is formed.

- Experiments and theories
- Density functional theory
- Virial theorem
- Bonding in a  $H_2$  molecule
- Electronic structures of simple molecules

### Question time

### Virial theorem

According to Per-Olov Löwdin, J. Mol. Spec. 3. 46 (1959). we will derive the vivial theorem. The system consists of Nelectrons and Mnuclei, whose Hamiltonian is given by  $\hat{T} = \sum_{i} \left( -\frac{1}{2} \nabla_{i}^{2} \right)$  $\hat{H} = \hat{T} + \hat{U}$  $\hat{U} = \sum_{i>j} \frac{1}{|k_i - k_j|} + \sum_{n>n'} \frac{Z_n Z_{n'}}{|R_n - R_n'|} + \sum_{i=n} \frac{Z_n}{|k_i - R_n|}$ ---- (1) Shrödinger eg. We consider the derivation AY = EY within adiabatic approximation. But the generalization is possible.  $E = \langle \Psi | \hat{H} | \Psi \rangle = (\Psi^* \hat{H} + dV)$ ~ - - - r (2)  $dv = dv_1 dv_2 dv_3 \cdots dv_N, \quad dv_1 = dx_1 dy_1 dz_1$ Now we introduce a scaling for variables.  $\mathbf{h}_{i} = \mathbf{S}^{-1} \left( \mathbf{S} \mathbf{h}_{i} \right) = \mathbf{S}^{-1} \overline{\mathbf{h}}_{i}$ - - - - (3)  $\mathbb{R}_{n} = S^{-1}\left(\underline{S} | \underline{R}_{n}\right) = S^{-1}\overline{\mathbb{R}}_{n}$ We further consider a scaled wave function ts:  $Y_{s} = S^{\frac{3N}{2}} \psi(sn, Sh_{2}, ---, Sh_{N}) \cdots (4)$ 

Noting the following velation:  

$$dV_{1} = dx_{1} dy_{1} dz_{1} = S^{-3} d(Sx_{1}) d(Sy_{1}) d(Sz_{1})$$

$$= S^{-3} d\tilde{x}_{1} dy_{1} d\tilde{z}_{1} = S^{-3} d\tilde{x}_{1}$$

$$dv = dv_{1} dv_{2} \dots dv_{N} = S^{-3N} d\tilde{v}_{1} d\tilde{v}_{2} \dots d\tilde{v}_{N}$$

$$dv = S^{-3N} d\tilde{v} d\tilde{v}$$
We can confirm that  $\psi$  is normalized.  

$$\int dv \ \psi_{s}^{*} \ \psi_{s} = S^{3N} \int dv \ \psi^{*}(\tilde{w}_{1}, \tilde{w}_{2}, \dots, \tilde{w}_{N}) \psi(\tilde{w}_{1}, \tilde{v}_{2}, \dots, \tilde{w}_{N})$$

$$= S^{3N} S^{-3N} \int d\tilde{v} \ \psi^{*}(\tilde{w}_{1}, \tilde{w}_{2}, \dots, \tilde{w}_{N}) \psi(\tilde{w}_{1}, \tilde{v}_{2}, \dots, \tilde{w}_{N})$$

$$Ising the Scaled  $\psi, we calculate the expectation value for  $\hat{T}.$ 

$$S^{-3N} d\tilde{v}$$

$$(\psi_{s} | \tilde{T} | \psi_{s} \rangle = S^{3N} \int dv \ \psi^{*}(\tilde{w}_{1}, \tilde{w}_{2}, \dots, \tilde{w}_{N}) \hat{T} \ \psi(\tilde{w}_{1}, \tilde{w}_{2}, \dots, \tilde{w})$$

$$Noting that$$

$$\nabla_{i}^{2} = \left(\frac{d^{2}}{dx_{i}^{2}} + \frac{d^{2}}{dy_{i}^{2}} + \frac{d^{2}}{dz_{i}^{2}}\right) = S^{2} \left(\frac{d^{2}}{d\tilde{w}_{i}^{2}} + \frac{d^{2}}{d\tilde{w}_{i}^{2}}\right)$$
We have  

$$\langle \psi_{s} | \tilde{T} | \psi_{s} \rangle = S^{2} \langle \psi_{s} | \tilde{T}_{s} | \psi_{s} \rangle$$

$$For (SFS),$$
the expectation of  $\tilde{T}$  is calculate with S=1.$$$

Next we calculate 
$$\langle \Psi_{S} | \hat{U} | \Psi_{S} \rangle$$
  
 $\langle \Psi_{S} | \hat{U} | \Psi_{S} \rangle = S^{3N} \int dV \Psi^{*}(\overline{\mu}, \overline{\mu}_{S}, ..., \overline{\mu}_{N}) \hat{U} \Psi(\overline{\mu}, \overline{\mu}_{S}, ..., \overline{\mu})$   
where  $\hat{U} = S \hat{U} (\{\overline{\mu}, \overline{\mu}_{S}\}), dV = S^{-3N} d\overline{V}$   
we have  
 $\langle \Psi_{S} | \hat{U} | \Psi_{S} \rangle = S \langle \Psi_{S} | \hat{U}_{S} | \Psi_{S} \rangle$   
 $= S U(1, \{SR\}) = S U(S) \dots (7)$   
For  $\{SR\}, \text{ the expectation of U is calculated}$   
From (6) and (7), we have  
 $With S = 1.$   
 $E(S) = \langle \Psi_{S} | \hat{T} | \Psi_{S} \rangle + \langle \Psi_{S} | \hat{U} | \Psi_{S} \rangle$   
 $= S^{2} T(S) + S U(S) \dots (8)$   
At  $S = 1.$   $\Psi_{S}$  be come the true Wave function.  
Thus, we have  
 $\left(\frac{\partial E(S)}{\partial S}\right)_{S=1}^{S=1} + S^{2} \sum_{n,p}^{2} \frac{\partial T(S)}{\partial \overline{R}_{np}} + S \sum_{n,p}^{2} \frac{\partial U(S)}{\partial \overline{R}_{np}} + \frac{\partial \overline{R}_{np}}{\partial \overline{R}_{np}} = 0$ 

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$$\begin{array}{c} \textcircled{\bullet}\\ 2 \ T(1) \ + \ U(1) \ = \ \prod_{n} \ \mathbb{F}_{n} \ \cdot \mathbb{R}_{n} \qquad (9) \\ & \mathbb{F}_{n} \ = - \frac{\partial}{\partial \mathbb{R}_{n}} \left( \ \top \ + \ U \right) \qquad \cdots \qquad (10) \\ (9) \ \text{is the Virial theorem, where the right hand} \\ & \underline{\text{side is calle 6 virial.}} \\ \hline (9) \ \text{is the Virial theorem, where the right hand} \\ & \underline{\text{side is calle 6 virial.}} \\ \hline (9) \ \text{is the Virial theorem, where the right hand} \\ & \underline{\text{side is calle 6 virial.}} \\ \hline (9) \ \text{is the Virial theorem, where the right hand} \\ & \underline{\text{side is calle 6 virial.}} \\ \hline (9) \ \text{is the Virial theorem, where the right hand} \\ & \underline{\text{side is calle 6 virial.}} \\ \hline \text{Let's consider a large bulk, and cut it} \\ \hline \text{to have Surface as shown below.} \\ \hline & \frac{d }{d } \qquad After \ \text{cutting.} \\ \hline & \frac{d }{d } \ \ After \ \text{cutting.} \\ \hline & \frac{d }{d } \ \ After \ After \ After \ After \ After \ After \ Afte$$

Cohesive energy At the equilibrium and atomic state, forces acting on atoms should be Zero. Thus, from the Virial theorem. We have Atom(at) Equilibrium (eq) 2 Tat + Vat = 2 Teg + Veg = The energy is given by from (14)  $I_{a+t} = -\overline{I}_{a+t} = \frac{1}{2}V_{a+t}$ Eat = Tat + Uat = - Tat Eeq = Teq + Ueq = -Teq- Veg 2 · · (15) The cohesive energy is given by Ecoh - (Eeg - Eat) = Eat - Eeg Ξ  $Teq - Tat = \frac{1}{2} (Vat - Veq)$ - ~- ( (6 ) In order to be Ecoh >0, we have the following Conditions: Teg > Tat, Veg < Uat --. (17)