Student ID number: ___________________ Name: ________________

Midterm exam –(MSA251) Materials Engineering– Spring (2023/4/20)

Show your calculations if necessary.

Ch2. ATOMIC STRUCTURE AND INTERATOMIC BONDING

1. (5 pts) *Sodium chloride (NaCl) exhibits predominantly ionic bonding. The Na^+ and Cl^- ions have electron structures that are identical to which two inert gases?*
- NaCl 에서 Na+와 Cl-는 어떤 원소의 전자구조와 동일한가?

Neon, Argon

2. (30 pts) *For a hypothetical X+-Y- ion pair, attractive and repulsive energies E_A and E_R, respectively, depend on the distance between the ions r, according to*

$$E_A = -\frac{A}{r}, \quad E_R = \frac{B}{r^n}$$

The equilibrium interionic spacing and bonding energy values of the ion pair are 0.35 nm and -6.13 eV, respectively. The net energy E_N is the sum of the two expressions above. If n = 10, calculate A and B. Show your calculation. (Don't forget to write down the answers with the ***unit****.)*

임의의 양이온 음이온 쌍에서 attractive 에너지와 repulsive 에너지 식음 다음과 같다. 두 이온의 평형상태에서 원자간 거리는 0.35nm 이고 이때 결합 에너지는 -6.13eV 이다. n=10 일때, A 와 B 를 구하시오.

$$\frac{dE_N}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} + \frac{d\left(\frac{B}{r^n}\right)}{dr}$$

$$= \frac{A}{r^{(1\,+\,1)}} - \frac{nB}{r^{(n\,+\,1)}} = 0$$

Now, solving for r (= r_0)

$$\frac{A}{r_0^2} = \frac{nB}{r_0^{(n+1)}}$$

or

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1-n)}$$

$$0.35\ \text{nm} = \left(\frac{A}{10\,B}\right)^{1/(1-10)} = \left(\frac{A}{10\,B}\right)^{-1/9}$$

and

$$-6.13\ \text{eV} = -\frac{A}{\left(\frac{A}{10\,B}\right)^{1/(1-10)}} + \frac{B}{\left(\frac{A}{10\,B}\right)^{10/(1-10)}}$$

$$= -\frac{A}{\left(\frac{A}{10B}\right)^{-1/9}} + \frac{B}{\left(\frac{A}{10B}\right)^{-10/9}}$$

$$\frac{A}{10B} = (0.35\ \text{nm})^{-9}$$

$$A = 10B(0.35\ \text{nm})^{-9}$$

following results

$$-6.13\ \text{eV} = = -\frac{A}{\left(\frac{A}{10B}\right)^{-1/9}} + \frac{B}{\left(\frac{A}{10B}\right)^{-10/9}}$$

$$= -\frac{10B(0.35\ \text{nm})^{-9}}{\left[(0.35\ \text{nm})^{-9}\right]^{-1/9}} + \frac{B}{\left[(0.35\ \text{nm})^{-9}\right]^{-10/9}}$$

$$= -\frac{10B(0.35\ \text{nm})^{-9}}{0.35\ \text{nm}} + \frac{B}{(0.35\ \text{nm})^{10}}$$

Or

$$-6.13\ \text{eV} = = -\frac{10B}{(0.35\ \text{nm})^{10}} + \frac{B}{(0.35\ \text{nm})^{10}} = -\frac{9B}{(0.35\ \text{nm})^{10}}$$

Solving for B from this equation yields

$$B = 1.88 \times 10^{-5} \text{ eV-nm}^{10}$$

Furthermore, the value of *A* is determined from one of the previous equations, as follows:

$$A = 10B(0.35 \text{ nm})^{-9} = (10)\left(1.88 \times 10^{-5} \text{ eV-nm}^{10}\right)(0.35 \text{ nm})^{-9}$$

$$= 2.39 \text{ eV-nm}$$

Ch3. STRUCTURES OF METALS AND CERAMICS

3. (30 pts) *Molybdenum has a BCC crystal structure and an atomic radius of 0.1363 nm. Calculate the interplanar spacing (nm) for the (111) set of plane. The answer should be rounded to the nearest thousandths. (정답은 소수점 넷째자리에서 반올림해서 셋째자리까지 쓸 것.)*

Mo 는 bcc 구조를 갖고 있고 원자 반지름이 0.1363nm 이다. (111) 면의 면간 거리(d)를 계산하시오

Solution

the lattice parameter *a* may be computed as

$$a = \frac{4R}{\sqrt{3}} = \frac{(4)(0.1363\ \text{nm})}{\sqrt{3}} = 0.3148\ \text{nm}$$

Now, the interplanar spacing d_{111} maybe determined using this equation

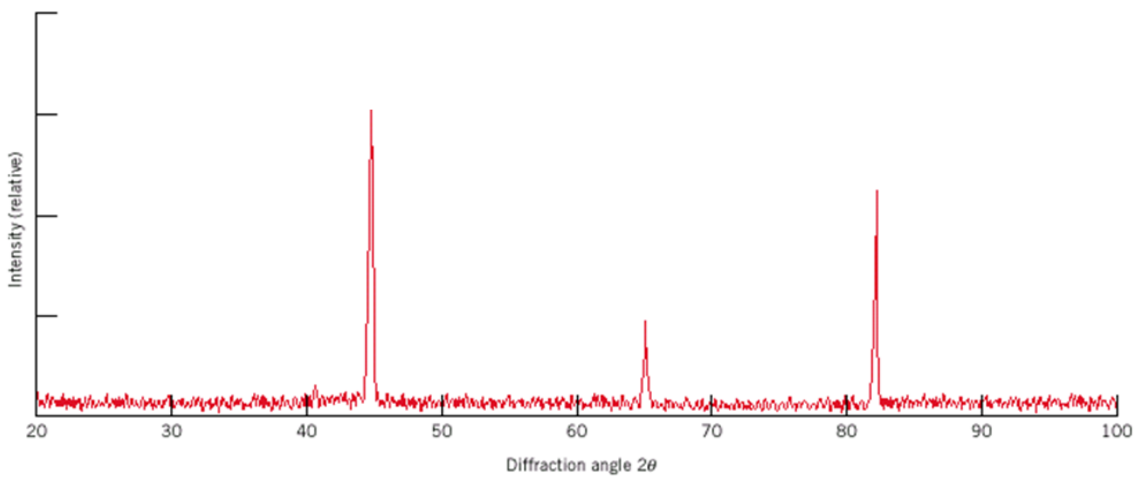
$$d_{111} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (1)^2}} = \frac{0.3148\ \text{nm}}{\sqrt{3}} = 0.1817\ \text{nm} \rightarrow \mathbf{0.182\ nm}$$

4. (15 pt)

(1) (5 pt) What is Brag's law? Write down the equation.
브래그 법칙을 쓰시오.

$\lambda = 2d_{hkl} \sin\theta$

(2) (5 pt) It is a XRD profile of BCC structure. Write down each (hkl) plane of the three peaks.
아래 그림이 bcc 구조의 xrd 그래프이다. 3 개의 픽의 면지수를 쓰시오.



(110) (200) (211)

(3) (5 pt) If the first peak position is 44 degrees, what is the d-spacing of this plane (x-ray source: 1.54 angstrom)
첫번째 픽의 2θ 값이 44 도 일 때, 이 면의 면간거리(d) 를 구하시오

$\lambda = 2d_{hkl} \sin\theta$

Sin22 = 0.37, 1.54A / 0.37 /2 = 2.08 A

1. (Hydrogen atom)
   (5 pts) Total energy is the sum of potential energy and kinetic energy. What would be the equation for the ground state energy of a hydrogen atom if we treat it only with classical mechanics?

총 에너지는 위치에너지와 운동에너지의 합이다. 만약에 고전역학으로 수소원자의 바닥상태를 수식으로 표현하면 어떻게 되는가?

$$E = -\frac{e^2}{|r|} + \frac{|p|^2}{2m}$$

2. (Hydrogen atom)
   (a) (5 pts) In quantum mechanics, what is the definition of wave function?
   양자역학에서 파동함수의 정의는?

- A function of position (r) that describes the probability of finding the electron at position r.
- Contain information of position and momentum

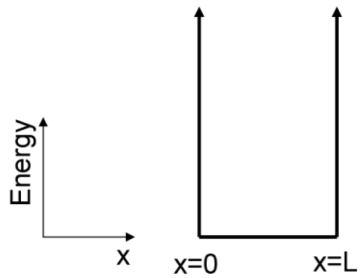
   (b) (5 pts) What is the meaning of "wave function is zero?"
   파동함수가 0 이 의미하는 바가 무엇인가?

electron doesn't exist

3. (Hydrogen atom)
   (10 pts) Write down the expression for the expectation value of the **kinetic energy** for the H atom (considering the proton to be fixed in space) in terms of the electronic wave function Ψ in spherical coordinate.
   수소 원자의 운동에너지 기대값을 구좌표계의 파동함수를 이용하여 수식으로 쓰시오. (가정, 양성자는 위치가 고정되어 있다)

$$K = -\frac{\hbar^2}{2m}\int \psi \nabla^2 \psi d^3 r$$

4. (Particle in a box)



To find the possible states (wave functions) of the electron in the box, we need to solve Schrodinger equation. Potential energy inside the box is zero and infinite outside the box.

위 그림의 박스내에 존재하는 전자의 파동함수를 구하기 위해서 슈뢰딩거 방정식을 풀어야 한다. 박스 내부 포텐셜 에너지는 zero 이고 외부는 무한대이다.

(a) (5 pts) write down (1) the Schrodinger equation for the particle in the box and (2) the boundary condition.
위 박스 조건에 맞는 슈뢰딩거 방정식과 경계조건을 쓰시오.

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x)$$

$$\psi(x=0)=0 \quad \psi(x=L)=0$$

(b) (5pt) Solve the Schrodinger equation in (a) using the trial function below. The answer should be wave function and energy.

아래의 trial 함수를 사용하여 위 슈뢰딩거 방정식을 풀어라

$$\psi(x) = A\sin(kx)$$

.

$$\psi_n(x) = A\sin\left(\frac{n\pi}{L}x\right) \qquad E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2$$

(b) (20 pts) What is the A in the wave function that you obtained in (b)? You can achieve A by normalization. Show your calculation.

Normalization 을 통해서 A 값을 구하라.

$$\int \sin^2(ax)\,dx = \frac{x}{2} - \frac{1}{4a}\sin(2ax)$$

$$\therefore \int_0^L \sin^2\left(\frac{n\pi}{L}x\right)dx = \frac{x}{2} - \frac{L}{4n\pi}\sin\left(\frac{2n\pi}{L}x\right)\Bigg|_0^L = \left(\frac{L}{2} - 0\right) - (0-0) = \frac{L}{2}$$

$$\therefore B^2\frac{L}{2} = 1 \quad \Rightarrow B = \sqrt{\frac{2}{L}}$$

$$\therefore \Psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

5. (Hydrogen atom) (**<u>Expectation value of the potential energy)</u>** As we have seen in the lectures, the 1s wave function of H atom is given by:
수소원자 바닥상태 (1s 오비탈)의 파동함수는 다음과 같다.

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} \exp(-\frac{r}{a_0})$$

(a) (5 pts) What is the ground state energy of hydrogen atom? The answer should contain *e* and a_0.
수소원자의 바닥상태 에너지는 몇인가?

-1/2 x e^2/a_0

(b) (10 pts) What is the expectation value of the potential energy of hydrogen atom? Show your calculation step by step.
수소원자 내 전자의 포텐셜 에너지의 기대값은 무엇인가?

$$\langle V \rangle = \int_0^\infty 4\pi r^2 \frac{1}{\sqrt{r_0^3 \pi}} \exp\left(-\frac{r}{r_0}\right)\left(\frac{-e^2}{r}\right)\frac{1}{\sqrt{r_0^3 \pi}} \exp\left(-\frac{r}{r_0}\right) dr =$$

$$= -\frac{4e^2}{r_0^3}\int_0^\infty r \exp\left(-\frac{2r}{r_0}\right) dr$$

$$= -\frac{4e^2}{r_0^3}\int_0^\infty r \exp\left(-\frac{2r}{r_0}\right) dr \qquad \frac{2r}{r_0} = r' \quad \frac{2}{r_0} dr = dr'$$

$$= -\frac{4e^2}{r_0^3}\int_0^\infty \left(\frac{r_0}{2}\right)^2 r' e^{-r'} dr' = -\frac{e^2}{r_0}\underbrace{\int_0^\infty r' e^{-r'} dr'}_{1} =$$

$$\langle V \rangle = -\frac{e^2}{r_0}$$ Equivalent to electron being at r_0

(위 파란색 풀이 중에서 밑줄 긋고 1 이라고 쓰여있는 적분계산의 풀이과정을 정확히 써야함. (xy)' = x'y + xy' 미분 공식에 양변을 적분한 수식을 적용하여야함.

X 를 r’, 그리고 y’를 exp(-r’)이라 놓으면, 적분내의 r’을 제거하여 적분 계산할 수 있음.)

(c) (5 pt) Based on the answer (a) and (b), what is the kinetic energy of the electron in hydrogen?

위 계산을 바탕으로 수소원자 내 전자의 운동에너지를 구하시오

Total Energy = -0.5e^2/a_0
Potential Energy = -e^2/a_0
Kinetic energy = total energy - potential energy = -0.5e^2/a_0 + e^2/a_0 = 0.5e^2/a_0

6. (10pt, Hydrogen atom) We can solve real H atom with Schrodinger equation expressed like below.

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{e^2}{|\vec{r}|}\right]\psi(\vec{r})=E\psi(\vec{r})$$ -------------(1)

Due to the fact that the ground state wave function of H atom is independent of orientation, spherical coordinate allows us to more easily solve the Schrodinger equation than x-y-z coordinate. In the spherical coordinate, Schrodinger equation can be written in like below.

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)-\frac{Ze^2}{r}\right]R(r)=ER(r)$$ -------------------(2)

Show how to convert the Eq. (1) to Eq.(2). (write down on the next page)

직각좌표계로 표현된 수식 1 을 구형좌표계 수식 2 로 변형시키시오.

$r^2 = x^2+y^2+z^2$

$\left(\frac{\partial r}{\partial z}\right)_{x,y} = \frac{\partial}{\partial z}\sqrt{x^2+y^2+z^2} = \frac{z}{r}$

(Another way. $2r\,dr = 2z\,dz$, so, $\frac{\partial r}{\partial z} = \frac{z}{r}$

$\left|\frac{\partial}{\partial z} f(r)\right|_{x-y} = \left(\frac{\partial r}{\partial z}\right)_{x-y}\left(\frac{\partial f}{\partial r}\right) = \frac{z}{r} f'(r)$

$\frac{\partial^2}{\partial z^2} f(r) = \frac{\partial}{\partial z}\left(\frac{\partial f}{\partial z}\right) = \frac{\partial}{\partial z}\left(\frac{z}{r} f'(r)\right)$

$= \frac{1}{r} f'(r) + z\cdot\frac{\partial}{\partial z}\left(\frac{f'(r)}{r}\right)$

$= \quad '' \quad + z\,\frac{\partial r}{\partial z}\cdot\frac{\partial}{\partial r}\left(\frac{f'(r)}{r}\right)$

$= \quad '' \quad + z\,\frac{\partial r}{\partial z}\left(-\frac{f'(r)}{r^2}+\frac{f''(r)}{r}\right)$

$= \quad '' \quad + \frac{z^2}{r}\left(-\frac{f'(r)}{r^2}+\frac{f''(r)}{r}\right)$

$= \left(\frac{1}{r}-\frac{z^2}{r^3}\right)f'(r) + \frac{z^2}{r^2} f''(r)$

combinding with $\frac{\partial^2}{\partial x^2} f(r)$ and $\frac{\partial^2}{\partial y^2} f(r)$ leads to

$\nabla^2 f(r) = f''(r) + \frac{2}{r} f'(r)$

동일한 방식으로 $(dr/dy)^2$, $(dr/dx)^2$ 구하고 합하여

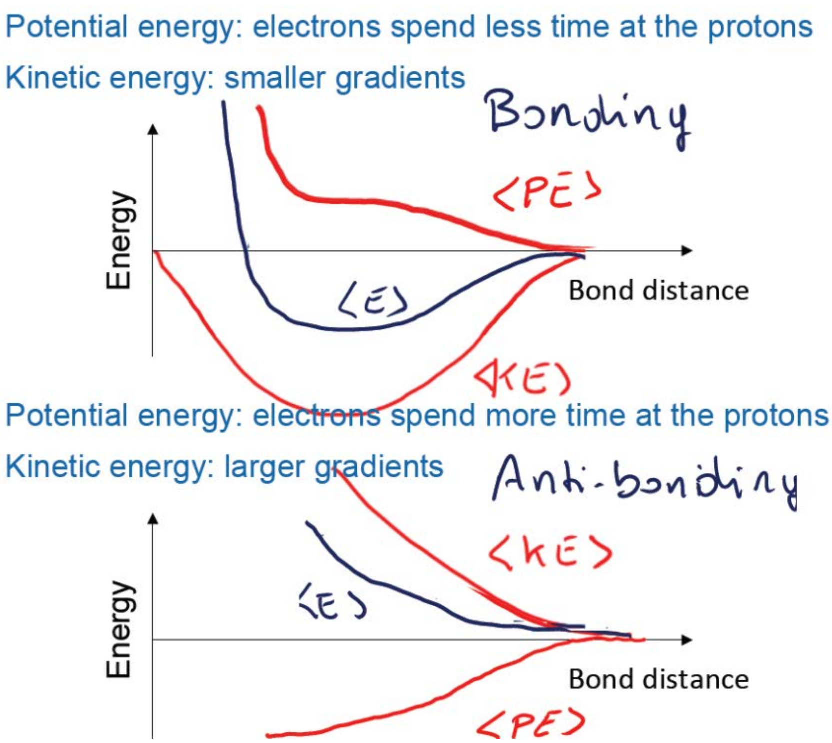
$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$이 $\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)$이 됨을 보임.

7. (15pt, H_2^+ molecules) Explain why He atoms do not exist as He_2 in terms of energy. For the explanation, you may need to use H_2^+ energy states that are achieved by the molecular wave functions approximated by LCAO. In your answer, you should show symmetric and anti-symmetric configuration of H^2+.

왜 He_2 분자는 존재하지 않는지 설명하시오. 이를 위해 H_2^+ 에너지 상태를 이용해야 함.

H2+ 분자의 energy state 을 계산하기 위해서 LCAO (linear combination of atomic orbital) approximation 이 필요함.

LCAO 를 이용하면 symmetric 과 anti-symmetric state 이 존재하게 되는데



두 state 의 KE (kinetic E)와 PE(potential E)는 원자간 거리에 따라 위 그림과 같이 변함.

KE 와 PE 의 합인 total energy <E>는 symmetric 상태 (위 그래프)가 낮고 anti-symmetric 상태는 두 원자가 멀리 떨어져 있을때보다 에너지가 높아짐. 낮은 에너지 상태를 bonding state, 높은 것을 anti-bonding state 이라고 함.

He_2 분자도 H2+와 유사하다고 가정하면 두 원자가 가까워 지면 bonding state 과 anti-bonding state 이 존재하게 되는데 He 하나당 각각 2 개의 전자가 있기 때문에 만약 두 He 이 가까워지면 anti-bonding state 에 전자가 채워져야함.

하지만 anti-bonding state 의 에너지가 He 이 원자상태로 존재할때의 에너지 상태보다 높기 때문에 전자가 더 높은 에너지 상태인 anti-bonding state 에 전자를 채우면서까지 존재하려 하지 않음. 따라서 He 는 He2 로 존재하지 않음.