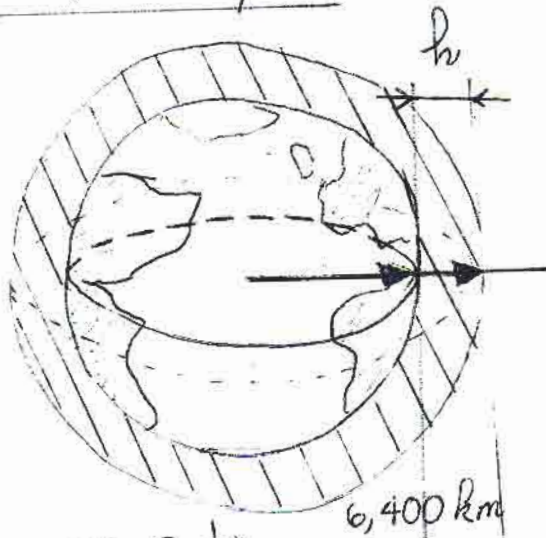
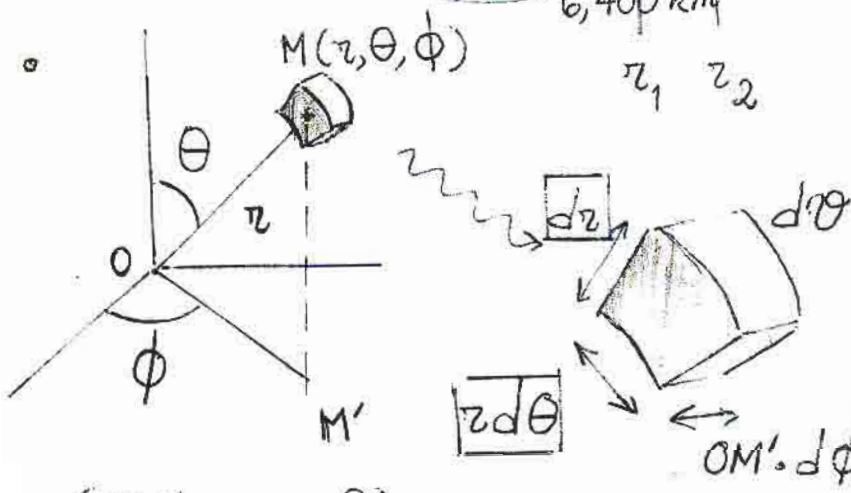


3.012 Bonding : PST solution

1. Earth's atmosphere 10 km



$$\left\{ \begin{array}{l} r_1 = 6,400 \text{ km} \\ r_2 = r_1 + h \\ r_2 = 6,400 \text{ km} + 10 \text{ km} \\ r_2 = 6,410 \text{ km} \end{array} \right.$$



volume element in spherical coordinates:

$$dV = dr r d\theta r \sin \theta d\phi$$

$$dV = r^2 \sin \theta dr d\theta d\phi$$

$(OM' = r \sin \theta)$

The volume of the Earth's atmosphere can be written as:

$$V_a = \int_{r=r_1}^{r=r_2} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \underbrace{r^2 \sin \theta}_{dV} dr d\theta d\phi$$

$$V_a = \int_{r_1}^{r_2} r^2 dr \left\{ \int_{\theta=0}^{\theta=\pi} \sin \theta d\theta \left(\int_{\phi=0}^{2\pi} d\phi \right) \right\}$$

$$\int_{\phi=0}^{2\pi} d\phi = [\phi]_0^{2\pi} = 2\pi \quad ; \quad \int_{\theta=0}^{\theta=\pi} \sin \theta d\theta = [-\cos \theta]_0^{\pi} = 2$$

$$\int_{r_1}^{r_2} r^2 dr = \left[\frac{r^3}{3} \right]_{r_1}^{r_2} = \frac{1}{3} (r_2^3 - r_1^3)$$

As a result, $V_a = \frac{1}{3} (r_2^3 - r_1^3) \{ 2 (2\pi) \}$

$$V_a = \frac{4\pi}{3} (r_2^3 - r_1^3)$$

$$= V_2 - V_1$$

V_2 : volume of a sphere
of radius r_2

V_1 : " " " " r_1

$$V_a = \frac{4\pi}{3} (6,410^3 - 6,400^3) \text{ km}^3$$

$$V_a = 5.155 \times 10^9 \text{ km}^3$$

2. a) \hat{x} (real) ($\longrightarrow x$)

- α_1, α_2 : complex numbers
- ϕ_1, ϕ_2 : wavefunctions

$$x(\alpha_1 \phi_1(x) + \alpha_2 \phi_2(x)) = \alpha_1(x \phi_1(x)) + \alpha_2(x \phi_2(x))$$

thus, x is linear

$$\langle \phi_1 | x \phi_2 \rangle = \int_{-\infty}^{+\infty} (\phi_1(x))^* (x \phi_2(x)) dx$$

$$= \int_{-\infty}^{+\infty} x^* (\phi_1(x))^* \phi_2(x) dx$$

($x = x^*$ because
 x is a real
number)

$$= \int_{-\infty}^{+\infty} (x \phi_1(x))^* \phi_2(x) dx$$

$$\langle \phi_1 | x \phi_2 \rangle = \langle x \phi_1 | \phi_2 \rangle$$

x is hermitian

b) [optional]

$$\underline{[\hat{x}, \hat{p}_x]} (\longrightarrow [x, -i\hbar \frac{\partial}{\partial x}])$$

$$\bullet [\hat{x}, \hat{p}_x] \phi(x) = [x, -i\hbar \frac{\partial}{\partial x}] \phi(x)$$

$$= x \left(-i\hbar \frac{\partial}{\partial x} \phi(x) \right) - \left\{ -i\hbar \frac{\partial}{\partial x} (x \phi(x)) \right\}$$

$$= -i\hbar x \frac{d}{dx} \phi(x) + i\hbar \left(\frac{d}{dx} x \right) \phi(x) + i\hbar x \frac{d}{dx} \phi(x)$$

$$\Rightarrow \underline{[\hat{x}, \hat{p}_x] \phi(x) = i\hbar \phi(x)}$$

• α_1, α_2 : complex numbers ; ϕ_1, ϕ_2 : wavefunctions

$$\begin{aligned} [\hat{x}, \hat{p}_x] \{ \alpha_1 \phi_1(x) + \alpha_2 \phi_2(x) \} &= i\hbar \{ \alpha_1 \phi_1(x) + \alpha_2 \phi_2(x) \} \\ &= \alpha_1 (i\hbar \phi_1(x)) + \alpha_2 (i\hbar \phi_2(x)) \\ [\hat{x}, \hat{p}_x] \{ \alpha_1 \phi_1(x) + \alpha_2 \phi_2(x) \} &= \alpha_1 ([\hat{x}, \hat{p}_x] \phi_1(x)) \\ &\quad + \alpha_2 ([\hat{x}, \hat{p}_x] \phi_2(x)) \end{aligned}$$

• $\langle \phi_1 | [\hat{x}, \hat{p}_x] \phi_2 \rangle = \langle \phi_1 | i\hbar \phi_2 \rangle$

$$\begin{aligned} &= \int_{-\infty}^{+\infty} (\phi_1(x))^* i\hbar \phi_2(x) dx \\ &= \int_{-\infty}^{+\infty} -(i\hbar)^* (\phi_1(x))^* \phi_2(x) dx \quad (i^* = -i) \\ &= - \int_{-\infty}^{+\infty} (i\hbar \phi_1(x))^* \phi_2(x) dx \\ \langle \phi_1 | [\hat{x}, \hat{p}_x] \phi_2 \rangle &= - \langle [\hat{x}, \hat{p}_x] \phi_1 | \phi_2 \rangle \neq \langle [\hat{x}, \hat{p}_x] \phi_1 | \phi_2 \rangle \end{aligned}$$

$[\hat{x}, \hat{p}_x]$ is not hermitian

c) $i \frac{d^2}{dx^2}$

• α_1, α_2 : complex numbers ; ϕ_1, ϕ_2 : wavefunctions

$$i \frac{d^2}{dx^2} \{ \alpha_1 \phi_1(x) + \alpha_2 \phi_2(x) \} = \alpha_1 \left(i \frac{d^2}{dx^2} \phi_1(x) \right) + \alpha_2 \left(i \frac{d^2}{dx^2} \phi_2(x) \right)$$

$i \frac{d^2}{dx^2}$ is linear

$$\langle \phi_1 | i \frac{d^2}{dx^2} \phi_2 \rangle = \int_{-\infty}^{+\infty} (\phi_1(x))^* \left(i \frac{d^2}{dx^2} \phi_2(x) \right) dx$$

$$= i \int_{-\infty}^{+\infty} (\phi_1(x))^* \frac{d^2}{dx^2} \phi_2(x) dx$$

integration by parts

$$\int_{-\infty}^{+\infty} u(x) \frac{dv}{dx}(x) dx = \left[u(x)v(x) \right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \frac{du}{dx}(x) v(x) dx$$

$$\left\{ \begin{array}{l} u(x) = (\phi_1(x))^* \\ v(x) = \frac{d}{dx} \phi_2(x) \\ \frac{du}{dx}(x) = \frac{d}{dx} (\phi_1(x))^* \\ \quad = \left(\frac{d}{dx} \phi_1(x) \right)^* \\ \frac{dv}{dx}(x) = \frac{d^2}{dx^2} \phi_2(x) \end{array} \right.$$

as a result, $\langle \phi_1 | i \frac{d^2}{dx^2} \phi_2 \rangle = i \left\{ \left[(\phi_1(x))^* \frac{d}{dx} \phi_2(x) \right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \left(\frac{d}{dx} \phi_1(x) \right)^* \frac{d}{dx} \phi_2(x) dx \right\}$

$$= -i \left(0 - \left\langle \frac{d}{dx} \phi_1 \middle| \frac{d}{dx} \phi_2 \right\rangle dx \right)$$

($\phi_1(x)$ vanishes when x goes to $\pm\infty$: the probability to find a non-free particle at $x = \pm\infty$ is null)

$$\Rightarrow \langle \phi_1 | i \frac{d^2}{dx^2} \phi_2 \rangle = -i \left\langle \frac{d}{dx} \phi_1 \middle| \frac{d}{dx} \phi_2 \right\rangle \quad (I)$$

similarly

$$\langle i \frac{d^2}{dx^2} \phi_1 | \phi_2 \rangle = i^* \left\langle \frac{d^2}{dx^2} \phi_1 \middle| \phi_2 \right\rangle$$

$$= -i \left\langle \frac{d^2}{dx^2} \phi_1 \middle| \phi_2 \right\rangle$$

$$\Rightarrow \langle i \frac{d^2}{dx^2} \phi_1 | \phi_2 \rangle = +i \langle \frac{d}{dx} \phi_1 | \phi_2 \rangle \quad (\text{II}) \quad (\text{integration by parts})$$

from (I) & (II) we conclude

$$\left\{ \begin{array}{l} \langle \phi_1 | i \frac{d^2}{dx^2} \phi_2 \rangle \neq \langle i \frac{d^2}{dx^2} \phi_1 | \phi_2 \rangle \\ \underline{i \frac{d^2}{dx^2} \text{ is not hermitian.}} \end{array} \right.$$

3. [optional]

$$\hat{L}_x = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y$$

$$\hat{p}_y$$

since

$$\hat{L} = \underbrace{\begin{bmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{bmatrix}}_{\hat{r}} \times \underbrace{\begin{bmatrix} \hat{p}_x \\ \hat{p}_y \\ \hat{p}_z \end{bmatrix}}_{\hat{p}}$$

$$[\hat{L}_x, \hat{p}_y] = [\hat{y} \hat{p}_z - \hat{z} \hat{p}_y, \hat{p}_y]$$

$$= (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y) \hat{p}_y - \hat{p}_y (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y)$$

$$[\hat{L}_x, \hat{p}_y] = \hat{y} \hat{p}_z \hat{p}_y - \hat{z} \hat{p}_y^2 - \hat{p}_y \hat{y} \hat{p}_z + \hat{p}_y \hat{z} \hat{p}_y \quad (\text{III})$$

To calculate $[\hat{L}_x, \hat{p}_y]$ it is convenient to introduce $\phi(x, y, z)$

$$[\hat{L}_x, \hat{p}_y] \phi(x, y, z) = \left\{ y \frac{\hbar}{i} \frac{\partial}{\partial z} \frac{\hbar}{i} \frac{\partial}{\partial y} - z \frac{\hbar}{i} \frac{\partial}{\partial y} \frac{\hbar}{i} \frac{\partial}{\partial y} - \frac{\hbar}{i} \frac{\partial}{\partial y} y \frac{\hbar}{i} \frac{\partial}{\partial z} + \frac{\hbar}{i} \frac{\partial}{\partial y} z \frac{\hbar}{i} \frac{\partial}{\partial y} \right\} \phi(x, y, z)$$

(correspondence principle)

$$[\hat{L}_x, \hat{p}_y] \phi(x, y, z) = \left(y \frac{\hbar}{i} \frac{\partial}{\partial z} \frac{\hbar}{i} \frac{\partial}{\partial y} - \frac{\hbar}{i} \frac{\partial}{\partial y} \left(y \frac{\hbar}{i} \frac{\partial}{\partial z} \right) \right) \phi(x, y, z) \\ + \left(-z \frac{\hbar}{i} \frac{\partial}{\partial y} \frac{\hbar}{i} \frac{\partial}{\partial y} + \frac{\hbar}{i} \frac{\partial}{\partial y} \left(z \frac{\hbar}{i} \frac{\partial}{\partial y} \right) \right) \phi(x, y, z)$$

$$[\hat{L}_x, \hat{p}_y] \phi(x, y, z) = \left(y \frac{\hbar}{i} \frac{\partial}{\partial z} \frac{\hbar}{i} \frac{\partial}{\partial y} - \frac{\hbar}{i} \mathbf{1} \frac{\hbar}{i} \frac{\partial}{\partial z} + \frac{\hbar}{i} y \frac{\partial}{\partial z} \frac{\hbar}{i} \frac{\partial}{\partial z} \right) \phi(x, y, z) \\ = -\frac{\hbar}{i} \left\{ \frac{\hbar}{i} \frac{\partial}{\partial z} \phi(x, y, z) \right\} \\ = -\frac{\hbar}{i} \hat{p}_z \phi(x) = i\hbar \hat{p}_z \phi(x)$$

Consequently $[\hat{L}_x, \hat{p}_y] = i\hbar \hat{p}_z$

4. Summarize the steps that allows us to obtain spherical harmonics as solutions of the eigenvalue equation for the expectation values of L^2

* Hydrogen atom eigenfunctions (2-body central force system)

$$\Psi = \Psi_c(x, y, z) \Psi(x, y, z)$$

$$\Psi = \Psi_c(x, y, z) R_{nl}(r) Y_{lm}(\theta, \phi)$$

$$\boxed{\Psi = \Psi_c(x, y, z) R_{nl}(r) \Theta(\theta) \Phi(\phi)}$$

where

$$\begin{cases} X = \frac{m_e x_e + m_n x_n}{M} \approx x_n & (m_n \gg m_e) \\ Y = \frac{m_e y_e + m_n y_n}{M} \approx y_n \\ Z = \frac{m_e z_e + m_n z_n}{M} \approx z_n \end{cases} \quad (\text{center-of-mass coordinates})$$

$M = m_e + m_n$ (total mass)

$$\begin{cases} x = x_e - x_n \\ y = y_e - y_n \\ z = z_e - z_n \end{cases} \quad (\text{fictitious particle coordinates / relative coordinates})$$

$$\mu = \frac{m_e m_n}{m_e + m_n} \approx m_e \quad (\text{reduced mass})$$

Ψ_c : center-of-mass wavefunction \times wavefunction of the nucleus which satisfies

$$\hat{H}_c \Psi_c = -\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) \Psi_c = E_c \Psi_c$$

• ψ : relative wavefunction \approx wavefunction of the electron

$$\hat{H}_r \psi = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + V(\sqrt{x^2+y^2+z^2}) \psi = E_r \psi$$

$$\hat{H}_r \psi = -\frac{\hbar^2}{2\mu} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) \right) + \frac{1}{r^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2} \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + V(r) \psi = E_r \psi$$

($\Psi = \psi_c \psi =$ total wavefunction of the system)
 ($E = E_c + E_r =$ total energy of the system)

• R : radial part of ψ

$$-\frac{\hbar^2}{2\mu} \left(\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \right) + \frac{\hbar^2 K}{2\mu r^2} R + V(r) R = E_r R$$

Y : angular part of ψ

$$-\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = \hbar^2 K Y$$

$$\boxed{\hat{L}^2 Y = \hbar^2 K Y} \quad (I)$$

K constant (eigenvalue of the square of the angular momentum operator)

* To solve the eigenvalue equation (I), we perform a separation of variables:

$$Y = \Theta(\theta) \Phi(\phi)$$

We obtain:

$$\frac{1}{\Theta} \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\sin^2 \theta} \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -K$$

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + K \sin^2 \theta + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = 0$$

θ -dependent

ϕ -dependent

Consequently:

$$\begin{cases} \frac{d^2 \Phi}{d\phi^2} = -C \Phi & C \text{ constant} \\ \sin \theta \frac{d}{d\theta} \sin \theta \frac{d\Theta}{d\theta} + K \sin^2 \theta \Theta = +C \Theta \end{cases}$$

$$\Rightarrow \begin{cases} \Phi(\phi) = A e^{i C^{1/2} \phi} + B e^{-i C^{1/2} \phi} & (A, B \text{ constant}) \\ \Phi(2\pi) = \Phi(0) & (\Phi \text{ is } 2\pi\text{-periodic}) \end{cases}$$

Thus $C^{1/2}$ is an integer $C^{1/2} = m$ ($m = 0, 1, 2, \dots$)

$$\boxed{\begin{cases} \Phi = A e^{im\phi} + B e^{-im\phi} \\ \sin \theta \frac{d}{d\theta} \sin \theta \frac{d\Theta}{d\theta} + K \sin^2 \theta \Theta = m^2 \Theta & \text{(II)} \\ Y = \Theta(\theta) \Phi(\phi) \end{cases} \begin{cases} m = 0, 1, 2, \dots \\ K \text{ constant} \end{cases}}$$

* To solve (II), we introduce the following change of variables

$$y = \cos \theta \quad P(y) = \mathbb{H}(\theta) = P(\cos \theta)$$

$$\begin{cases} \sin \theta = \sqrt{1-y^2} & (0 \leq \theta \leq \pi) \\ \frac{d}{d\theta} = -\sin \theta \frac{d}{d(\cos \theta)} = -\sqrt{1-y^2} \frac{d}{dy} \end{cases}$$

(II) is thus rewritten as

$$\boxed{(1-y^2) \frac{d^2 P}{dy^2} - 2y \frac{dP}{dy} - \frac{m^2}{1-y^2} P + KP = 0 \quad (\text{III})}$$

[Proof: $\sin \theta \frac{d}{d\theta} \sin \theta \frac{d\mathbb{H}}{d\theta} = -\sin^2 \theta \frac{d}{d(\cos \theta)} (-\sin^2 \theta) \frac{dP}{d\cos \theta}$

$$= + (1-y^2) \frac{d}{dy} (1-y^2) \frac{dP}{dy}$$

$$\sin \theta \frac{d}{d\theta} \sin \theta \frac{d\mathbb{H}}{d\theta} = (1-y^2)^2 \frac{d^2 P}{dy^2} + (1-y^2) (-2y) \frac{dP}{dy}$$

(+) $K \sin^2 \theta \mathbb{H} = K (1-y^2) P$

(+) $-m^2 \mathbb{H} = -m^2 P$

(=) $\sin \theta \frac{d}{d\theta} \sin \theta \frac{d\mathbb{H}}{d\theta} + K \sin^2 \theta \mathbb{H} - m^2 \mathbb{H} = (1-y^2)$

$$\times \left\{ (1-y^2) \frac{d^2 P}{dy^2} - 2y \frac{dP}{dy} + KP - m^2 P \right\}$$

The solutions of (III) are known as the associated Legendre functions $P_e^m(y)$ (see F.3)

$$\boxed{\mathbb{H}_{lm}(\theta) = D P_e^m(y)}$$

D normalization constant
PSTB10

The corresponding eigenvalue K equals $l(l+1)$ (l integer)
Moreover we admit that (III) can be solved only if $m \leq l$

* To sum up

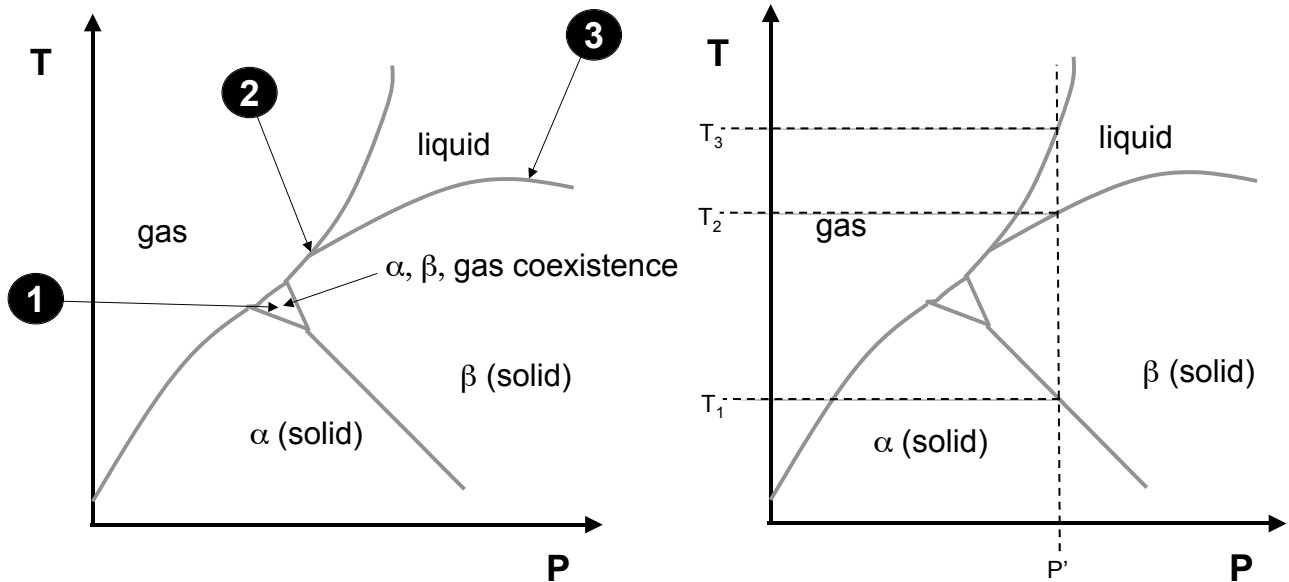
$$\Phi_m = A e^{im\phi} + B e^{-im\phi} ; (m = 0, 1, 2, \dots, (l-1), l)$$

$$\Theta_{lm} = D P_l^m(y) ; (l = 0, 1, 2, \dots)$$

$$Y_{lm} = \Theta(\theta) \Phi(\phi) ; \hat{L}^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$$

THERMODYNAMICS

1. **single-component phase diagrams.** Shown below is a hypothetical phase diagram for a single-component closed system. Answer the following questions about this diagram:
 - a. Apply the phase rule to each of the marked locations 1, 2, and 3, and determine whether those points on the diagram correctly mark stable equilibria.
 - b. Is the molar volume change of transformation $\Delta \bar{V}_{\alpha \rightarrow gas}$ for the transformation of solid α to the gas phase positive or negative?
 - c. For the fixed pressure P' , draw a qualitative plot of the Gibbs free energy of this material for each phase as a function of temperature over the range shown.



(a) The Gibbs phase rule for single-component phase diagrams is:

$$D + P = C + 2$$

Since the number of components $C = 1$, we have:

$$D + P = 3$$

The number of degrees of freedom (D) added to the number of phases present (P) must be = 3 for a stable equilibrium.

Examining the marked points on the diagram:

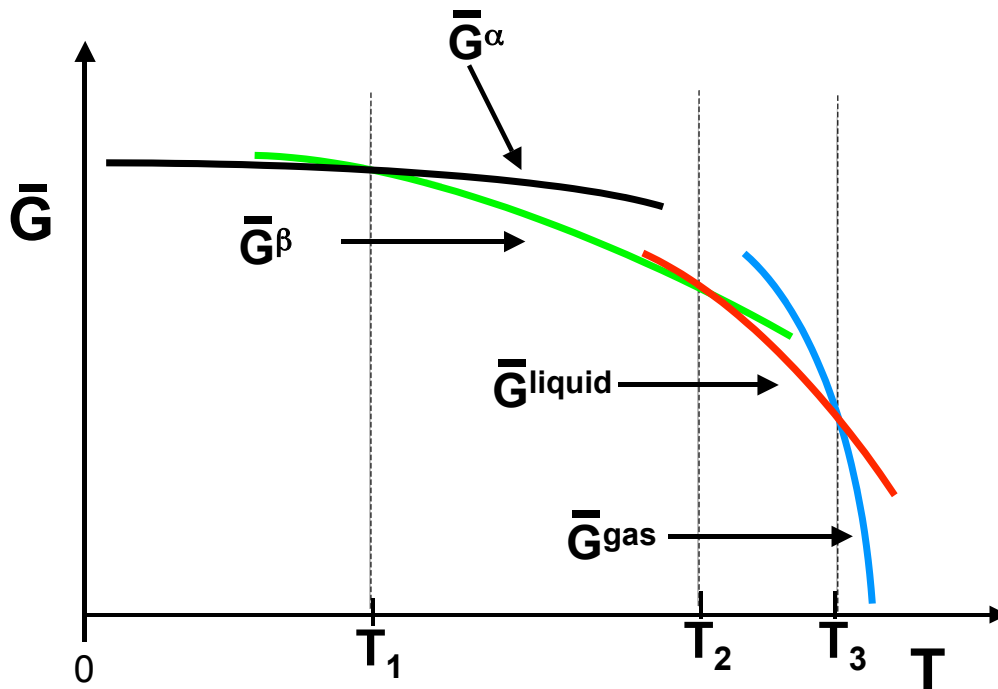
- (1) a 3-phase field- a region with two degrees of freedom (temperature and pressure can be varied independently within the field and the same equilibrium is maintained). Plugging into the phase rule:
 $D + P = 2 + 3 = 5$
...thus this is definitely **not** a stable equilibrium.
- (2) Point 2 marks the intersection of three single-phase regions: it is a triple point where liquid, gas, and the solid phase b are in equilibrium at a single temperature and pressure:
 $D + P = 0 + 3 = 3$
...this phase equilibrium is stable.
- (3) Point 3 marks liquid-solid b equilibrium, with one degree of freedom- if the temperature is changed, the pressure required to maintain the two-phase equilibrium is predetermined. Likewise, if the pressure is changed, the temperature is predetermined:
 $D + P = 1 + 2 = 3$
...this is a stable phase equilibrium.

(b) The Clausius-Clapeyron equation relates the slope of the pressure vs. temperature phase boundary to the enthalpy change, temperature, and volume change at a phase transition:

$$\left. \frac{dP}{dT} \right|_{\text{equilibrium}} = \frac{\Delta \bar{H}_{\text{trans}}}{T_{\text{trans}} \Delta \bar{V}_{\text{trans}}}$$

The enthalpy change of first-order phase transitions must be positive (remember, the entropy is always increasing with temperature for stability, and at a phase transition $\Delta \bar{H}_{\text{trans}} = T_{\text{trans}} \Delta \bar{S}_{\text{trans}}$; absolute temperature must be positive therefore enthalpy changes at the transition must be positive). Since the enthalpy change and T_{trans} are positive, the sign on the phase transition volume change is the same as the sign of the slope of the P vs. T phase boundary. Looking at the phase diagram, we see that along the α /gas phase boundary, the pressure increases as temperature increases- dP/dT is positive. Thus, the volume change on transformation of solid α to gas is positive.

(c). Using the information from the phase diagram, we can construct the following qualitative diagram:



...the diagram must exhibit: (1) negative slope and curvature for each free energy curve (requirements for stability), and (2) free energy curves of phases cross at points of two-phase equilibrium; the stable phase at each temperature must exhibit the lowest free energy.

2. **Free energy behavior of solutions** [DJI1][DJI2]. Shown on the following page is a diagram of free energies for a two-component A-B system at a fixed temperature of 500 K and fixed pressure of 1 atm. This system exists in 3 different phases- liquid, and two solid phases α and β . Two copies of the diagram are provided to sketch on. Use this diagram to answer the questions below:

- Using the top copy of the free energy diagram, draw common tangents that identify composition regions of two-phase equilibrium at this temperature and pressure. Draw a 'composition bar' at the bottom of the diagram as in lecture, and denote which phases are present as a function of composition.
- At the composition marked X' on the diagram, the system is in equilibrium with 2 phases in coexistence.
 - What two phases are present?
 - What are the phase fractions, in terms of parameters given on the diagram?
 - What is the composition of each phase that is present?
- On the lower copy of the phase diagram, draw constructions or mark points as necessary to identify the following quantities for a system with composition X':
 - The chemical potential of A in each phase, and B in each phase present.

ii. The standard state chemical potential of A and B in each phase present.

(a) See diagram below.

(b) (i) Liquid and solid α .

(ii) To identify the relevant compositions, points X_B^α and X_B^L are marked on the top free energy diagram below. Applying the lever rule:

$$f^\alpha = \frac{(X_B^L - X')}{(X_B^L - X_B^\alpha)}$$
$$f^L = \frac{(X' - X_B^\alpha)}{(X_B^L - X_B^\alpha)}$$

(iii) The compositions are given by the points where the common tangent touches each free energy curve:

Liquid has composition X_B^L
Solid a has composition X_B^α

(c) See the diagram below. We must extrapolate the free energy curves to get the intercepts with the $X_B = 0$ and $X_B = 1$ axes for the standard state chemical potentials.

