Phonon Statistics

- Crystal vibrations: There are two kinds of "quantization";
 - The limitation of the allowed frequencies in a finite crystal to the normal modes by the boundary conditions. (classical atoms and classical waves;, *only specific wavelengths*, $m\lambda=2L$, and their corresponding frequencies, ω_m , are allowed)
 - The limitation of the allowed energies in one of specific mode of an oscillator. (quantum mechanical; we consider the individual atoms are now "particles" with wave-like properties. The energy in a vibration with a particular allowed mode (state), *n*, must be of the form $E_n = (n + \frac{1}{2})\hbar\omega$
 - Both limitations must be satisfied by the vibration in a crystal, i.e.,

$$E_{mn} = (n + \frac{1}{2})\hbar\omega_m$$

:The energy corresponding to the *n*th state of the *m*th mode.

Phonon statics

• What is the average number of phonons with frequency ω_m at temperature T?

(N possible modes – ω_m is a particular mode)

 $E_{mn} = n\hbar\omega_m$: Energy corresponding to *n*th state of *m*th mode, i.e., the state with *n* phonons, each with energy of $\hbar\omega$

(1) P_{mn} = probability of exciting the state with E_{mn} in the crystal at temperature T $P_{mn} = \frac{e^{-E_{mn}/kT}}{\sum_{n=0}^{\infty} e^{-E_{mn}/kT}}$

If
$$|x| < 1$$
, $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$
 $x^n = e^{-\frac{E_{mn}}{kT}}$, $x = e^{-\frac{\hbar\omega}{kT}}$
 $P_{mn} = e^{-\frac{E_{mn}}{kT}} [1 - e^{-\frac{\hbar\omega}{kT}}]$

Phonon statics

(2) average energy of the *m*th mode

$$\bar{E}_m = \sum_{\substack{n=0\\\infty}}^{\infty} P_{mn} E_{mn}$$
$$= \sum_{\substack{n=1\\n=1}}^{\infty} n\hbar\omega_m e^{-\frac{n\hbar\omega_m}{kT}} [1 - e^{-\frac{\hbar\omega}{kT}}] + E_{m0} \qquad \text{(zero point energy)}$$
$$\sum_{\substack{n=1\\\infty}}^{\infty} nx^n = \sum_{\substack{n=1\\n=1}}^{\infty} nx^n = \frac{x}{k}$$

$$\sum_{n=0}^{\infty} nx^n = \sum_{n=1}^{\infty} nx^n = \frac{x}{(1-x)^2}$$
$$\bar{E}_m - E_{m0} = \frac{\hbar\omega_n}{e^{\hbar\omega_n/kT} - 1}$$

(3) average number of phonon with ω_m

$$\bar{n}_{m} = \frac{\bar{E}_{m} - E_{m0}}{\frac{\hbar\omega}{1}}$$

$$\bar{n}_{m} = \frac{1}{\frac{e^{\frac{\hbar\omega}{kT}} - 1}{e^{\frac{\hbar\omega}{kT}} - 1}}$$
[Bose – Einstein distribution]
: Applicable to both phonons and photons

Phonon statics



If $\hbar \omega \gg kT$, the Bose-Einstein distribution reduces to the simple Boltzmann distribution.

If
$$\frac{\hbar\omega}{kT} \ll 1$$
 (large T), $\bar{E}_m - E_0 = \frac{\hbar\omega}{1 + \frac{\hbar\omega}{kT} - 1} = kT$

$$\frac{1}{2}kT$$
: kinetic energy, $\frac{1}{2}kT$: potential energy

Total energy (there are 3N total number of modes in three dimensions)

$$\bar{E} = \sum_{n=1}^{3N} \bar{E}_m = 3NkT$$

The Hydrogen atom

- A single electron bound to a single proton by a Coulomb attractive force.
- An understanding of the solution for the hydrogen atom allow at least a qualitative understanding of elementary atomic structure.



Spherical coordinate system

$$x = r \sin \theta \cos \phi$$
$$y = r \sin \theta \sin \phi$$
$$z = r \cos \phi$$

The Hydrogen atom

• The Schrödinger equation for the hydrogen atom is

$$\nabla^2 \psi + (\frac{2m}{\hbar^2}) \{ \mathbf{E} - \mathbf{V}(r) \} \psi = 0$$

where the potential energy V(r) is Coulomb attraction

between postive proton and negative electron.

 $V(r) = -\frac{q^2}{4\pi\varepsilon_0 r}$:central force field (only a function of distance from the center of force and independent of the particular direction)

• For spherical coordinates,

$$\frac{1}{r^2}\frac{\delta}{\delta r}\left[r^2\frac{\delta}{\delta r}\right]\psi + \frac{1}{r^2\sin\theta}\frac{\delta}{\delta\theta}\left(\sin\theta\frac{\delta}{\delta\theta}\right)\psi + \frac{1}{r^2\sin\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}\left(\frac{q^2}{4\pi\varepsilon_0r} + E\right)\psi = 0$$

• Solutions by seeking a separation of the variables

 $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$

The Hydrogen atom

• The resulting differential equations for each of the variables are

$$-\frac{1}{\Phi}\frac{\partial^{2}\Phi}{\partial\phi^{2}} = A$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(B - \frac{A}{\sin^{2}\theta}\right)\Theta = 0 \qquad (A \& B \text{ are constants})$$

$$\frac{d^{2}R}{dr^{2}} + \frac{2}{r}\frac{dR}{dr} + \left(\frac{2m}{\hbar}\{E - V(r)\} - \frac{B}{r^{2}}\right)R = 0$$

Angular parts [the equations for Φ(φ) & Θ(θ)] are independent of V(r) and are the same for all central force-field systems.
: expressible in "spherical harmonics" and do not affect the allowed

energies for the free hydrogen atom.

- Quantization is expected because an electron is confined physically. But, there are no geometric boundary conditions.
- However, the requirement is that the wave function should be mathematically well behaved.
- There are three quantum numbers because there are three kinds of variables.

The solutions of $\Phi(\phi)$, $\Theta(\theta)$

$$\Phi(\phi) = c_1 e^{iA^{1/2}\phi} + c_2 e^{-iA^{1/2}\phi}$$

- In order for $\Phi(\phi)$ to be single valued, $\Phi(\phi + 2\pi) = \Phi(\phi)$ $\Rightarrow A^{\frac{1}{2}} = m_l, \ m_l = 0, \ \pm 1, \ \pm 2$

 m_l : the magnetic quantum number

E in a free hydrogen atom does not depend on m_l unless magnetic field is present. (Zeeman effect)

• Θ(θ)

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- $\Theta(\theta)$ involves polynomials in sin θ and cos θ .
- For $\Theta(\theta)$ to be finite, a polynomial must be terminated after a finite number of terms.
- The termination condition introduces another quantum number ℓ such that

 $B = \ell(\ell+1)$ $\ell = 0, 1, 2, \cdots$

 $|m_l| \leq \ell$

 ℓ : angular momentum quantum number

- The total angular momentum for a given state of the hydrogen is

$$\hbar\big\{\ell(\ell+1)\big\}^{\frac{1}{2}}$$

The solutions of $\Phi(\phi)$, $\Theta(\theta)$

Θ(θ)

$$\Theta(\theta) = P_l^{m_l}(\cos\theta) = \frac{1}{2^l l!} (1 - \cos^2\theta)^{|m_l|/2} \frac{d^{l+|m_l|}(\cos^2\theta - 1)^l}{d(\cos\theta)^{l+|m_l|}}$$

[associated Legendre functions]

Spectroscopic designation	I	m _l	$P_l^{m_l}(\cos\theta)$	$\Phi(\phi)$		
S	0	0	1	1		
р	1	0	$\cos \theta$	1		
р	1	±1	sinθ	exp(±iφ)		
d	2	0	(3cos ² θ–1)/2	1		
d	2	±1	3sin0cos0	exp(±iφ)		
d	2	±2	$3sin^2\theta$	exp(±i2¢)		

The solution for R(r)

• For R(r), the differential equation becomes

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left\{\left(E + \frac{q^2}{4\pi\varepsilon_0 r}\right) - \frac{\ell(\ell+1)}{r^2}\right\}R = 0$$

- The solution of the above equation can once again be written in the form of a polynomial that must be terminated after a finite number of terms in order for R(*r*) to be finite and well behaved.
- The termination conditions introduce the third quantum number, *n*, so called the *principal quantum number*, because the energy depends only on the value of *n* in the hydrogen atom.

The solution for R(r)

• The radial wave functions have the form

$$R_{n,\ell}(r) = -\rho^{\ell} exp(-\frac{\rho/2}{2}) \frac{d^{2\ell+1}}{d\rho^{2\ell+1}} \left[exp(\rho) \frac{d^{n+\ell}}{d\rho^{n+\ell}} (\rho^{n+\ell} e^{-\rho}) \right]$$
Laguerre polynomials

$$\ell \leq (n-1)$$
 $n = 1, 2, \cdots$
 $\rho = 2r/na_0$
 $a_0 = 4\pi\varepsilon_0\hbar^2/mq^2$: Bohr radius - the radius of the circular
orbit of the lowest energy state (ground
state)

• Combine the various portions of the wave functions:

$$\phi_{n,\ell,m,m_s} = R_{n,\ell}(r)\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi)$$

Energy of the hydrogen atom

• Allowed energies in the hydrogen atom

$$E_n = -\frac{mq^4}{32\pi^2\varepsilon_0{}^2\hbar^2} \cdot \frac{1}{n^2}$$

- *m* is the reduced mass of the hydrogen atom, which is defined as $m_N \cdot m_e / (m_N + m_e)$. Since $m_N \ge m_e$, the reduced mass of the hydrogen atom reduces to m_e . The difference between the reduced mass and the electron mass is 0.05%
- Ground state of the hydrogen atom corresponds to an energy of $E_1 = -13.5 \ eV$, called 1 Rydberg.
- When an electron in energy state E_n undergoes a transition to the ground state, the energy difference $(E_n E_1)$ is emitted as a photon.

$$\Delta E_n = (E_n - E_1) = \left(\frac{mq^4}{2\hbar^2}\right) \left(1 - \left(\frac{1}{n^2}\right)\right)$$

"Lyman series" of optical emission lines for hydrogen atm

Energy of the hydrogen atom

Electron transitions for the Hydrogen atom



Visible Spectrum



Hydrogen Absorption Spectrum



Hydrogen Emission Spectrum



Electron Spin

- In addition to the orbital angular momentum described by ℓ, the electron also has a kind of intrinsic angular momentum called "electron spin".
- The treatment of the spin angular momentum is closely analogous to the treatment of orbital angular momentum.

The spin angular momentum vector *S* $|S| = S = \sqrt{s(s+1)}\hbar$ *s*: spin quantum number

• The *z*(arbitrary) component of the spin angular momentum

$$S_z = m_s \hbar$$
 m_s : spin quantum number
 $m_s = \pm \frac{1}{2}$
 $+ \frac{1}{2}$: spin up
 $- \frac{1}{2}$: spin down

Orbital of hydrogen atom

• Allowed energies depend only on *n*

$$E_n = -(\frac{mq^4}{32\pi\varepsilon_0^2\hbar^2})\frac{1}{n^2}$$

• Example

(1) 1s:
$$n = 1, \ell = 0, m_{\ell} = 0$$

 $\Theta(\theta)$ and $\Phi(\phi)$ are constants. \rightarrow Spherical symmetry state



Two spin quantum numbers (m_s) \rightarrow two s states with the same energy

Orbital of hydrogen atom

(2) p state:

$$n = 2, \ell = 1, m_{\ell} = -1, 0, +1, m_s = \pm \frac{1}{2}$$

- *p* states have 3 orbital states.
- Due to spin, *p* states have 6 possible states.
- All the states have the same energy in hydrogen atom.
- When the states with different spatial distributions (set of quantum numbers) have the same energy, it is said to as "degenerate".
- Wave functions for the degenerate states:

 $\psi_{n,l,+1} = R_{n,l}(r) \sin \theta e^{i\phi}$ $\psi_{n,l,0} = R_{n,l}(r) \cos \theta$ $\psi_{n,l,-1} = R_{n,l}(r) \sin \theta e^{-i\phi}$ Angular distribution of the p state, $|\psi_{n,l,m_s}|^2$, is symmetry about the z axis. (Lobes of probability density)

Distribution of wave functions (Probability density)

	$s~(\ell=0)$		$p(\ell = 1$	$(\ell=1) \qquad \qquad d \ (\ell=2)$						f (ℓ = 3)						
	<i>m</i> = 0 <i>s</i>	m = 0 Pz	$m = \pm 1$		<i>m</i> = 0	$m = \pm 1$		$m = \pm 2$	<i>m</i> = 0	$m = \pm 1$		$m = \pm 2$		m = ±3		
			p _x	py dz²	d _{z²}	d _{xz}	dyz	d _{xy}	$d_{x^2-y^2}$	r 1z2	f _{x2²}	1yz2	f _{xyz}	$f_{z(x^2-y^2)}$	fx(x2-3y2)	$f_{y(3x^2-y^2)}$
n = 1																
n = 2	•	8		0												
n = 3	•	2			-	*	8									
n = 4	•	2	••	0	-	*	2		••	\$	*	*	*	*	••••	
n = 5	•	2	••	0	-	*	2	()	•							
n = 6		2	••	٩								•••		•••	•••	
n = 7	0															

Pauli Exclusion Principle

- "No two electrons in the same system can have all the quantum numbers the same, n, ℓ, m_s, m_e ."
- "The wave function for any system of electrons must be antisymmetric with respect to the interchange of any two electrons.

 $m_s: 2$ for $\ell = 0$ (s) $m_\ell: 3$ for $\ell = 1$ (p) $m_\ell: 5$ for $\ell = 2$ (d) $m_\ell: 7$ for $\ell = 3$ (f)

 \therefore s has two states, p: 6 states, d: 10 states, f: 14 states

Pauli Exclusion Principle

$$H : 1s^{1} \\ He : 1s^{2} \\ Li : 1s^{2}2s^{2} \\ Be : 1s^{2}2s^{2} \\ for the term of the term of the term of the term of term$$