Lecture 3

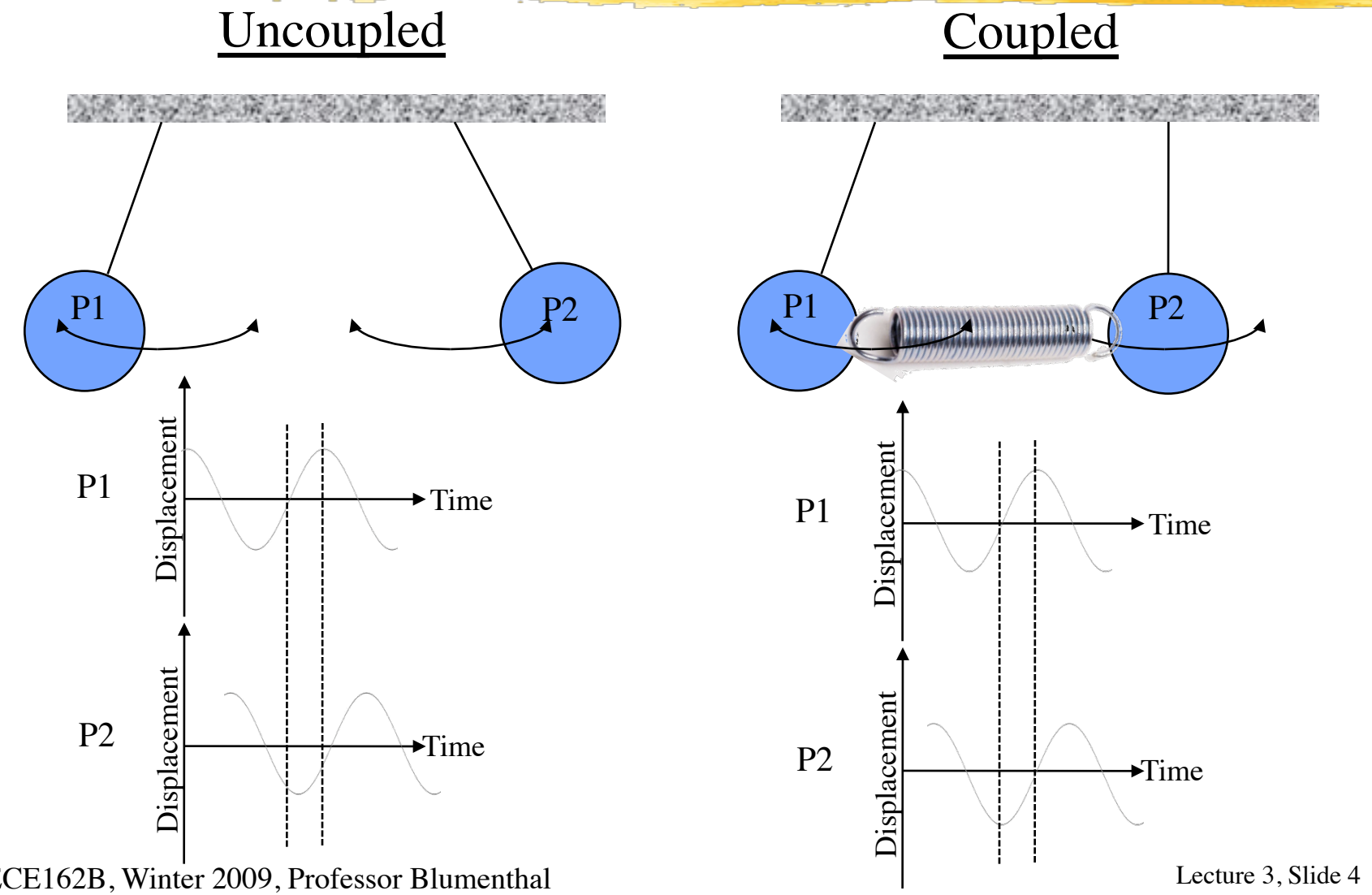
Last Class

- Properties of Bonds
- Bond Types
  - Ionic bonds
  - Metallic bonds
  - Covalent bond
  - Van der Waals bond
  - Mixed bonds

Continue Chapter 5 on Bonds

- Coupled Mode Theory
  - Take two oscillating systems each described by their own physical equation of motion.
  - Now physically couple them together
  - Coupled mode theory lets us re-write the equations of motion to include the coupling

Example: Pendulums



Feynman's Coupled Mode Approach

- Richard Feynman, Physicist, Nobel Laureate (see Feynman Lectures on Physics, Addison Wesley Longman, ISBN-13: 978-0201021158)
  - Developed an approach that can be used to describe all physical systems that are coupled
  - Sometimes called coupled mode theory
  - Other examples besides pendulums include electrical oscillators, atoms, acoustics and vibrational systems, etc.
  - Step 1: Write a model for each part of the system by itself
  - Step 2: Introduce a coupling factor in each equation that describes how each part of the system interacts with the other parts of the system
  - This couple can be in time, space, time and space or other manner

Schrodinger's Equation

- Describes how a particle of mass (m) evolves in time (t) and space (∇) in a spatial potential (V). All possible solutions of motion to this evolution in space and time are given by any (ψ) that satisfies this equation for a particular m and V.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Schrodinger's Equation

- Lumping all spatial components (∇ and V) into one term, called an operator, we can define the Hamiltonian (H) and simplify the equation. Note the H operates on the spatial part of ψ

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

$$H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)$$

Schrodinger's Equation

- This a partial differential equation (PDE). We have learned to solve these many times before. We guess at a viable solution. In this case, since there is both space and time, we will guess that the solution has both space and time in it, and further more, we will assume the solution is separable (i.e. made up of two functions, one only a function of space and the other only a function of time).

$$\psi = \omega(t)\psi(r)$$

- Further more, we will use the concept similar to Fourier series, where any function can be represented by the correct combination of finite or infinite sum of individual functions (e.g. harmonics). Any solution (function) that we are interested in can be composed of the linear sum of a set of separable functions.

$$\psi = \sum_j \omega_j(t)\psi_j(r)$$

Schrodinger's Equation

- For now lets consider only time dependence of the Schrodinger Equation described by ω(t).
- The following steps are a technique to eliminate the spatial variation in the PDE. Using the Hamiltonian operator and fact that ψ_j is not dependent on time so is constant w.r.t time

$$H\Psi = H\sum_j \omega_j(t)\psi_j(r) = i\hbar\frac{\partial\Psi}{\partial t} = i\hbar\sum_j \psi_j \frac{\partial\left(\omega_j(t)\right)}{\partial t}$$

- Multiplying both sides by ψ_k and integrating over the volume element dv (note that time only functions come outside spatial integrals)

$$\sum_j \omega_j(t)\int \psi_k H\psi_j dv = i\hbar\sum_j \psi_j \frac{d\left(\omega_j(t)\right)}{dt}\int \psi_k\psi_j dv$$

Schrodinger's Equation

- Now there is an important relationship between the two different solutions ψ_j and ψ_k that each satisfy the SE. They are *orthogonal* to each other and satisfy the following relationship

$$\int \psi_k \psi_j d\upsilon = \begin{cases} C_{kj} \text{ if } k = j \\ 0 \text{ if } k \neq j \end{cases}$$

- Assuming that $C_{kj} = 1$ for now, and defining H_{kj} as follows, we can simplify the differential equation for each value of k

$$H_{kj} = \int \psi_k H \psi_j d\upsilon$$

$$i\hbar \frac{d(\omega_k(t))}{dt} = \sum_j H_{kj} \omega_j(t)$$

Coupled Schrodinger's Equations

- Lets consider the simplest case where there are two solutions j=1 and j=2.
- Our two Diff. equations will look like

$$i\hbar \frac{d(\omega_1(t))}{dt} = H_{11}\omega_1(t) + H_{12}\omega_2(t)$$

$$i\hbar \frac{d(\omega_2(t))}{dt} = H_{21}\omega_1(t) + H_{22}\omega_2(t)$$

Coupling Term

Coupling Term

Uncoupled Solution

- If the two equations are not coupled (e.g. no spring in the pendulum example) then $H_{12}=H_{21}=0$ and

$$i\hbar\frac{d(\omega_1(t))}{dt} = H_{11}\omega_1(t)$$

$$i\hbar\frac{d(\omega_2(t))}{dt} = H_{22}\omega_2(t)$$

- Which each have solutions

$$\omega_1(t) = K_1 e^{-i\frac{H_{11}}{\hbar}t}$$

$$\omega_2(t) = K2e^{-i\frac{H_{22}}{\hbar}t}$$

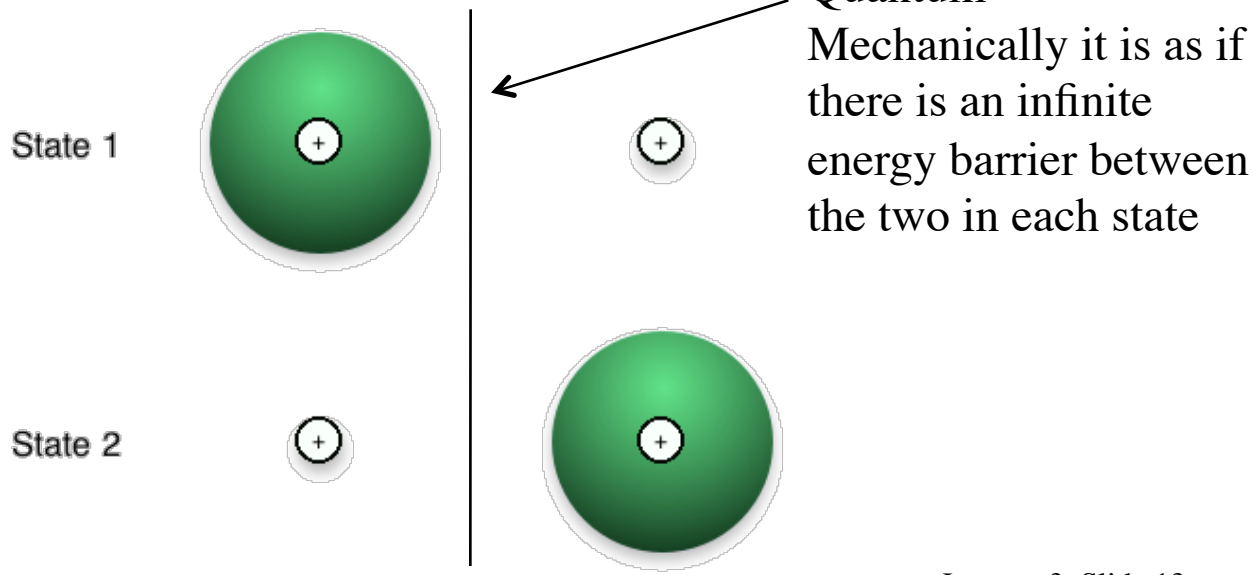
- We define the probability of being in a state (1 or 2) at time *t* as given by

$$\text{Prob(State 1)} = \left|\omega_1(t)\right|^2 = \left|K_1\right|^2$$

$$\text{Prob(State 2)} = \left|\omega_2(t)\right|^2 = \left|K_2\right|^2$$

Uncoupled Solution

- This solution tells us whatever state the system is in at a certain time, it will stay in that state. If nothing is done to the system from the outside, once in state 1 it stays in state 1 or once in state 2 it stays in state 2.
- An example of uncoupled states for a hydrogen atom and Proton in a system is illustrated below



Coupled States

- Now, lets assume there is not an infinite barrier, that the closer the H atom and nucleus get, the more there is a probability that the electron can jump from on nucleus to the other, moving the system from state 1 to state 2 or visa versa.
- Our coupled differential equations must contain the coupling terms H_{12} and H_{21}.
- We are going to introduce a new term "weak coupling." This means that although the system can move between states, it can also stay in one state. That way we can talk about the states as individual independent states that can vary with time.

Coupled States

- Reintroducing the coupling terms and defining constants E_0 and A and assuming the coupling is symmetric

$$H_{11} = H_{22} = E_0$$
$$H_{21} = H_{12} = -A$$

- Then we can write the coupled differential equations in matrix formulation

$$i\hbar \frac{d(\omega_1(t))}{dt} = E_0\omega_1(t) - A\omega_2(t)$$
$$i\hbar \frac{d(\omega_2(t))}{dt} = -A\omega_1(t) + E_0\omega_2(t)$$
$$i\hbar \frac{d}{dt}\begin{bmatrix}\omega_1(t)\\ \omega_2(t)\end{bmatrix} = \begin{bmatrix}E_0 & -A\\ -A & E_0\end{bmatrix}\begin{bmatrix}\omega_1(t)\\ \omega_2(t)\end{bmatrix}$$

Coupled States

- Substituting our typical solutions

$$\omega_1(t) = K_1 e^{-i\frac{E}{\hbar}t} \text{ and } \omega_2(t) = K_2 e^{-i\frac{E}{\hbar}t}$$

$$K_1 E = E_0 K_1 - A K_2$$

$$K_2 E = -A K_1 + E_0 K_2$$

$$E\begin{bmatrix} K_1 \\ K_2 \end{bmatrix} = \begin{bmatrix} E_0 & -A \\ -A & E_0 \end{bmatrix}\begin{bmatrix} K_1 \\ K_2 \end{bmatrix}$$

- Which from Linear Algebra Theory has a solution only if the matrix determinant is equal to zero

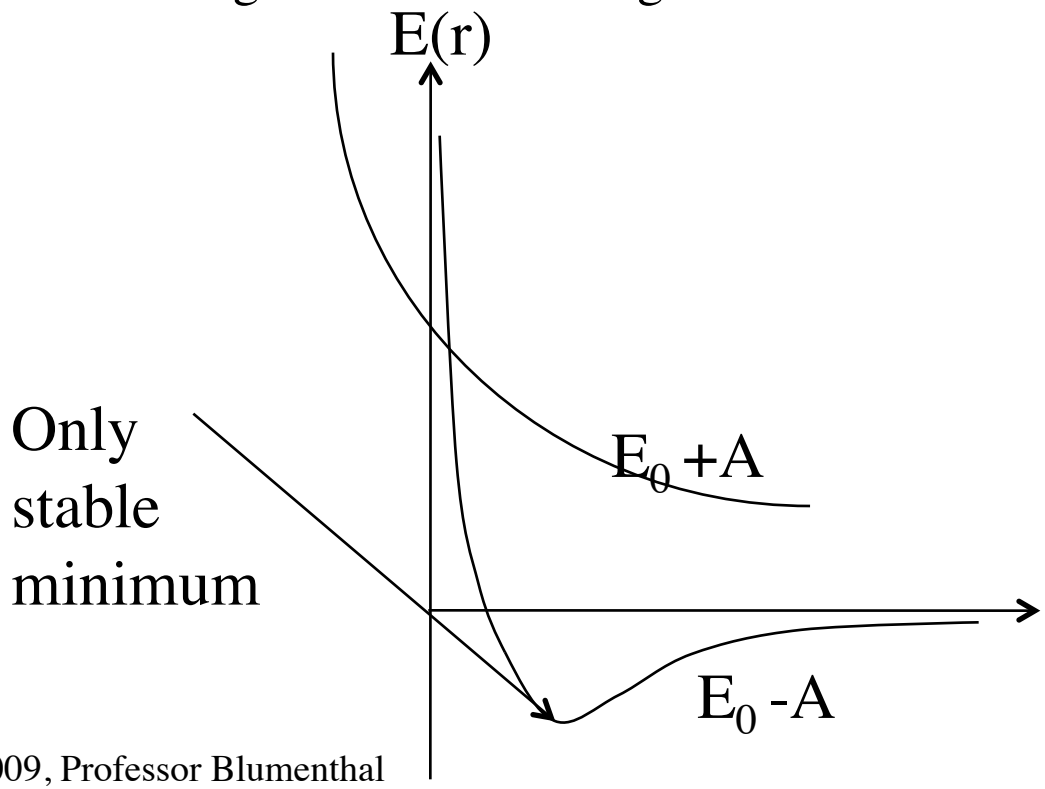
$$\begin{vmatrix} E_0 - E & -A \\ -A & E_0 - E \end{vmatrix} = 0$$

$$(E_0 - E)^2 = A^2$$

$$E = E_0 \pm A$$

Coupled States

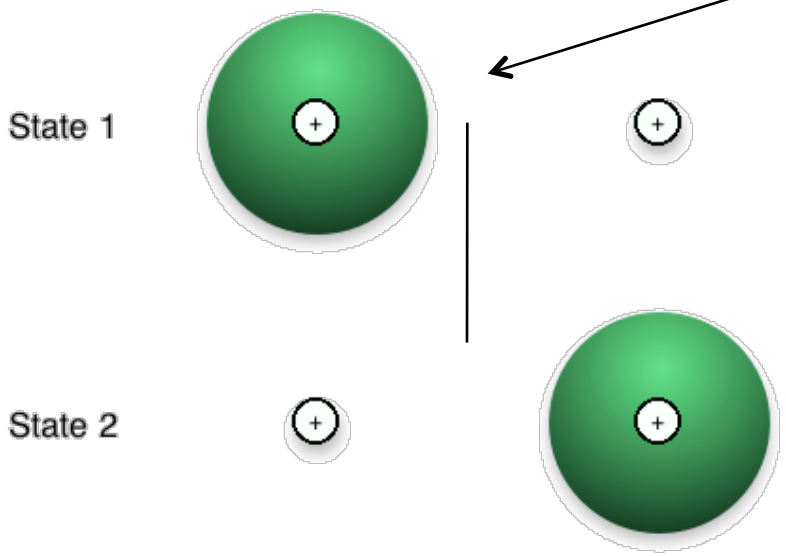
- As the two are brought together from infinity, only one solution has attractive and repulsive forces balance out to a stable solution.
- In the time dynamic solution, the electron can jump from one nucleus to the other and a sharing can occur forming a bond.



Coupled States

- If there is no coupling, $E=E_0$
- If there is coupling, the energy level is split into two new levels E_0+A and E_0-A

Coupled Interaction



Quantum Mechanically it is as if there is an finite energy barrier between the two in each state. But it is a balanced system, so there will be a stable solution as shown in the energy minimum in the previous slide.