

Basic Concept:

- Solve Schrödinger equation with added U_{sf} :

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U_N(r) + U_{sf}(r) \right] \Psi_\alpha = E_\alpha \Psi_\alpha$$

\downarrow \downarrow
 e -Nuclei interaction e - e interaction

- Simplest method is the Hartree Approximation (U_H) with an additional negative term, U_{xc} .

$$U_{sf} = U_H + U_{xc}$$

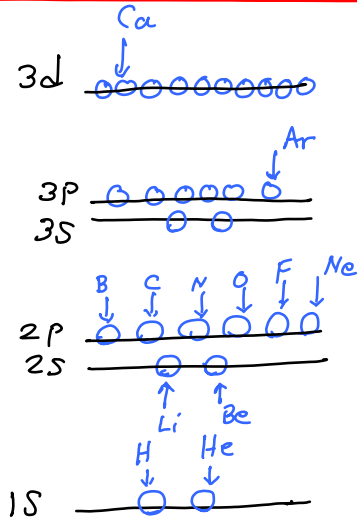
- With this approach we can more or less understand all observed atomic spectra.
- Valence electrons are the most important ones. Their energy levels periodically goes up and down versus atomic number.

Valence electrons are the electrons in the outer most orbits. They affect the **chemical** properties of an element. We are not concerned about the core electrons. They are valuable

for diagnostic purposes, for example, to find what impurities are present in Silicon.

Electrical and optical properties are all about valence electrons.

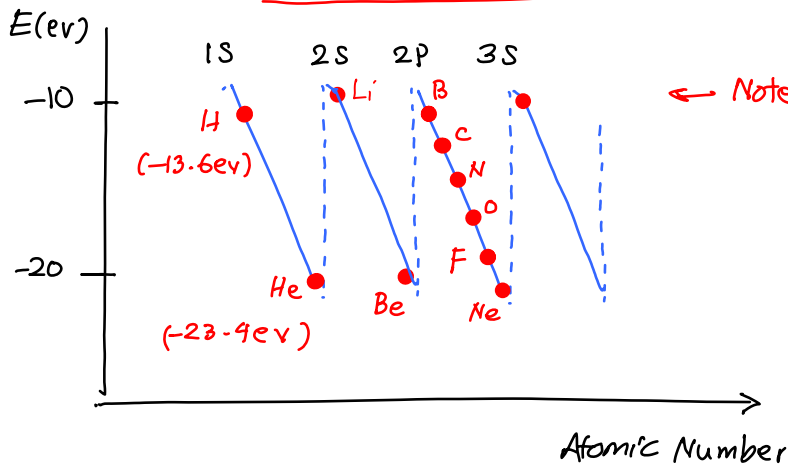
Filling up valence electrons



Periodic Table
(without the transition metals)

H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr

Valence levels

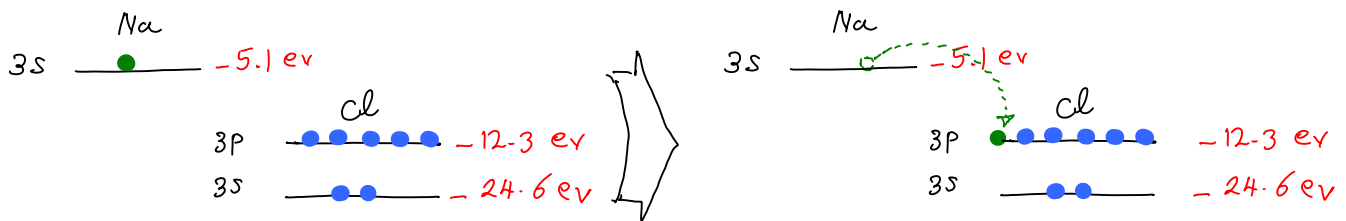


← Note periodic nature.

- As a level (say p) fills, energy level becomes more negative (i.e. it is harder to ionize the atom).
- As we go down the rows and right along the columns, the valence levels fill.

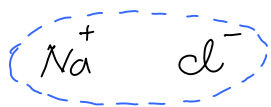
Ionic Bonding

Ionic bonding forms between atoms on the opposite side of the periodic table. For example take Na and Cl:



When they join together, we may expect the electron from 3s level in Na moves to a lower energy state in Cl, and loses $12.3 - 5.1 = 7.2 \text{ eV}$ energy during this transfer.

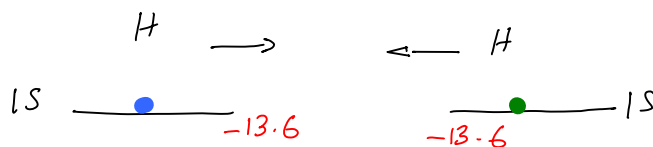
However, this number is **WRONG**. The actual bonding energy is **4 eV**. To get this correct values, we must see how the electrostatic changes when $\text{Na}^+ \text{Cl}^-$ is formed:



Covalent bonding

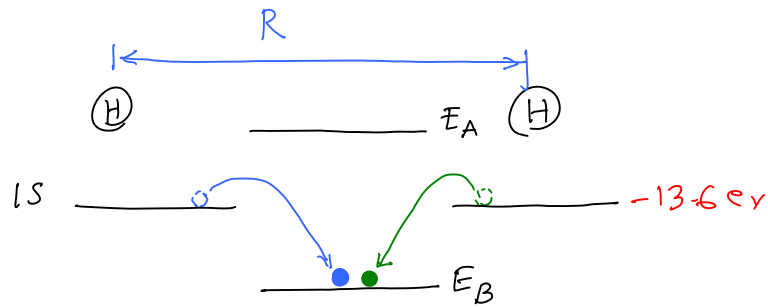
Many electronic materials, such as Silicon, form through covalent bonding.

The simplest example is H_2 :



But why two hydrogen atoms want to join and form a bond?

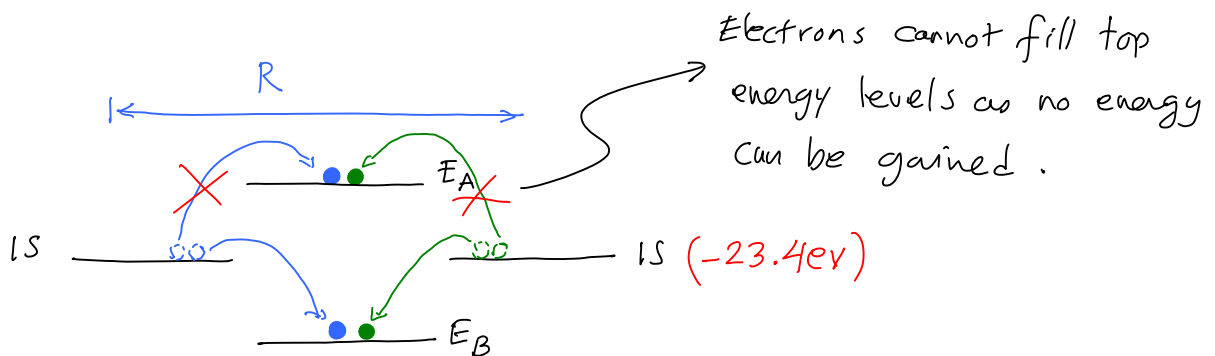
We must first solve the Schrodinger equation for two hydrogen atoms at a distance R . We will see that two energy levels form, one level a little lower than -13.6 eV , and one a little higher:



So energy can be gained through bonding.

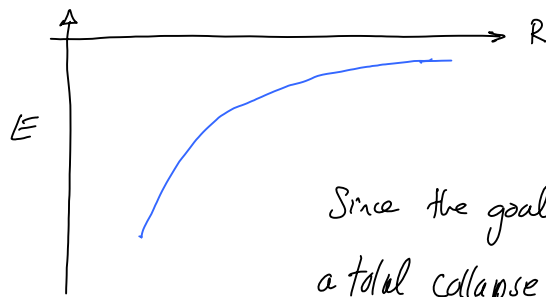
So why doesn't this happen for He?

Each He has two electrons, so they would need to fill two energy levels. So the two electrons would need to move to the higher energy level E_A , which is not possible.



Covalent bonding works between partially filled valence bands, like group 4 elements: C, Si, Ge, etc.

For the case hydrogen molecule, why the two H atoms do not collapse since E_B continues falling (and E_A continues rising) as the atoms approach each other?



Since the goal is to minimize energy, a total collapse $R=0$, would make sense!

However, we are ignoring key electron and nuclear interactions:

$$\text{Bonding energy: } E_B = E(H_2) - E(2H)$$

$$E(2H) = U_{eN} + U_{e'N'} = 2E_0 \quad (E_0 = -13.6 \text{ eV})$$

$$E(H_2) = U_{eN} + U_{e'N'} + U_{ee'} + U_{NN'} + U_{e'N} + U_{eN'}$$

just solving for 2-nuclei we get:

$$U_{eN} + U_{e'N'} = E_{B0}$$

$$U_{e'N} + U_{eN'} = E_{B0}$$

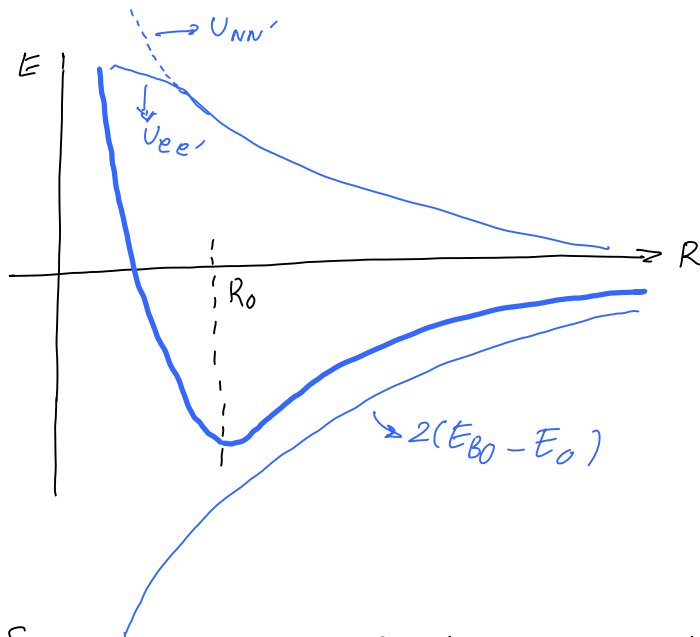
$$\text{Thus: } E(2H) - E(H_2) = 2E_{B0} - 2E_0 + U_{ee'} + U_{NN'}$$

$$U_{NN'} \text{ is easily Coulomb interaction of: } U_{NN'} = \frac{e^2}{4\pi\epsilon_0 R}$$

But $U_{ee'}$ is difficult to calculate (since electrons move and have different separations). We can approximate:

$$U_{ee'} = \frac{e^2}{4\pi\epsilon_0\sqrt{R^2 + a_0^2}} \quad (a_0 \text{ is the Bohr radius})$$

If we now plot energy:



So there exists a finite R_0 for the minimum energy

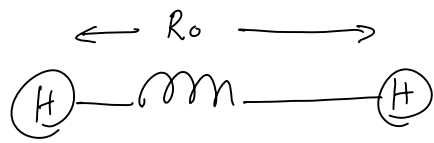
What is the ionization energy of H_2^+ :

$$\text{Since } E(H_2^+) = U_{eN} + U_{eN'} + U_{NN'} \Rightarrow$$

$$E(H_2) - E(H_2^+) = E_{B0} + U_{ee'} = E_B$$

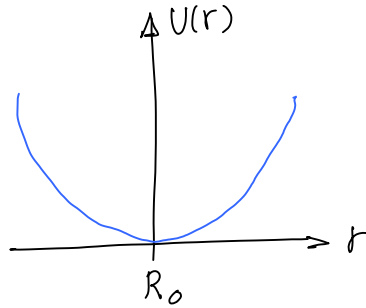
So the ionization energy E_B is greater than the non-interacting value E_{B0} .

Covalent bond can be considered as a spring connection, meaning that R is changing with an equilibrium value at R_0 .



So $U(r) = \frac{1}{2} kr^2$

This curve is not parabolic in real molecule.



But for a small region around R_0 , we can assume parabolic, and the spring constant k is:

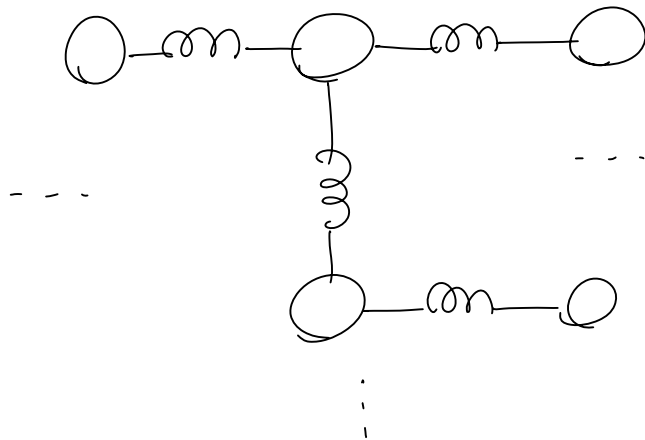
$$k = \left. \frac{d^2 U}{dr^2} \right|_{r=R_0}$$

The frequency of vibration of H_2 is then:

$$f_0 = \sqrt{\frac{2k}{m}}$$

This bonding picture can be extended to large systems

such as solids:



Basis Functions

We now concentrate on method of basis functions.

Schrodinger equation:

$$H\phi_\alpha = E_\alpha \phi_\alpha$$

Hamiltonian Operator eigenfunction eigenvalue (energy level)

We can expand ϕ_α as a linear combination of a set of basis functions, $u_m(r)$:

$$\phi_\alpha(r) = \sum_m \varphi_m u_m(\vec{r})$$

Coefficient basis functions

So for a given basis functions, we can represent ϕ_α by the vector of coefficients:

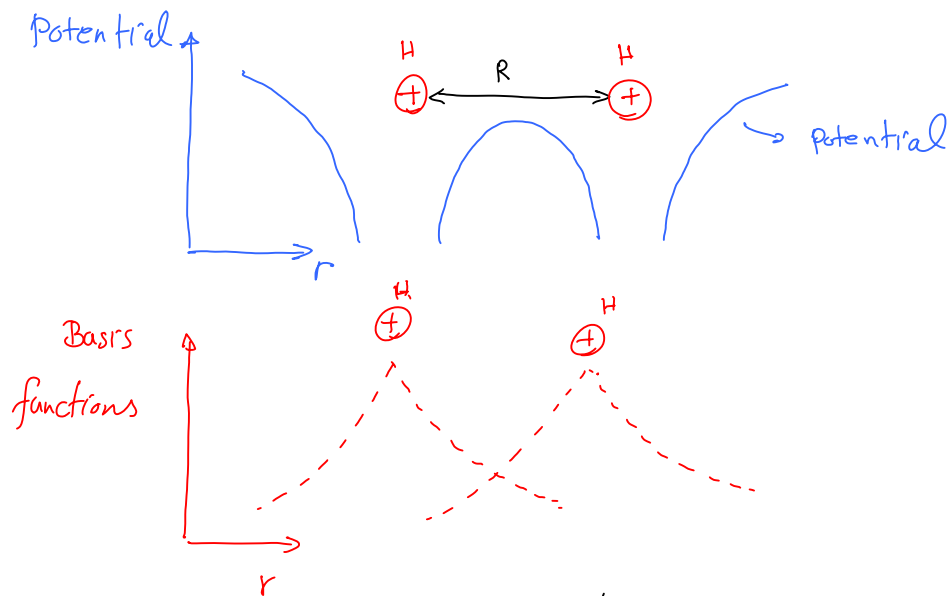
$$\Phi(r) = \begin{Bmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_M \end{Bmatrix}$$

We usually like to choose u_m 's so they look like ϕ_α , so we can use less number of u_m 's to expand ϕ_α .

For example, look at Hydrogen molecule:

Since the spherical symmetry is lacked, finite difference solution of the Schrodinger equ. is very difficult.

Let's use only two functions $U_L(r)$ and $U_R(r)$ as our basis:



We can now represent the Hamiltonian with a 2×2 matrix, rather than 1000×1000 in a finite difference approach.

$$H_{op} \phi(r) = E \phi(r)$$

$$\text{Substitute: } \phi(r) = \sum_m \varphi_m U_m(r) = \varphi_L U_L(r) + \varphi_R U_R(r) \Rightarrow$$

$$H_{op} \sum_m \varphi_m U_m(\vec{r}) = E \sum_m \varphi_m U_m(\vec{r})$$

$$\times \int U_n^*(r) dr \text{ on both side } \Rightarrow$$

$$\int d\vec{r} U_n^*(\vec{r}) H_{op} \sum_m \varphi_m U_m(r) = \int d\vec{r} U_n^*(r) E \sum_m \varphi_m U_m(\vec{r})$$

$$\sum_m \underbrace{\left[\int d\vec{r} U_n^*(r) H_{op} U_m(r) \right]}_{\equiv H_{nm} \text{ Matrix element}} \varphi_m = E \sum_m \underbrace{\left[\int d\vec{r} U_n^*(r) U_m(\vec{r}) \right]}_{\equiv S_{nm} \text{ overlap integral}} \varphi_m$$

$$\sum_m H_{nm} \varphi_m = E \sum_m S_{nm} \varphi_m \quad \text{in Matrix form} \rightarrow$$

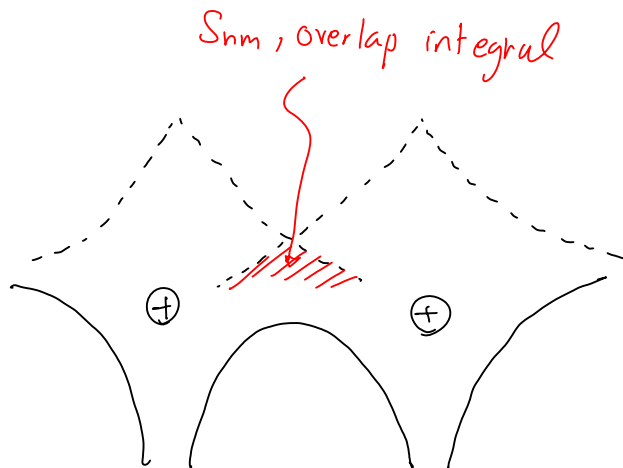
$$\boxed{[H] \{\varphi\} = E [S] \{\varphi\}}$$

It's always convenient to choose *orthogonal* basis functions:

$$\int u_n^*(r) u_m(r) d\vec{r} = \delta_{nm} = \begin{cases} 1 & n=m \\ 0 & n \neq m \end{cases} \quad \text{Kronecker delta}$$

$$\Rightarrow S_{nm} = \delta_{nm}$$

But in numerical calculations, it is more convenient to choose non-orthogonal basis.



Let's try our approach to solve for H_2 .

Let's ignore all electron interactions:

$$H_{op} \phi = E \phi$$

$$H_{op} = -\frac{\hbar^2}{2m} \nabla^2 + U_{N_L}(r) + U_{N_R}$$

H_2 basis functions are given by:

$$\text{Left atom: } \left[-\frac{\hbar^2}{2m} \nabla^2 + U_{N_L}(r) \right] u_L(\vec{r}) = E_0 u_L(\vec{r})$$

$$\text{Right atom: } \left[-\frac{\hbar^2}{2m} \nabla^2 + U_{N_R}(r) \right] u_R(\vec{r}) = E_0 u_R(\vec{r})$$

So we can expand $\phi(r)$:

$$\phi(\vec{r}) = \varphi_L u_L(\vec{r}) + \varphi_R u_R(\vec{r})$$

So the Schrodinger equation in 2x2 Matrix form is:

$$[H] \begin{Bmatrix} \varphi_L \\ \varphi_R \end{Bmatrix} = E [S] \begin{Bmatrix} \varphi_L \\ \varphi_R \end{Bmatrix}$$

$\underbrace{\hspace{10em}}_{\text{Coefficients}}$

Where for $[S]$, we have:

$$\begin{aligned} S_{11} &= \int dr u_L^*(r) u_L(r) = 1 \\ S_{22} &= \int dr u_R^*(r) u_R(r) = 1 \\ S_{12} &= \int dr u_L^*(r) u_R(r) = s \\ S_{21} &= \int dr u_R^*(r) u_L(r) = s \end{aligned} \quad \left. \vphantom{\begin{aligned} S_{11} \\ S_{22} \\ S_{12} \\ S_{21} \end{aligned}} \right\} [S] = \begin{bmatrix} 1 & s \\ s & 1 \end{bmatrix}$$

For $[H]$ we have:

$$\begin{aligned} H_{11} &= \int dr u_L^* H_{op} u_L = \int dr u_L^* \left(\overbrace{-\frac{\hbar^2}{2m} \nabla^2 + U_{N_L}(r)}^{E_0 u_L} + \underbrace{U_{N_R}(r)}_{\downarrow} \right) u_L \\ &= \int dr u_L^* (E_0 u_L + U_{N_R} u_L) = E_0 \underbrace{\int dr u_L^* u_L}_{=1} + \underbrace{\int dr u_L^* U_{N_R} u_L}_{\equiv a} \\ &= E_0 + a \end{aligned}$$

Similarly $H_{22} = E_0 + a$

$$H_{21} = \int dr u_R^* H_{op} u_L = \int dr u_R^* [E_0 u_L + U_{NR} u_L]$$

$$= E_0 \underbrace{\int dr u_R^* u_L}_{\equiv s} + \underbrace{\int dr u_R^* U_{NR} u_L}_{\equiv b}$$

calculate these integral usually numerically.
 $= E_0 s + b$

Similarly $H_{21} = E_0 s + b$. So $[H]$ is:

$$[H] = \begin{bmatrix} E_0 + a & E_0 s + b \\ \underbrace{E_0 s + b}_{\equiv B} & \underbrace{E_0 + a}_{\equiv A} \end{bmatrix}$$

$$[H] \{ \varphi \} = E [S] \{ \varphi \} \Rightarrow [S]^{-1} [H] \{ \varphi \} = E \{ \varphi \}$$

$$\begin{bmatrix} 1 & s \\ s & 1 \end{bmatrix}^{-1} \begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{Bmatrix} \varphi_L \\ \varphi_R \end{Bmatrix} = E \begin{Bmatrix} \varphi_L \\ \varphi_R \end{Bmatrix}$$

$$\frac{1}{1-s^2} \begin{bmatrix} 1 & -s \\ -s & 1 \end{bmatrix} \begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{Bmatrix} \varphi_L \\ \varphi_R \end{Bmatrix} = E \begin{Bmatrix} \varphi_L \\ \varphi_R \end{Bmatrix}$$

$$\frac{1}{1-s^2} \begin{bmatrix} A - Bs & B - sA \\ B - sA & A - Bs \end{bmatrix} \begin{Bmatrix} \varphi_L \\ \varphi_R \end{Bmatrix} = E \begin{Bmatrix} \varphi_L \\ \varphi_R \end{Bmatrix}$$

$$\begin{bmatrix} \frac{A-BS}{1-s^2} - E & \frac{B-SA}{1-s^2} \\ \frac{B-SA}{1-s^2} & \frac{A-BS}{1-s^2} - E \end{bmatrix} \begin{Bmatrix} \phi_L \\ \phi_R \end{Bmatrix} = 0$$

$$\det \begin{bmatrix} \frac{A-BS}{1-s^2} - E & \frac{B-SA}{1-s^2} \\ \frac{B-SA}{1-s^2} & \frac{A-BS}{1-s^2} - E \end{bmatrix} = 0 \Rightarrow$$

$$\frac{A-BS}{1-s^2} - E = \pm \frac{B-SA}{1-s^2}$$

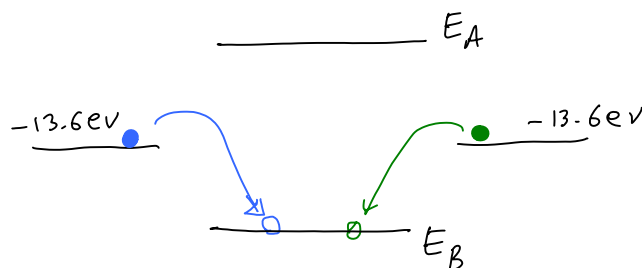
$$A-BS - (1-s^2)E = \pm (B-SA)$$

$$E = \frac{A-BS \pm (B-SA)}{1-s^2} = \begin{cases} \frac{A(1-s) + B(1-s)}{1-s^2} \\ \frac{A(1+s) - B(1+s)}{1-s^2} \end{cases}$$

$$E_B = \frac{A+B}{1+s} = E_0 + \frac{a+b}{1+s} \rightarrow \text{eigenvector } \begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$$

$$\rightarrow E_A = \frac{A-B}{1-s} = E_0 + \frac{a-b}{1-s} \rightarrow \text{eigenvector } \begin{Bmatrix} 1 \\ -1 \end{Bmatrix}$$

(a and b are negative)



With only a 2×2 matrix, we were able to get such an accurate result! This is because the bounding level in Hydrogen

is largely made up of 1s wavefunctions.

How do we know that we can ignore the upper basis levels (such as $2s, 2p_x, 2p_y, 2p_z$, etc.)?

As a general rule given:

$$[S]^{-1} [H] = \begin{bmatrix} E_1 & M \\ M & E_2 \end{bmatrix}$$

if the off-diagonal elements M are $\ll |E_1 - E_2|$ then their effect is relatively small.

Hilbert Space

We know that a function can be expanded versus a basis. This is analogous to 3D space where any vector can be written as a linear combination of the Cartesian unit vectors:

Vector space:

$$\vec{V} = V_x \hat{x} + V_y \hat{y} + V_z \hat{z}$$

unit vectors

$$\vec{a} \cdot \vec{b} = a_x b_x + a_y b_y + a_z b_z$$

dot product

Hilbert space:

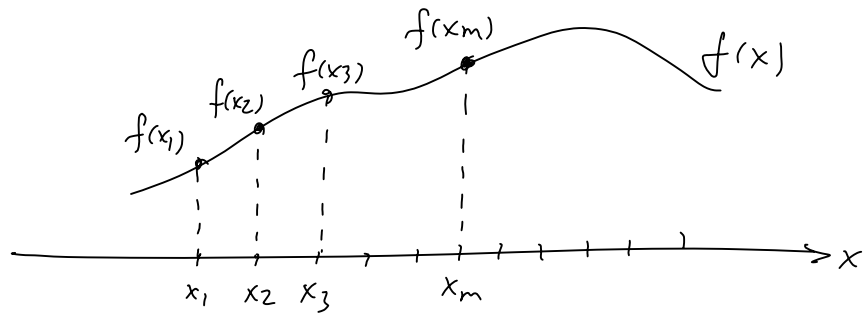
$$\Phi(r) = \varphi_1 u_1 + \varphi_2 u_2 + \varphi_3 u_3 + \dots$$

basis functions

$$\int d\vec{r} f^*(\vec{r}) g(\vec{r})$$

In a discrete 1D lattice, we may write the dot product in the Hilbert space as:

$$\int dx f^*(x) g(x) = a \sum_m f^*(x_m) g(x_m)$$



Orthogonal functions: $\int d\vec{r} u_m(\vec{r}) u_n(\vec{r}) = \delta_{mn}$ Kronecker delta

For non-orthogonal functions, we may transform them into a set of orthogonal functions. One way to do this is:

$$\tilde{u}_i(\vec{r}) = \sum_n [S^{-1/2}]_{ni} u_n(\vec{r}) \quad \text{Recall: } S_{mn} = \int u_m^* u_n d\vec{r} \text{ overlap integral}$$

The proof is as follows:

$$\text{Let } \tilde{u}_j = \sum_m [S^{-1/2}]_{mj} u_m(\vec{r})$$

For orthogonality, let's calculate:

$$\int d\vec{r} \tilde{u}_i^* \tilde{u}_j = \int d\vec{r} \sum_n [S^{-1/2}]_{ni}^* u_n^*(\vec{r}) \sum_m [S^{-1/2}]_{mj} u_m(\vec{r})$$

$$= \sum_n \sum_m \underbrace{[S^{-1/2}]_{ni}^*}_{=[S^{-1/2}]_{in}} [S^{-1/2}]_{mj} \underbrace{\int dr U_n^*(r) U_m(r)}_{S_{nm}}$$

$$= \sum_n \sum_m [S^{-1/2}]_{in} S_{nm} [S^{-1/2}]_{mj}$$

$$= [S^{-1/2} S S^{-1/2}]_{ij} = \delta_{ij}$$

So \tilde{u}_i 's are orthogonal:

$$\tilde{u}_i = \sum_n [S^{-1/2}]_{ni} u_n$$

orthogonal set
Transformation
non-orthogonal set

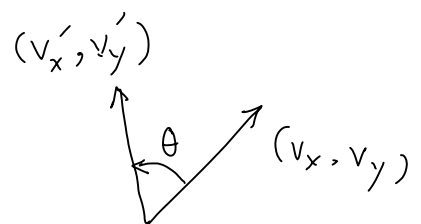
So we can always construct an orthogonal set from a non-orthogonal set.

Transformation:

In vector space we can rotate a vector by multiplying it

by a matrix:

$$\begin{Bmatrix} v'_x \\ v'_y \end{Bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{Bmatrix} v_x \\ v_y \end{Bmatrix}$$



In Hilbert space, the analogous action is matrix transformations.

For example

$$H_{nm} = \int d\vec{r} U_m^*(\vec{r}) H_{op} U_n(\vec{r})$$

is the projection of U_n on basis function U_m under the transformation H_{op} .

Changing Coordinate system

Given a function $\Phi(\vec{r}) = \sum_m \varphi_m U_m(\vec{r})$

if we were to change the basis from U_m to U'_m :

$$\Phi(\vec{r}) = \sum_i \varphi'_i U'_i(\vec{r})$$

how can we do it? Use a matrix transformation.

This matrix looks like:

$$[C] = \begin{matrix} & \xrightarrow{i} \\ \begin{matrix} \downarrow m \\ \left[\begin{array}{ccc|c|c|ccc} \cdot & \cdot & \cdot & | & | & | & \cdot & \cdot & \cdot \end{array} \right] \end{matrix} \end{matrix}$$

$$U'_i(\vec{r}) = \sum_m C_{mi} U_m(\vec{r})$$

So if we find $[C]$, we can use it to transform from one basis to another.

Let's check [C]. In the new basis set:

$$\begin{aligned}\phi(\vec{r}) &= \sum_i \phi'_i u'_i(\vec{r}) \\ &= \sum_i \phi'_i \sum_m C_{mi} u_m(\vec{r})\end{aligned}$$

$$= \sum_m u_m(\vec{r}) \sum_i C_{mi} \phi'_i$$

but this must be $= \sum_m \phi_m u_m(\vec{r}) \Rightarrow \phi_m = \sum_i C_{mi} \phi'_i$

m matrix form:

$$\{\phi\} = [C] \{\phi'\}$$

Unitary transformation

Unitary transformation preserves the length of a vector.

$$\sum_m |\phi_m|^2 = \sum_i |\phi'_i|^2$$

in vector form: $\{\phi\}^\dagger \{\phi\} = \{\phi'\}^\dagger \{\phi'\}$ †: Conjugate Transpose

For this, the matrix that makes the transformation has

to be unitary: $CC^\dagger = C^\dagger C = I$

why? let's look at $\{\phi\} = [C] \{\phi'\} \Rightarrow \{\phi\}^\dagger = \{\phi'\}^\dagger [C]^\dagger$

$$\Rightarrow \{\varphi\}^{\dagger} \{\varphi\} = \{\varphi'\}^{\dagger} [C]^{\dagger} [C] \{\varphi'\}$$

which must be equal to $\{\varphi'\}^{\dagger} \{\varphi'\}$. and the only way for this to happen is $[C]^{\dagger} [C] = I$

Summary of equations:

$$E\phi = H_{op} \phi$$

$$\phi(r) = \sum_m \varphi_m u_m(r)$$

$$= \sum_i \varphi'_i u'_i(r)$$

$$u'_i = \sum_m C_{mi} u_m(r)$$

$$\{\varphi\} = [C] \{\varphi'\}$$

In matrix notation, basis transformations are defined by:

$$[A'] = C^{\dagger} A C$$

To show this, we have:

$$A'_{ij} = \int dr u'_i{}^*(r) A_{op} u'_j(r)$$

$$= \int dr \sum_m C_{mi}{}^* u_m{}^*(r) A_{op} \sum_n C_{nj} u_n(r)$$

$$= \sum_m \sum_n C_{mi}{}^* A_{mn} C_{nj}$$

$$\text{But } C_{mi}^* = (C^\dagger)_{im} \Rightarrow$$

$$A'_{ij} = \sum_m \sum_n (C^\dagger)_{im} A_{mn} C_{nj} = [C^\dagger A C]_{ij}$$

$$\Rightarrow \hat{A} = C^\dagger A C$$

To visualize this consider finding the eigenvalues and eigenvectors of a Hamiltonian matrix:

in MATLAB:

$$[V, D] = \text{eig}(H)$$

square matrix
with eigenvector
as its columns

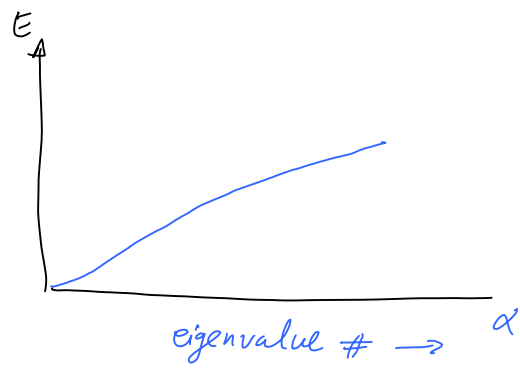
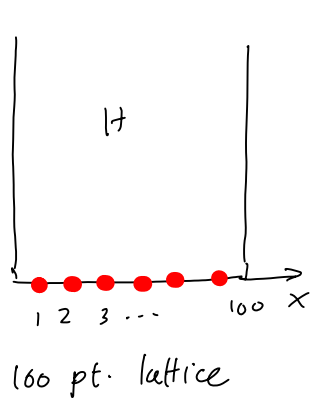
Diagonal matrix with
eigenvalues on the diagonal

This is like transforming $[H] \rightarrow [D]$

as a basis transformation from the *real space*
basis to the *eigenvector basis space*.

$$[D] = [V]^\dagger [H] [V]$$

As an example, let's calculate the electron density of
the "electrons in a box".



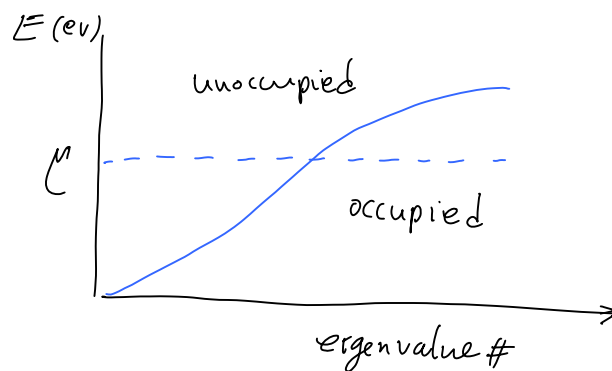
By the method of finite difference, we have:

$$H = \begin{pmatrix} 2t_0 & -t_0 & 0 & \dots \\ -t_0 & 2t_0 & & \ddots \\ 0 & \ddots & \ddots & 2t_0 \end{pmatrix}$$

we want to find electron density:

$$n(x) = \sum_{\text{occupied } \alpha} |\varphi_{\alpha}(x)|^2$$

we can redefine $n(x)$ by applying the Fermi function:



$$\begin{aligned} n(x) &= \sum_{\alpha} |\varphi_{\alpha}(x)|^2 f_{\alpha} \\ &= \sum_{\alpha} \varphi_{\alpha}(x) f_{\alpha} \varphi_{\alpha}^*(x) \end{aligned}$$

Summarizing, $\tilde{\rho} = V \rho V^\dagger$

$$\rho = V^\dagger \tilde{\rho} V$$

$\tilde{\rho}$ is in real space

ρ is in eigenstate space.

The diagonal elements of $\tilde{\rho}$ are equal to the electron density $n(x)$.

So in eigenstate basis or "space" ρ is a diagonal matrix with elements:

$$f_\alpha = \frac{1}{1 + e^{(E_\alpha - \mu)/k_B T}} = f_0(E_\alpha - \mu)$$

Let us generalize the density matrix for any space as ρ ,

where ρ is given by:

$$\rho = f_0([H] - \mu[I])$$

What does this mean? How is the "function" of a matrix calculated?

For a diagonal matrix it is simply the 'function' operated on all elements. How about matrices with off diagonal elements?

Example: Given $[H]$ with off-diagonal elements, calculate

$\sin[H]$.

Answer: Diagonalize $[H]$, operate $\sin(\)$, then transform $[H]$

back into original space.

(1) diagonalize $[H]$, $[D] = V^+ [H] V = \begin{bmatrix} D_{11} & & 0 \\ & D_{22} & \\ 0 & & \dots \end{bmatrix}$

(2) operate $\sin()$: $\begin{bmatrix} \sin(D_{11}) & & 0 \\ & \sin(D_{22}) & \\ 0 & & \dots \end{bmatrix}$

(3) Transform back to original space:

$$V \begin{bmatrix} \sin(D_{11}) & & 0 \\ & \sin(D_{22}) & \\ 0 & & \dots \end{bmatrix} V^+$$

Note: In MATLAB matrix functions & element by element functions are different.

$\sin([H]) \rightarrow$ element by element sine

$\sin m([H]) \rightarrow$ matrix operation

• Finally the expression for $\tilde{\rho}$ in real space is:

$$\tilde{\rho} = V \begin{bmatrix} f_0(E_1 - \mu) & & 0 \\ & f_0(E_2 - \mu) & \\ 0 & & \dots \\ & & & f_0(E_n - \mu) \end{bmatrix}$$

Interestingly, $\tilde{\rho}$ is only diagonal in the eigenvector basis. Off diagonal elements of $\tilde{\rho}$ in alternate basis sets are used in some calculations, but more often than not only the diagonal element of $\tilde{\rho}$ (which in any space provide electron density) are of interest.