

Presentation - Quantum many body

slide ②: What's so far;

- * Instructor gave us an idea about the couple cluster's theory and stuff.
 - and explained briefly about;
 - ⇒ Schrödinger eqⁿ.
 - ⇒ Quantum mechanics and Hartree fock method on H₂ atom.
 - then the roadmap to find the roots of the couple cluster eq^{ns}.

* Tim = 0

- basic ideas: States, Observables, measurements, uncertainty
 - ⇒ Schrödinger eqⁿ.
 - ⇒ Eigenfunⁿ of L²
 - ⇒ Hamiltonian in Real space.
 - ⇒ representing H₂ atom.

* Ben = 0

- ⇒ Stern - Grelach (dobut - on@nb) results.
- ⇒ Spin states and operators
- ⇒ Ansatz for spatial Component of wave funⁿ of H₂
- ⇒ Garlekin projection
- ⇒ Slater determinant.

Michal : second quantization I.

\Rightarrow spin orbitals

\Rightarrow Fock space and slater determinant.

\Rightarrow creation and annihilation operators

\Rightarrow ON operator \hookrightarrow (annihilated)

Then professor revised the second quantization.

\hookrightarrow 2nd quantization II.

Eddie: \hookrightarrow Slater - Condon rules, ~~and it's quantum~~

\Rightarrow Wick's thm.

~~etc~~

Slide ④

AO (Atomic orbitals)

Orbital

simple idea.

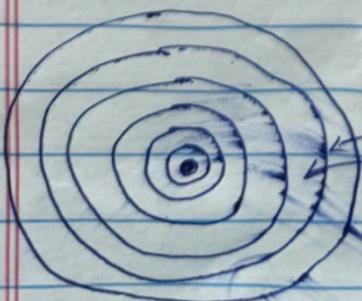
Orbital is a space where we are likely to find an electron and that space has the shape of an oscillation which is pinned to the nucleus at the center of an atom.

Orbital exists only if electron is there.
is it
How it is possible?

It is just a path which the energy is minimized. Therefore the probability of an electron is there is highly likely.

If we can capture the the path of an electron and overlap them together we can get the orbital.

Radial probability: (finding where is electron from the nucleus at a distance r from the nucleus)

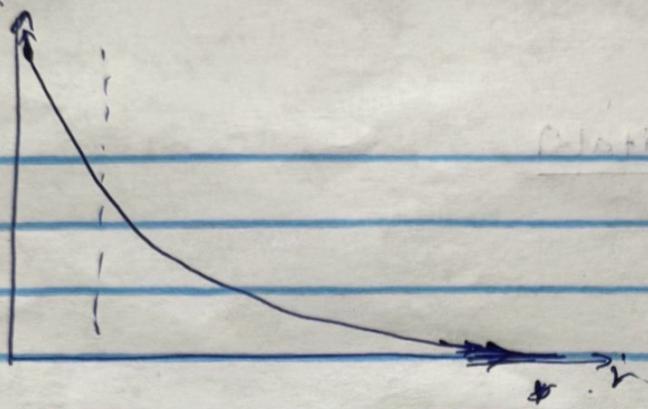


Concentric spherical shells

Is orbital imagined as an onion.

probability is greatest at $r=0$.

(probability) $\propto r^2$

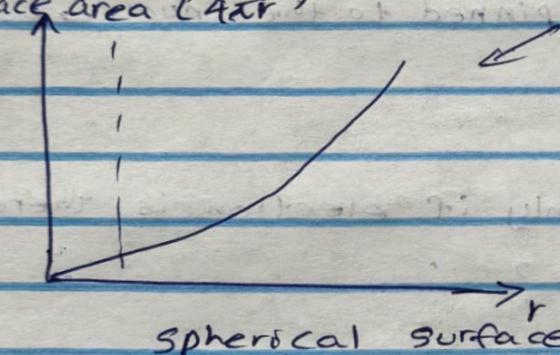


Probability density $\propto r^2$

probability density.

In contrast:

Surface area ($4\pi r^2$)



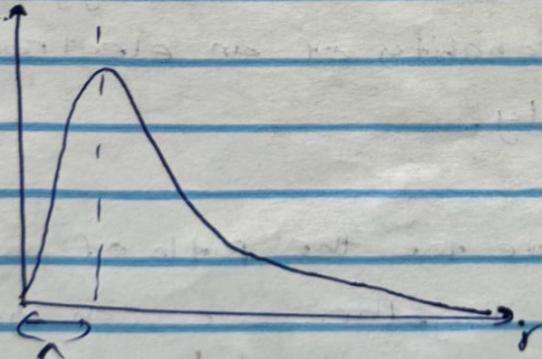
Increases the surface area more rapidly than decreases

spherical surface

probability density

radial probability

$|\psi|^2 r^2$



C for H₂ atom.

$$r = 0.529 \text{ \AA} \text{ or } 52.9 \text{ pm.}$$

Radial probability

$$\times 10^{-12} \text{ m.}$$

H₂ atom and atomic

spd_f orbitals Any orbital can have up to two electrons (with different spinning)

$S - O$ - spherical

$$P = \infty$$

A - 

energy levels and sub levels.

of energy levels = # of sublevels

		two filled	
energy levels -	n=1	$1s^2$	s - can hold 2 electrons
	n=2	$2s^2 \quad 2p^6$	p - " " 6 "
	n=3	$3s^2 \quad 3p^6 \quad 3d^{10}$	d - " " 10 "
	n=4	$4s^2 \quad 4p^6 \quad 4d^{10} \quad 4f^{14}$	f - " " 14 "
	↑ 3 orbitals.	↑ 7 orbitals.	
	1-orbital	s orbital	
			sub levels.
	$l=0$	$l=1$	$l=2$
	$l=3$		

Quantum numbers

n	$\ell = (n-1)$	m_ℓ	m_s
energy level	sublevel	orbital	electron spin.
1	s	0	+1/2 ↑
	p	-1 0 1	-1/2 ↓
	d	-2 -1 0 1 2	
	f		

How to identify a quantum number?

ex: $3p^5$

$n = 3$

~~For 3p there are 3 sublevels.~~

$l = 1$

$m_l \Rightarrow \{ -1, 0, 1 \} = 0$

$m_s = -\frac{1}{2}$

$\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2}$

electron configuration.

for \Rightarrow ~~phosphorus~~ phosphorus \rightarrow 15 electrons.

15
P

 $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^3$
2 2 6 2

6 \Rightarrow 6 - electrons

9 - p electrons:

2 8 6 10 14
 $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^{10}$
 $4s^2 \ 4p^6 \ 4d^{10} \ 4f^{14}$

Slide ⑥ spatial orbitals and spin orbitals.

We define an orbital as a wave funⁿ for a single particle, an electron.

Because we are concerned with molecular electronic structure, we will be using molecular orbitals for the wave funⁿs of the electron in a molecule.

Spatial Orbital. $\psi(r)$, is a funⁿ of the position vector r and describes the spatial distribution of an electron such that $|\psi_i(r)|^2 dr$ is the probability finding an electron in the small volume element dr surrounding r .

Spatial molecular orbitals will usually be assumed to form an orthonormal set

$$\int \psi_i^*(r) \psi_j(r) dr = \delta_{ij}$$

If the set of spatial orbitals $\{\psi_i\}$ were complete, then any arb. funⁿ $f(r)$ could be easily expanded as

$$f(r) = \sum_{i=1}^{\infty} a_i \psi_i(r)$$

where a_i are constant coefficients.

In general, the would have to be infinite to be complete.

However, in practice we will never have available a complete set, but only a finite set

$$\{\phi_i \mid i=1, 2, \dots, K\} \text{ of } K \text{ such orbitals.}$$

This finite set will only span a certain region of the complete space, but we can however, describe results as being "exact" within the subspace spanned by the finite set of orbitals.

To completely describe an electron, it is necessary to specify its spin.

A complete set for describing the spin of an electron consists of the 2 orthonormal fun^{ns}s $\alpha(\omega)$ and $\beta(\omega)$

i.e $\alpha(\omega)$ - Spin up

$\beta(\omega)$ - Spin down.

The wave funⁿ for an electron that describes both space and spin coordinates, $\psi(x)$

say $y \in \mathcal{Y} = \mathcal{Y}(r, \omega)$ indicates both space r and spin ω .

From each spatial orbital one can form 2 different spin orbitals \rightarrow one corresponding to spin up and one " " " " down.

by multiplying the spatial orbital by the α or β spin fun^{ns}s respectively.

i.e

$$\underline{\Phi}(x) = \begin{cases} \phi(r) \alpha(\omega) \\ \text{or} \\ \phi(r) \beta(\omega) \end{cases}$$

Given a set of K spatial orbitals

$$\{\phi_i | i=1, 2, \dots, K\}$$
 one can thus form a

set of $2K$ spin orbitals $\{\underline{\Phi}_i | i=1, \dots, 2K\}$ as

$$\begin{aligned} \underline{\Phi}_{2i-1}(x) &= \phi_i(r) \alpha(\omega) \\ \underline{\Phi}_{2i}(x) &= \phi_i(r) \beta(\omega) \end{aligned} \quad \left. \right\} i = 1, 2, \dots, K.$$

If the spatial orbitals are orthonormal, so are the spin orbitals

$$\int \underline{\Phi}_i^*(x) \underline{\Phi}_j(x) dx = \langle \underline{\Phi}_i, \underline{\Phi}_j \rangle = \delta_{ij}$$

Slide 5) AO's basis set exchange

Consider a molecule like H₂O

If we want a basis for this molecule,

2. we select relevant atoms.

(element you are using).

3. choose the format which suits your program.

~~Step~~

1. select the particular basis set you want.

4. click on "Get basis set"

Web portal we can use to get well studied basis sets.

at the moment 689 total basis sets
and 596 orbital basis.

Ex: 6-31++G* ⇒ split valence basis set, which includes both diffuse and polarization functions.

6 ⇒ refers to number of basis funⁿs describing the co-electrons of oxygen.

31 ⇒ refers splitting the valence shell into two levels.

one with 3 funⁿs and one with one funⁿ.

* = higher angular momentum funⁿ

D for oxygen.

H \Rightarrow diffuse basis funⁿs applied to both H and O

Small exponents describes orbitals stand far from nucleus.

↑ modeling H-bonds

H₂ atom and atomic orbitals

$$\text{peak } r \text{ (for radial probability)} \Rightarrow r = 0.529 \text{ Å}$$

In Bohr's model, he assume electron is there at this r 100% of time.

in quantum mechanics. \Rightarrow it is there ~~is~~ for some time.
not all the time.

difference \Rightarrow reasons,

1. wavelike behavior of the electron
2. Heisenberg uncertainty principle.

MOS-

In chemistry, molecular orbitals are functions describing the location and wave-like behavior of an electron in a molecule.

In an isolated atom, the orbital electrons location determined by function called ~~are~~ AOs.

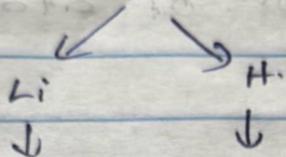
When multiple atoms combine chemically into a molecule by forming a valence chemical bond, the electrons locations are determined by the molecule as a whole, so the AOs combine to form MOs.

MOs are three types

1. bonding orbitals. ~~MO energy < AO energy~~
2. antibonding orbitals. ~~MO energy > AO.~~
3. non-bonding orbitals. Same energy

Ex: (4.1) (Lithium Hydride) $\rightarrow \text{LiH}$

$$d_{\text{nuc}} = 2 \text{ fm}$$



$$\text{atomic number } z_1 = 3, z_2 = 1$$

$$\Rightarrow \# \text{ of electrons} = d = z_1 + z_2 = 4.$$

two nuclei are fixed at locations R_1 and R_2 , whereas the 4 electrons have variable locations r_1, r_2, r_3, r_4 .

Here, ψ is a function of 12 scalar unknowns

It satisfies

$$\psi(r_1, r_2, r_3, r_4) = -\psi(r_2, r_1, r_3, r_4) = -\psi(r_1, r_2, r_4, r_3).$$

next-step (construct a finite-dimensional space of functions, along with a suitable basis)

which contain an approximate solution to the electronic Schrödinger eqn.

$$H = -\frac{1}{2} \sum_{i=1}^d \Delta r_i - \sum_{i=1}^d \sum_{j=1, j \neq i}^{d_{\text{nuc}}} \frac{z_j}{|r_i - r_j|} +$$

$$\sum_{i=1}^d \sum_{j=i+1}^d \frac{1}{|r_i - r_j|}$$

There are many ways to select a suitable basis.

↳ we apply the method called. LCAO

* linear combination of atomic orbitals.

LCAO

→ widely used in quantum chemistry.

→ starts with atomic orbitals.

We select a set of atomic orbitals.

let. $\{X_1, X_2, \dots, X_K\}$. → These are sufficiently smooth functions $X_i : \mathbb{R}^3 \rightarrow \mathbb{R}$.
and they are linearly independent.

* Notably, atomic orbital basis set for different atoms are well documented and available through online data resources like www.basis-set-exchange.org.

The number K of atomic orbitals is greater than or equal to the number d of electrons.

$$\text{i.e. } d \leq K$$

$$d = K \text{ can hold.}$$

* number K of AO determines the total count n of one particle basis functions used in the discretization.
we will be told shortly $n = 2K$

ex: (4-2) ($d = k = 4$),

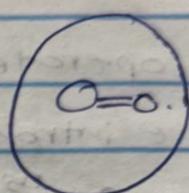
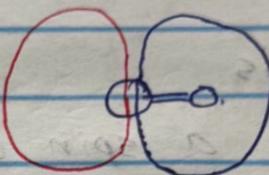
we select $k = 4$ AO

3 for Li

1 for H



AO surface



of 4 AO (Li: 1s, 2s, 2p₀; H: 1s) of LiH.

$$C = \pm 0.025 \Rightarrow \text{blue} + \text{red} -$$

The pictures are iso-surfaces for X_1, \dots, X_4 .

↑
has the form $\{ r \in \mathbb{R}^3 : X_i(r) = C \}$

Before proceeding with (LCAO) approach, we need to account for the electronic spin.

* The inclusion of spin doubles the size of our basis.

each AO X_i will be replaced by two functions.

Even the electronic Schrödinger eqⁿ does not explicitly include the electronic spin, it remains a significant factor in electronic structure calculations. This explains the eqⁿ next.

Note that $n \geq 2d$ (as $d \leq 2K$
and $n = 2K$.
 $2d \leq 2K \Rightarrow 2d \leq n$)

elec. spin \rightarrow spin up $+\frac{1}{2}$
spin down $-\frac{1}{2}$

To incorporate this

we introduce a spin variable set $\{ \pm \frac{1}{2} \}$ and 2 binary fun^{ns}.

$$m_0(s) = \begin{cases} 1 & \text{if } s = +\frac{1}{2} \\ 0 & \text{if } s = -\frac{1}{2} \end{cases} \quad \text{and} \quad m_1(s) = \begin{cases} 1 & \text{if } s = -\frac{1}{2} \\ 0 & \text{if } s = +\frac{1}{2} \end{cases}$$

The atomic orbitals can be separated into a spatial and spin components, namely

$$\phi_i(r, s) = \chi_i(r) m_0(s) \quad \text{and}$$

for $i = 1, \dots, K$

$$\phi_{k+i}(r, s) = \chi_i(r) m_1(s)$$

This factorization simplifies the treatment of electronic spin, making it possible to handle the spatial and spin degrees of freedom independently in calculations.

In order to simplify the notation, we replace \mathbb{R}^3 by

$$X := \mathbb{R}^3 \times \{ \pm \frac{1}{2} \}.$$

and we introduce compound coordinates

$$x = (r, s) \text{ on } X$$

Using these, we equip the atomic orbital space on X with inner product.

$$\langle \phi_i, \phi_j \rangle_{L^2(X)} = \int \phi_i(x) \phi_j(x) dx.$$

$$= \sum_{\substack{S \in \mathbb{Z}^n \\ S \subset \{-1, 0, 1\}}} m_{ij}(S) \int_{\mathbb{R}^3} X_i(r) X_j(r) dr$$

$\uparrow \quad \quad \quad \uparrow$
 $i \bmod (k+1)$ $j \bmod (k+1)$

where the indices of X_i and X_j in the right integral are understood as i and $j \bmod k+1$.

In principle, we obtained a Gaußien basis for H by passing from the ϕ_i to d -particle fun^{ns}s

However, LCAO method introduces an additional set of orthonormal fun^{ns}s known as molecular orbitals,

↑
describes the behavior
of individual electrons
within the molecule.

The molecular orbitals resemble the atomic orbitals.

These are linear combinations:

$$\varepsilon_i = \sum_{j=1}^n c_{j,i} \phi_j \quad \text{for } i = 1, 2, \dots, n.$$

Notably, the fun^{ns}s ε_i and ϕ_i span the same n -dimensional vector space.