

Presentation - Quantum many body

Slide 2: What's so far;

* Instructor gave us an idea about the Coupled cluster's theory and stuff.

and explained briefly about;

⇒ Schrödinger eqⁿ.

⇒ Quantum mechanics and Hartree fock method on H_2 atom.

then the roadmap to find the roots of the CC coupled cluster eq^{ns}.

* Tim ⇒

basic ideas: states, observables, measurements, uncertainty

⇒ Schrödinger eqⁿ.

⇒ Eigenfunⁿ of L^2

⇒ Hamiltonian in Real space.

⇒ representing H_2 atom.

* Ben ⇒

⇒ Stern - Gerlach (electron - magnet) results.

⇒ Spin states and operators

⇒ Ansatz for spatial component of wave fun^{ns} of H_2

⇒ Gorkin projection

⇒ Slater determinant.

Michal : second quantization I.

⇒ spin orbitals

⇒ Fock space and Slater determinant.

⇒ creation and annihilation operators

⇒ ON operator $\hookrightarrow (\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow)$

Then professor revised the second quantization.

2nd quantization II

Eddie: ⇒ Slater-Condon rules, Wick's th^m.

⇒ Wick's th^m.

~~⇒~~

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.

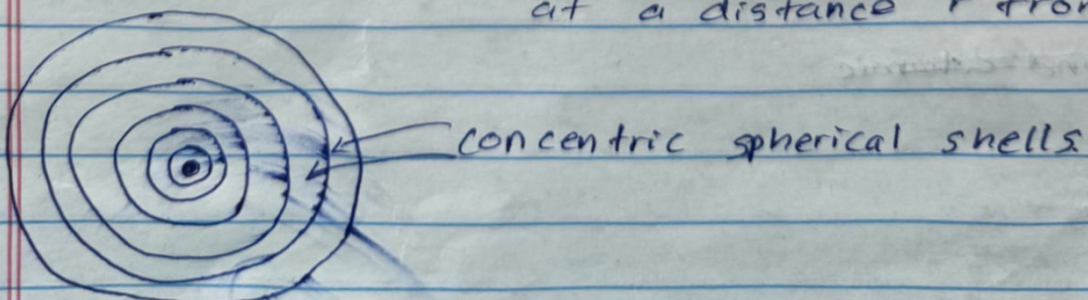
Orbital exists only if electron is there.

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.

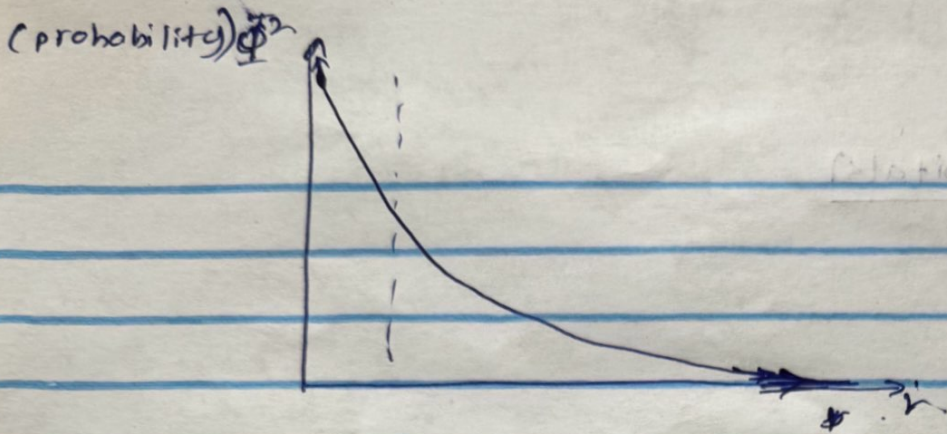
If we can capture the the path of an electron and overlap them together we can get the orbital.

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



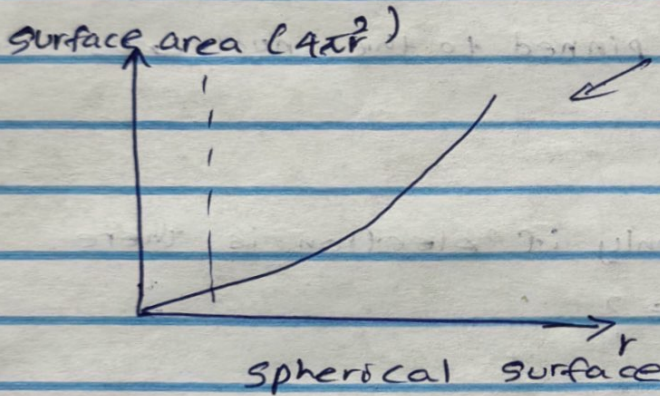
is orbital imagined as
an onion.

probability is greatest at $r=0$.



probability density.

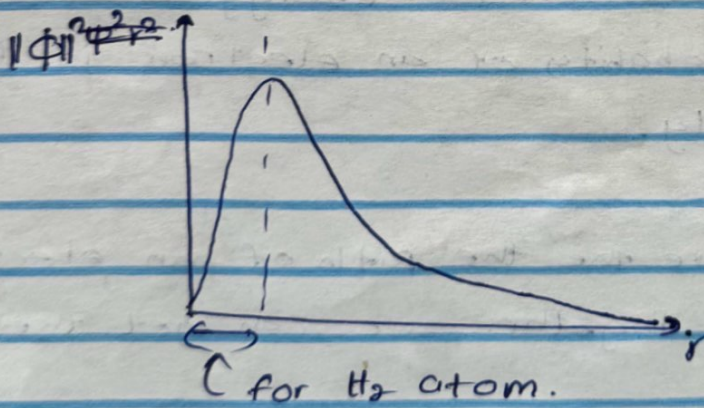
In contrast.



Increases the surface area more rapidly than decreases probability density.

spherical surface area.

radial probability has a maximum at a certain distance.



for H_2 atom.


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

radial probability


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

~~H_2 atom and atomic~~

spdf orbitals (any orbital can have up to two electrons (with different spinning))

s -  - spherical

p - 

d - 

energy levels and sub levels.

of energy levels = # of sublevels

energy levels	n=1	n=2	n=3	n=4	Electron Capacity
	1s ²	2s ² 2p ⁶	3s ² 3p ⁶ 3d ¹⁰	4s ² 4p ⁶ 4d ¹⁰ 4f ¹⁴	s - can hold 2 electrons
					p - " " 6 "
					d - " " 10 "
					f - " " 14 "
	↑ 1-orbital	↑ 3 orbitals	↑ 5 orbitals	↑ 7 orbitals	
	sub levels.				

$l=0$ $l=1$ $l=2$ $l=3$

Quantum numbers

n	l = (n-1)	m _l	m _s
energy level	sublevel	orbital	electron spin.
	s	0	+1/2 ↑
	p	-1 0 1	-1/2 ↓
	d	-2 -1 0 1 2	
	f		

How to identify a quantum number?

ex: $3p^5$

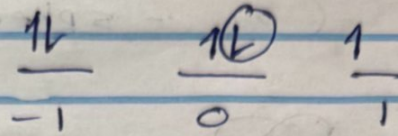
$n=3$

~~$l=2$~~

$l=1$

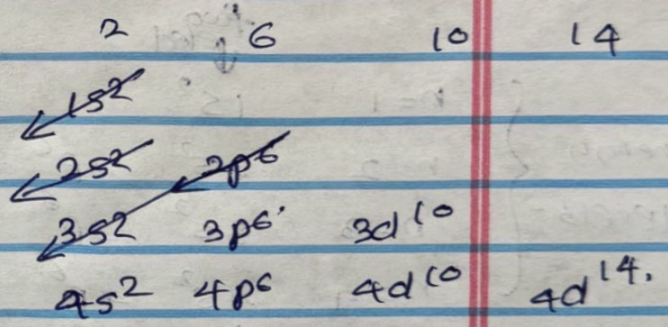
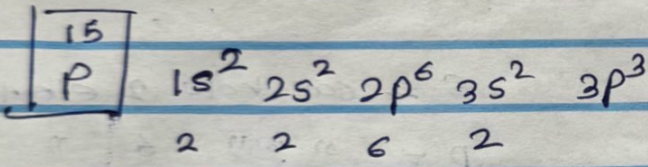
$m_l \Rightarrow [-1, 1] = 0$

$m_s = -1/2$



electron configuration.

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



~~6~~ 6 - s electrons
9 - p electrons

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 fun^s of the electron in a molecule.

Spatial orbital. $\phi_i(r)$, is a funⁿ of the position vector r and describes the spatial distribution of an electron such that $|\phi_i(r)|^2 \cdot dr$ 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

$$\int \phi_i^*(r) \phi_j(r) = \delta_{ij}$$

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

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

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

$\{\phi_i \mid i=1, 2, \dots, k\}$ of k 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} $\alpha(\omega)$ 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 $\psi(\vec{r} = \vec{r}(x, y, z))$

Indicates both space r and spin ω .

From each spatial orbital one can form a 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} 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

$$\underline{\Phi}_{2i-1}(x) = \phi_i(r) \alpha(\omega)$$

$$\underline{\Phi}_{2i}(x) = \phi_i(r) \beta(\omega) \quad \left. \vphantom{\underline{\Phi}_{2i}(x)} \right\} i = 1, 2, \dots, K.$$

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, 6 AO's basis set exchange

Consider a molecule like H_2O

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.

~~3.~~

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* \Rightarrow split valence basis set, which includes both diffuse and polarization functions.

6 \Rightarrow refers to number of basis functions describing the core-electrons of oxygen.

31 \Rightarrow refers splitting the valence shell into two levels.

one with 3 functions and one with one function.

* \Rightarrow higher angular momentum funⁿ
D for oxygen.

\Rightarrow diffuse basis funⁿs applied to both H and O

Small exponents describes orbitals stand far
from nucleus.

\uparrow modeling H-bonds

H₂ atom and atomic orbitals

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

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

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

difference \Rightarrow reasons,

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

MOS-

In chemistry, a molecular orbital is a function describing the location and wave-like behavior of an electron in a molecule.

In an isolated atom, the orbital electron location is determined by a function called ~~at~~ AOs.

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

MOs are three types

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

Ex: (4.1) (Lithium Hydride) \rightarrow LiH.

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



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.} Λ scalar unknowns

It satisfies

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

next - step (construct a finite-dimensional space of
fun^{ns}, along with a suitable basis)

↑
which contain an approximate solution
to the electronic Schrödinger
eqⁿ.

$$H = -\frac{1}{2} \sum_{i=1}^d \Delta_{r_i} - \sum_{i=1}^d \sum_{j=1}^{d_{\text{nuc}}} \frac{Z_j}{|r_i - R_j|} +$$

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

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. $\{ \chi_1, \chi_2, \dots, \chi_K \}$ → These are sufficiently smooth functions $\chi_i: \mathbb{R}^3 \rightarrow \mathbb{R}$ 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.

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

$d = K$ can hold.

* number K of AO determines the total count n of one particle basis functions used in the discretization.

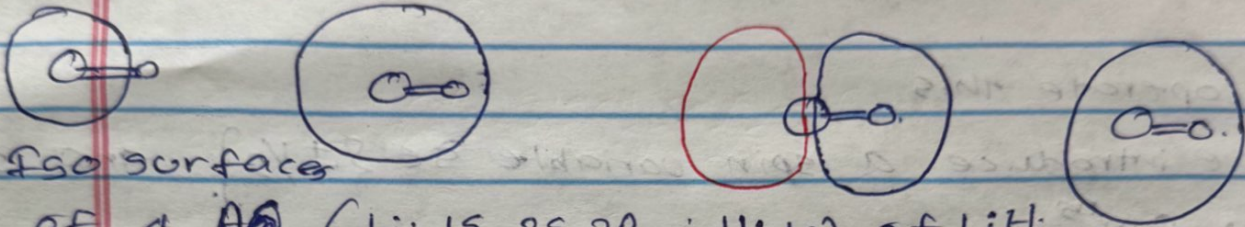
we will be led shortly $n = 2K$

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

we select $k=4$ AO

3 for Li

1 for H



iso surface

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

$C = \pm 0.025 \Rightarrow$ blue +
red -

The pictures are iso-surfaces for χ_1, \dots, χ_4 .

↑
has the form $\{r \in \mathbb{R}^3 : \chi_i(r) = c\}$
constant
can be \pm

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 χ_i will be replaced by two $\chi_i^{\uparrow, \downarrow}$

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 near k.

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 $s \in \{\pm \frac{1}{2}\}$ and a binary function

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

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 $x = (r, s)$ on X

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

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

$$\equiv \sum_{s \in \left\{ \pm \frac{1}{2} \right\}} m \begin{bmatrix} i \\ k+1 \end{bmatrix}^{(s)} \begin{bmatrix} m_j(s) \\ k+1 \end{bmatrix} \int_{\mathbb{R}^3} \chi_i(r) \chi_j(r) dr$$

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

where the indices of χ_i and χ_j in the right integral are understood as i and $j \bmod (k+1)$.

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

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

↑
describes the behavior of individual electrons within the molecule.

The molecular orbitals resemble the atomic orbitals.

They are linear combinations;

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

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