

# Quantum Mechanics in Chemistry.

Fall 2011 : Mainly electronic structure theory.

Organization of class:

prerequisites: introductory Quantum Linear algebra.

There will be no midterms or final exam.

Grades are based on extended assignments (~5)

There will be a final assignment due in exam period.

The first part of the course will use the book:

Modern Quantum Chemistry  
by Szabo and Ostlund.  
(available in bookstore \$20.-.)

The material covered in class is advanced and not easy.

Hard work is expected.

If you didn't succeed well in

Hilroy

In the quantum / linear algebras  
I do not recommend taking  
the class.

In the assignments we will  
make use of (Symbolic) Math  
programs (Mathcad, Matlab, ...)

I also plan to have you write  
programs (in Fortran) to do  
(small) calculations.

## Outline of topics to be covered (tentative).

- A) Outline of the electronic structure problem: The finite basis full CI model of quantum chemistry.
- B) Discussion on Symmetries and Spin  
permutational Symmetry  
Spin Symmetry  
Rudimentary group theory.
- C) Slater rules for matrix-elements  
Solving model problems for atoms.
- D) Hartree-Fock Theory  
The one-particle density matrix.
- E) Second Quantization
  - Operator solution for Harmonic oscillator (bosons)
  - Occupation number representation for electrons
  - Second quantized form of  $\hat{H}$ .
- F) Deriving equations using second quantization
  - CI Singles for excited states
  - CI Doubles mainly for ground states.

G) Normal order and Wick's theorem (Some diagrammatic techniques)

H) Using second quantization to discuss:

Configuration interaction

Single reference coupled cluster methods for excited states

(Equation of motion CC).

~~Graded~~ Analytical energy derivatives and density matrices.

I) Contemporary topics in Quantum Chemistry

- Local correlation
- Explicit correlation
- Multireference methods.

## Fundamentals of Quantum Chemistry

The fundamental starting point for non-relativistic quantum chemistry is the

Time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \quad \psi(t=0) = \psi_0$$

Here  $\hat{H}$  is the so-called Hamiltonian which relates to the classical energy.  $\psi$  is a wave function that depends on all coordinates

$$\psi = \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t)$$

of the particles in the system. It also depends on time.

This equation leaves out spin. We will introduce this later.

By integrating the T.D.S.E. one can calculate  $\psi(t)$  for all times, provided the wfn at  $t=0$  is known.



The time-dependent formulation is needed when one includes a time-dependent ~~for~~ external field, e.g. to study spectroscopy.

Also the T.D.S.E. is used often in problems involving the nuclei. It can be more efficient to solve time-dependent problems.

In electronic structure we often deal with the time-independent ~~Schrodinger~~ Schrodinger equation

If  $\hat{H}$  does not depend on time (e.g. no laser field) then

Formal solution to T.D.S.E.

$$\hat{H} \phi_n = E_n \phi_n \quad (\text{eigenstates})$$

$$\psi(t=0) = \sum_n c_n \phi_n$$

$c_n$  need to be specified, in principle arbitrary.

$$\psi(t) = \sum_n c_n e^{-iE_n t/\hbar} \phi_n$$

$\Rightarrow$  Easy to verify that

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi,$$

## Some notes on T.D.S.E.

probability to find ~~state~~  
energy  $E_m$  upon measurement:

$$c_m = \int \phi_m^* \sum_n c_n e^{-iE_n t/\hbar} \phi_n = c_m e^{-iE_m t/\hbar}$$

$$P_m = |c_m^{(t)}|^2 = |c_m^{(0)}|^2$$

$\Rightarrow$  Excited states do not decay.  
 $\Rightarrow$   $P_m$  do not change with time!

Also: T.D.S.E. does not lead  
to thermal equilibrium.

There are issues with TDSE that  
are not easily resolved.  
(fundamental physics!)

Let us use atomic units

$$\hbar = m_e = e = a_0 = 1$$

$$\Rightarrow 4\pi\epsilon_0 = 1$$

$H$ : kinetic energy + electro-statics  
(no magnetic interactions)

$$H = \sum_p \frac{p^2}{2m}$$

I would like to emphasize  
the essential simplicity.

In the basis of eigenstates,  
a time-dependent  $\psi(t)$  is  
given by a set of oscillating  
factors:  
 $c_1 e^{-iE_1 t/\hbar}, c_2 e^{-iE_2 t/\hbar}, \dots$

It is trivial to calculate  $\psi(t)$   
at a (much) later time;  
all independent phase factors

This is much easier than say  
solving Newton's equation of  
motion

Compare motion of nuclei for  
harmonic oscillator: each  
normal mode oscillates independently,  
with its own frequency.

- 1.) Overall motion (all normal  
modes) looks very complicated
- 2.) It is very easy to calculate  
configuration at later time  
(say, a year from now)

Formal quantum mechanics has  
same simplicity.

Design computer games using  
quantum mechanics ...!



In much of chemistry we are less interested in full time-dependent motion, but in equilibrium statistical mechanics. A slight extension in kinetics.

Also here eigenstate of  $\hat{H}$  play a crucial role. Properties are determined from a Boltzmann distribution.

$$P_n \sim e^{-E_n / kT}$$

$$\langle \hat{O} \rangle = \sum_n P_n \langle \psi_n | \hat{O} | \psi_n \rangle$$

$|\psi_n\rangle$  here includes full ligand state

translational, rotational, vibrational, (nuclear) spin, electronic degrees of freedom.

The formal solution is easy:

$$\text{Solve } H \phi_n = E_n \phi_n$$

→ determine equilibrium properties.

Since electronic excitation energies are large, we are interested in few, lowest electronic states.

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## Hamiltonian (non-relativistic) for Quantum Chemistry

Classical expression for  
energy of charged particles,  
neglecting magnetic effects:

$$E = \sum_{\alpha} \frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{q_{\alpha} q_{\beta}}{4\pi\epsilon_0 |\vec{r}_{\alpha} - \vec{r}_{\beta}|}$$

- Only electrostatic interactions
- No Lorentz forces / magnetism

Quantum Mechanics:

$$\hat{H} = \sum_{\alpha} -\frac{\nabla_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{q_{\alpha} q_{\beta}}{4\pi\epsilon_0 |\vec{r}_{\alpha} - \vec{r}_{\beta}|}$$

Use atomic units:  $\hbar = m_e = e = a_0 = 1$

$\sum_{\alpha}$  includes all particles:  
nuclei + electrons.

$$\hat{H} \phi_n(r_1, r_2, \dots, r_N, R_1, R_2, \dots, R_Z) \\ = E_n \phi_n$$

$r_i$ : electronic coordinate

$R_{\alpha}$ : nuclear coordinate

Direct solution of this problem is very complicated.

It has been done for very small molecules:  $\text{LiH}$ ,  $\text{BH}$  etc.

In practice one proceeds in steps

$$\hat{H} = \sum_{\alpha} -\frac{1}{2} \frac{\nabla_{\alpha}^2}{M_{\alpha}} - \sum_i \frac{1}{2} \frac{\nabla_i^2}{m_e} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}} - \sum_{\alpha, i} \frac{Z_{\alpha}}{r_{\alpha i}} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

$$= \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee}$$

define  $\hat{H}_{el} = \hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee}$

$\Rightarrow$  Solve for the clamped nuclei solutions

$$\hat{H}_{el} \psi_{\lambda}^{el}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; \vec{R}_1, \vec{R}_2, \dots, \vec{R}_Z) = E_{\lambda}(R) \psi_{\lambda}^{el}(\vec{r}; \vec{R})$$

Assume fixed positions of nuclei:

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The solution to the full  
Nuclear + electronic  
Schrödinger equation can  
then be written as

$$\phi = \sum_x \psi_x^{el}(\{\vec{r}\}; \{\vec{R}\}) \chi_x(\{\vec{R}\})$$

$\Rightarrow$  The electronic, clamped  
nuclear states are used  
as an expansion set (basis)

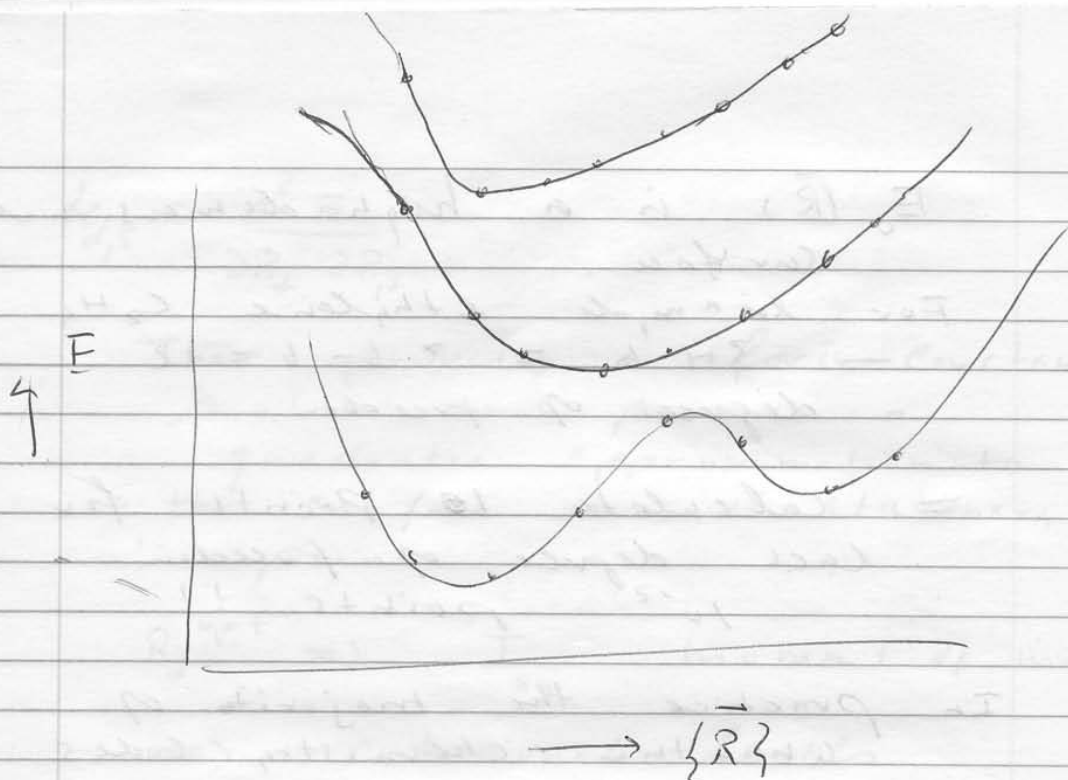
$$\begin{aligned} (\hat{T}_N + \hat{H}_{el}) \sum_x \psi_x^{el}(r; R) \chi_x(R) \\ = E \sum_x \psi_x^{el}(r; R) \chi_x(R) \end{aligned}$$

In this class I will not do  
much with this Nuclear  
Schrödinger equation.

I will post notes that cover  
this aspect (lectures given  
in summer 2011).

Our focus will be

$$\hat{H}_{el} \psi_x(\{\vec{r}\}; \{\vec{R}\}) = E_x(\vec{R}) \psi_x$$



Fixing  $\vec{R}$  we can attempt  
to solve for  $\psi_\lambda(\vec{r}, \vec{R}), E_\lambda(\vec{R})$

$\Rightarrow$  Ground and excited state  
potential energy surfaces.

Ground state is often well  
separated in energy

$\Rightarrow$  Born-Oppenheimer approximation

$$\phi_n = \psi_0^{\text{el}}(\vec{r}, \vec{R}) \chi_0(\vec{R})$$

Single electronic state in  
expansion



$E_0(\vec{R})$  is a high-dimensional surface.

For example ethylene  $C_2H_4$   
 $\rightarrow 3N - 6 = 3 \cdot 6 - 6 = 12$   
degrees of freedom.

$\Rightarrow$  Calculate  $10^{12}$  points for  
each degree of freedom  
 $10^{12}$  points !!

In practice the majority of  
quantum chemistry codes  
do the following.

- (1) Module to calculate  $E_\lambda(\vec{R}_\lambda)$   
at given point  $\{\vec{R}_\lambda\}$   
configuration
- (2) Calculate energy gradient

$$\frac{\partial E_\lambda}{\partial \vec{R}_\lambda} \text{ in } 3N \text{ directions}$$

at stationary point  $\nabla E = 0$   
Search for points at which  $\nabla E = 0$

$\Rightarrow$  optimize geometries  
- minima  
- transition states

- (3) at optimum Calculate  
Hessian

$$k_{\alpha\beta} = \frac{\partial^2 E}{\partial R_\alpha \partial R_\beta}$$

This provides a force constant matrix and provides a quadratic approximation to the surface around stationary point.

$R_\alpha^{opt} \Rightarrow \frac{I}{x_y}$  moment of inertia  
 $\Rightarrow$  rotational levels

$k_{\alpha\beta} \rightarrow$  harmonic frequencies  $\omega_x$ , normal modes  $q_x$

Transition state is characterized by one imaginary frequency  
 $\omega_x^2 < 0$

$E_x(R_\alpha^{opt})$  : electronic energy.

In the harmonic oscillator & Rigid rotor approximation one can calculate partition functions

$$Q = \sum_x e^{-E_x / k_B T}$$

$\Rightarrow$  Thermodynamic properties  
 Using info at Transition state  
 obtain rate constants (Transition state theory),  
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The crucial ingredient is the ability to solve

$$\hat{H}^{el}(\{\vec{R}\}) \psi_x^{el}(\vec{r}; \vec{R}) = E_x(\vec{R}) \psi_x^{el}(\vec{r}; \vec{R})$$

From now on I will suppress the  $\vec{R}$  dependence, and drop the subscript 'el'.

$$\hat{H} \psi(\vec{r}) = E \psi(\vec{r})$$

$$\hat{H} = \hat{T} + V^{He} + V^{ee}$$

$$= \sum_i -\frac{1}{2} \vec{p}_i^2 + \sum_{\alpha, i} \frac{Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|} + \frac{1}{2} \sum_{i < j} \frac{1}{r_{ij}}$$

$$= \sum_i \left( -\frac{1}{2} \vec{p}_i^2 + V(r_i) \right) + \frac{1}{2} \sum_{i < j} \frac{1}{r_{ij}}$$

$$\equiv \sum_i h(i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

$$\equiv \hat{h} + \hat{V}$$

↓  
One-electron operator

Two-electron operator

$V_{NN}$  is just a constant which can be added to energy.

## General solution to electronic Schrödinger equation.

$$\hat{H} = \sum_i h(i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

To understand the structure of solution let us consider first a one-body Hamiltonian.

$$\hat{h} = \sum_i \hat{h}(i)$$

We can solve the S.E. for this problem by postulating that the wave function is a product of one-electron functions (orbitals)

$$\Psi(1, 2, \dots, N) = \psi_a(1) \psi_b(2) \dots \psi_z(N)$$

Then

$$\begin{aligned} & (h(1) + h(2) + \dots + h(N)) (\psi_a(1) \dots \psi_z(N)) \\ &= (\hat{h}(1) \psi_a(1)) \psi_b(2) \dots \psi_z(N) + \\ &+ (\hat{h}(2) \psi_b(2)) \psi_a(1) \dots \psi_z(N) \\ &+ \dots \\ &+ (\hat{h}(N) \psi_z(N)) \psi_a(1) \dots \psi_{z-1}(N) \end{aligned}$$

Why?  $h(1) = -\frac{1}{2} \nabla_1^2 + V(1)$

The derivative acts only on  $\psi_a(1)$ , multiplication is done once, etc.

Hilroy

Therefore if I use ~~solutions~~  
divide by  $\Psi$ , we get

$$\frac{h(1) \psi_a(1)}{\psi_a(1)} + \frac{h(2) \psi_b(2)}{\psi_b(2)} + \dots \frac{h(N) \psi_z(N)}{\psi_z(N)} \\ = \frac{E \Psi}{\Psi} = E$$

Following standard reasoning in  
separation of variables,  
Each term has to be constant

$$h(1) \psi_a(1) = \epsilon_a \psi_a(1)$$

$$h(2) \psi_b(2) = \epsilon_b \psi_b(2)$$

$$E = \epsilon_a + \epsilon_b + \dots \epsilon_z$$

Moreover being  $h(i)$  is the  
same operator, only coordinate  
is named differently.

$\Rightarrow$

Solve one electron problem

$$h(1) \psi_a(1) = \epsilon_a \psi_a(1)$$

$\epsilon_a$ : orbital energies

$\psi_a(1)$ : orbitals: one-electron  
eigenfunctions of  $\hat{h}(1)$



Once I have solved the one-electron problem, one can write solutions for many-electron wfn's.

$$\Psi_x = \varphi_a(1) \varphi_b(2) \dots \varphi_z(N)$$

$$E_x = \epsilon_a + \epsilon_b + \dots \epsilon_z$$

$\Rightarrow$  pick  $N$  orbitals  
 $\Rightarrow \varphi, E$

Question (I may have asked you before) :

What is the ground state of this Hamiltonian  $\hat{H}$ ?

Answer: put all electrons in lowest energy orbital

$$\Psi = \varphi_0(1) \varphi_0(2) \dots \varphi_0(N)$$

$$E = N \cdot \epsilon_0$$

For electrons this is totally inadequate (qualitatively ridiculous!)

There are quantum mechanical systems for which this is correct, however!

(Boson  $^4\text{He}$  for example, superfluid)

What is missing? The Pauli exclusion principle.

I will discuss this issue in more detail later.

There are two complications

- 1) antisymmetry
- 2) spin.

Let me first give the qualitative picture: If orbital levels are as follows:

$\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array}$ 
Pauli: put at most 2 electrons in each orbital of opposite spin.

$\uparrow \downarrow$  2, 3
  $\uparrow$  or  $\downarrow$

$\uparrow \downarrow$  0

$\Rightarrow$  These are the only allowed wfn's

$$\psi_0(1) \quad \bar{\psi}_0(2) \quad \psi_1(3) \quad \bar{\psi}_1(4) \quad \dots$$

$$E = \sum_i \epsilon_i$$

With this empirical rule (Pauli), we can understand orbital level structure of atoms and molecules.

A slightly more rigorous formulation (still only a rule) can be formulated in this fashion:

Orbitals also depend on spin.

The easiest way to define is

that orbitals are either

of  $\alpha$ - or  $\beta$  type. This

indicates the eigenvalue of

the  $S_z$  operator as  $\frac{1}{2}$ ,  $-\frac{1}{2}$

$$\hat{S}_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle$$

$$S_z |\beta\rangle = -\frac{1}{2} |\beta\rangle$$

( $\hbar=1$ )

"spin-orbitals"

$$\psi_a \alpha, \psi_a \beta, \psi_b \alpha, \psi_b \beta, \dots$$

or

$$\psi_a, \bar{\psi}_a, \psi_b, \bar{\psi}_b$$

where a overbar labels  $\beta$  spin.

So after introducing spin, we can think of product functions

$$\psi_a(1) \bar{\psi}_a(2) \psi_b(3) \bar{\psi}_b(4) \dots$$

Spin can be introduced in Hilroy

Multiple ways. The above is easy, but does not incorporate many features. We will have a fuller discussion later.

The additional postulate is that a wave function for electrons has to change sign under interchange of a pair of electron labels

$$\begin{aligned}\psi(1, 2, 3, 4) &= -\psi(2, 1, 3, 4) \\ &= -\psi(1, 2, 4, 3) \\ &= +\psi(2, 1, 4, 3) \quad \text{etc.} \\ &= +\psi(2, 3, 1, 4)\end{aligned}$$

For a product function this can be incorporated as antisymmetrizing the product (spin-orbitals)

$$A(\psi_a(1) \psi_b(2)) = \psi_a(1) \psi_b(2) - \psi_a(2) \psi_b(1)$$

$$A(\psi_a(1) \psi_b(2) \psi_c(3)) = \psi_a(1) \psi_b(2) \psi_c(3) - \psi_a(2) \psi_b(1) \psi_c(3)$$

$$\begin{array}{l} 1 \ 2 \ 3 \\ 2 \ 1 \ 3 \\ 3 \ 2 \ 1 \\ 1 \ 3 \ 2 \end{array} \left. \vphantom{\begin{array}{l} 1 \ 2 \ 3 \\ 2 \ 1 \ 3 \\ 3 \ 2 \ 1 \\ 1 \ 3 \ 2 \end{array}} \right\} \ominus$$

$$\begin{array}{l} 3 \ 1 \ 2 \\ 2 \ 3 \ 1 \end{array} \left. \vphantom{\begin{array}{l} 3 \ 1 \ 2 \\ 2 \ 3 \ 1 \end{array}} \right\} \oplus$$

$$- \psi_a(3) \psi_b(1) \psi_c(2)$$

$$- \psi_a(1) \psi_b(3) \psi_c(2)$$

$$+ \psi_a(3) \psi_b(1) \psi_c(2)$$

$$+ \psi_a(2) \psi_b(3) \psi_c(1)$$

$$A = \sum_{i=1}^{N!} (-1)^{P_i} P_i$$

$P_i$  is called the parity of the permutation.

(+): even # of interchanges

(-): odd # of interchanges

It is readily verified that each of the terms have the same energy eigenvalue

$$E = \epsilon_a + \epsilon_b + \dots + \epsilon_z$$

because  $\hat{h}(a) = \hat{h}(b) = \dots = \hat{h}(N)$

$$\sum_i h(i) A(\psi_a^{(1)} \dots \psi_z^{(N)})$$

$$= A\left(\sum_i h(i) (\psi_a^{(1)} \dots \psi_z^{(N)})\right)$$

$$= A[(\epsilon_a + \epsilon_b + \dots + \epsilon_z) (\psi_a^{(1)} \dots \psi_z^{(N)})]$$

$$= E A(\psi_a^{(1)} \dots \psi_z^{(N)})$$

The antisymmetrized product can be thought of in another (fully equivalent) way



A Slater determinant  $\hat{B}$   
generates an antisymmetrized  
product

$$\begin{vmatrix} \psi_a(1) & \psi_a(2) \\ \psi_b(1) & \psi_b(2) \end{vmatrix} = \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)$$

$$\begin{vmatrix} \psi_a(1) & \psi_b(2) & \psi_a(3) \\ \psi_b(1) & \psi_b(2) & \psi_b(3) \\ \psi_c(1) & \psi_c(2) & \psi_c(3) \end{vmatrix} =$$

$$\begin{aligned} & \psi_a(1) (\psi_b(2)\psi_c(3) - \psi_b(3)\psi_c(2)) \\ & - \psi_b(1) (\psi_c(2)\psi_c(3) - \psi_a(3)\psi_c(2)) \\ & + \psi_c(1) (\psi_a(2)\psi_b(3) - \psi_b(3)\psi_a(2)) \\ & = \dots \text{ Same as what I had before.} \end{aligned}$$

From determinant picture it  
is easy to see that interchange  
of electron labels, interchanges  
two columns in determinant  
 $\Rightarrow$  change of sign.

$$\Rightarrow \text{Solutions to } H\psi = E\psi$$

$$\hat{H} = \sum_i h(i)$$

Can be expressed as Slater determinants = antisymmetrized products. Energy is sum of orbital energies.

In Slater determinant, every spin-orbital can at most be occupied once.

Pauli principle is a consequence of antisymmetry requirement.

$\Rightarrow$  After consideration of Antisymmetry & spin we can solve the one-electron problem:

(i)  $\hat{h}(i) \phi_a(i) = \epsilon_a \phi_a(i)$   
Solve one-electron S.E. (spatial orbs.)

(ii) Define spin orbitals  $|\phi_a(i)\alpha\rangle, |\phi_a(i)\beta\rangle$   
 $= |\phi_a\rangle, |\bar{\phi}_a\rangle$

(iii) Define N-electron Slater determinants: pick N diff distinct spin orbitals

$$|\Phi\rangle = |\phi_a(1), \phi_b(2), \dots, \phi_z(N)|$$

$$a < b < c < \dots < z$$

Hilroy