

We can order the orbitals,  
as changing the order in  
a determinant introduces a  
sign at most.

Including spin we might  
also say

$$|\Phi_\lambda\rangle = |\varphi_a(1) \varphi_b(2) \dots \varphi_{\frac{M}{2}}(M) \bar{\varphi}_a(1) \bar{\varphi}_b(2) \dots \bar{\varphi}_{\frac{M}{2}}(M)|$$

(first include  $M_\alpha$  orbitals,  
then ~~and~~  $M_\beta$  orbitals.

If one has  $M$  spatial orbitals,  
the number of distinct  
determinants with  $M_\alpha, M_\beta$   
is

$$\binom{M}{M_\alpha} \binom{M}{M_\beta},$$

Each of these determinants is  
eigenstate of  $\hat{h} = \sum \hat{h}(i)$  with  
energy  $\sum \epsilon_i$ . Also eigenstate of  
 $\hat{S}_z = \frac{1}{2} (M_\alpha - M_\beta)$ .

$\Rightarrow$  One has to use correct orbitals!

If the orbitals are chosen to  
be orthonormal, these states  
are orthogonal. To normalize  
one has to introduce a  
factor  $\frac{1}{\sqrt{N!}}$  (Proot later)

$\Rightarrow |\Phi_\lambda\rangle = \frac{1}{\sqrt{N!}} A(\varphi_a(1) \dots \varphi_{\frac{M}{2}}(M))$   
orthonormal basis for Hilbert space.

## Inclusion of Electron repulsion:

$$V = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

Application of the linear variational principle: The full CI model of quantum chemistry.

The eigenstates of the one-electron Hamiltonian can be used as a basis for the true many-electron problem.

Then we can write

$$|\psi\rangle = \sum_x c_x |\phi_x\rangle$$

The  $|\phi_x\rangle$  form an in principle complete basis.

To obtain the coefficients we can apply the variational principle:

$$\text{Minimize } \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \langle H \rangle = E$$

This leads to a matrix eigenvalue problem (see Chapter 1, Szabo and Ostlund)

$$\sum_{\mu} \langle \phi_x | H | \phi_{\mu} \rangle c_{\mu} = E c_x$$

$$H C = C E$$

Hilroy



This presents the best solution within the basis set

Is this a practical approach to quantum chemistry?

If we assume we have  $M$  orbitals of both  $\alpha$  spin and  $\beta$  spin.  
(This is determined by basis set used to expand orbitals)

~~The~~

$M$  spatial orbitals  
 $M_\alpha$   $\alpha$  electrons  
 $M_\beta$   $\beta$  electrons

$$(M_\alpha - M_\beta) = 2 \quad (S_z)$$

# of determinants

$$\binom{M}{M_\alpha} \cdot \binom{M}{M_\beta}$$

choose  $M_\alpha$   $\alpha$ -orbitals out of  $M$   
choose  $M_\beta$   $\beta$ -orbitals out of  $M$

e.g. for ethylene:

$$M \approx 100$$

$$M_\alpha \approx 10 = M_\beta$$

$$\binom{100}{10} = \frac{100 \cdot 99 \cdots 91}{10 \cdot 9 \cdots 1} \approx \left(\frac{100}{10}\right)^{10} = 10^{10}$$

$$\# \text{ of determinants} = 10^{10} \times 10^{10} = 10^{20} !!$$

the number of matrix-elements

$$\langle \phi_x | H | \phi_y \rangle \approx 10^{20} \cdot 10^{20} = 10^{40}$$

Absolutely impossible to ~~set~~ store  
Hamiltonian matrix, let alone  
diagonalize. Even to store solution  
 $C_\mu$ , is impractical / impossible

This is called the Full CI  
solution. Such calculations are  
done for small molecules,  
small basis sets.

FCI: In principle exact solution,  
in complete one-particle basis  
 $\Rightarrow$  model to start from when  
approximating.

- Also "exact solution" in  
finite / small basis  $\Rightarrow$  A  
rigorous benchmark to compare  
against.

- Conceptually simple. Insight  
in solutions to S.E.

- Only requires  $\langle \phi_x | H | \phi_y \rangle$ .

~~It is also~~

It is evident one needs to make  
approximations. We will see how  
to do this without losing accuracy.  
Hilroy (much)

## Hartree Fock approximation

This is a cornerstone of most wave function based electronic structure approaches.

$|\Psi\rangle$  is approximated by a single determinant  $|\Phi\rangle$

$$|\Phi\rangle = \frac{1}{\sqrt{N!}} |\psi_1(1) \psi_2(2) \dots \psi_N(N)|$$

The orbitals are optimized such that the energy is minimized

$\langle \Phi | H | \Phi \rangle$  is minimum

$$\langle \psi_a | \psi_b \rangle = \delta_{ab}$$

Orbitals are orthonormal

I will here briefly state the equations, we will discuss in more detail later.

Introduce a finite (atomic) basis set  $|\chi_\mu\rangle$

$$\psi_a(1) = \sum_{\mu} \chi_{\mu}(1) c_{\mu a}$$

MO's are linear combinations of (atomic) orbitals.

Important quantities:

overlap integral  $\langle \chi_\mu | \chi_\nu \rangle = S_{\mu\nu}$

one-electron integrals  $\langle \chi_\mu | \hat{h} | \chi_\nu \rangle = h_{\mu\nu}$

$$h_{\mu\nu} = \int \chi_\mu^*(1) \hat{h}(1) \chi_\nu(1) d1$$

two-electron integrals

$$\langle \chi_\mu \chi_\nu | \frac{1}{r_{12}} | \chi_\lambda \chi_\sigma \rangle \equiv \langle \mu\nu | \lambda\sigma \rangle$$

$$\langle \mu\nu | \lambda\sigma \rangle = \int \chi_\mu^*(1) \chi_\nu^*(2) \frac{1}{r_{12}} \chi_\lambda(1) \chi_\sigma(2) d1 d2$$

Note  $\chi_\mu$  indicate spin-orbitals  
here  $\Rightarrow$  Integration involves also  
treatment of spin.

Anti-symmetrised 2-electron integrals

$$\langle \mu\nu || \lambda\sigma \rangle = \langle \mu\nu | \lambda\sigma \rangle - \langle \mu\nu | \sigma\lambda \rangle$$

These integrals are calculated  
to at the start of a calculation.



A Hartree - Fock calculation works as follows.

→ assume a guess for MO's  
 $C_{\mu i} \quad i=1, N$

Steps:

1) Calculate density matrix

$$P_{\mu\nu} = \sum_{i=1, N} C_{\mu i} C_{\nu i} \quad (\text{occupied orbitals})$$

2) Calculate Fock - matrix

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda, \sigma} \langle \mu\lambda | \nu\sigma \rangle D_{\lambda\sigma}$$

3) Solve (generalized) eigenvalue problem

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \sum_{\lambda} \int_{\mu\lambda} C_{\lambda i} \epsilon_i$$

⇒ Molecular orbitals  $C_{\nu i}$   
Orbital energies  $\epsilon_i$

If new orbitals from (5)  
agree with input orbitals:  
converged

Otherwise go back to 1.

Iterate until IF, ID, < no  
longer change.

This is called a self-consistent field procedure.

At self-consistency, when

$$D^{(in)} \rightarrow F \rightarrow \text{Diagonalize} \rightarrow D^{(out)},$$

when  $D^{(in)} = D^{(out)}$ :

The energy of determinant is optimal (stationary).

In practice one uses smart convergence techniques. HF calculations are cumbersome, sometimes.

Note (more discussion later),

- The determinant in HF is unique (up to a phase)
- The density matrix is unique (given the basis set)
- Molecular orbitals are not unique

$$\sum_i C_{pi} C_{vi} = D_{pv}$$

One can rotate ~~the~~ occupied orbitals  $C'_{pi} = \sum_j U_{ji} C_{pj}$

$U_{ji}$  is unitary.

If  $C = SC \Rightarrow$  Canonical Mo's.  
Hilbert



## Martree-Fock in practice:

- Decent results for geometry optimization (small basis sets)
- reasonable harmonic frequencies
- Very poor for thermochemistry, energy differences.
- Not good for potential energy surfaces.

However: total energies in HF are remarkably accurate

$$E_{\text{HF}} \approx 99.5 \% \text{ of } E_{\text{FCI}}$$

Total energies are huge, e.g.

water  $-76 \text{ a.u.} \approx$   
 $-760 \text{ kJ mol}^{-1}$

$\Rightarrow$  1% error  $\approx 100 \text{ kJ mol}^{-1}$

For this reason HF by itself is not good enough.

One needs to go beyond:

Inclusion of electron correlation.

HF is often the starting point.

## Symmetry in Quantum Mechanics

This is a vast topic. I wish to discuss here the general principles. I will not go into full detail. In a next section I will discuss the permutation group, angular momentum and spin.

### General principles:

Suppose that we know the solutions to the S.E:

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle, \quad \langle\phi_n|\phi_m\rangle = \delta_{nm}$$

These solutions form an orthonormal basis for the Hilbert space.

Question: Can I find operator(s)

$\hat{U}$  such that

$\hat{U}|\phi_n\rangle$  also form an orthonormal basis, while having the same energies  $E_n$

$$\text{i.e. } (\hat{U}|\phi_n\rangle)^\dagger |\hat{U}|\phi_m\rangle = \delta_{nm}$$

$$\hat{H} \hat{U}|\phi_n\rangle = E_n \hat{U}|\phi_n\rangle \quad ?$$

1) The orthonormality condition implies  $\langle\phi_n|\hat{U}^\dagger \hat{U}|\phi_n\rangle = \langle\phi_n|\phi_n\rangle$

$$\Rightarrow U^\dagger U = 1 \quad \hat{U}^\dagger = \hat{U}^{-1}$$

Hilroy

i.e. 1)  $\hat{U}$  is a Unitary operator.  
(linear)

(Note in physics some symmetries are anti Unitary (time-reversal))

$$\text{then } (U\phi | U\psi) = (\phi | \psi)^*$$

This is not our usual inner product).

$$\begin{aligned} 2) \quad \hat{U} \text{ commutes with } \hat{H} \\ \hat{H} \hat{U} |\phi_n\rangle &= \hat{U} |\phi_n\rangle E_n \\ &= \hat{U} \hat{H} |\phi_n\rangle \quad \forall \phi_n \\ \hat{H} \hat{U} &= \hat{U} \hat{H} \end{aligned}$$

3) if  $\hat{U}$  commutes with  $H$ ,  
then also  $\hat{U}^\dagger = \hat{U}^{-1}$ :

$$\begin{aligned} \hat{H} \hat{U} &= \hat{U} \hat{H} \\ \hat{U}^\dagger \hat{H} \hat{U} &= \hat{U}^\dagger \hat{U} \hat{H} = \hat{H} \end{aligned}$$

$$\hat{U}^{-1} H (U \hat{U}^{-1}) = H \hat{U}^{-1}$$

$$\hat{U}^{-1} H = H \hat{U}^{-1}$$

$$\hat{U}^\dagger H = H \hat{U}^\dagger$$

4) if  $\hat{U}_1$  and  $\hat{U}_2$  commute,  
and unitary, then also  $\hat{U}_1^\dagger \hat{U}_2^\dagger$

$$a) \quad \hat{H} \hat{U}_1 \hat{U}_2 = \hat{U}_1 \hat{H} \hat{U}_2 = \hat{U}_1 \hat{U}_2 \hat{H}$$

$$\begin{aligned} b) \quad (\hat{U}_1, \hat{U}_2)^\dagger (\hat{U}_1, \hat{U}_2) &= \\ \hat{U}_1^\dagger \hat{U}_2^\dagger \hat{U}_2 \hat{U}_1 &= \hat{U}_1^\dagger \hat{U}_1 = 1 \end{aligned}$$

5) Linear operators are associative  
 $\hat{U}_1 (\hat{U}_2 \hat{U}_3) = (\hat{U}_1 \hat{U}_2) \hat{U}_3 = \hat{U}_1 \hat{U}_2 \hat{U}_3$   
(always holds for matrix multiplication)



It follows that the (full) set  
of symmetry operations  $\hat{U}_i$   
form a mathematical group.

Definition of a group:

~~Set of elements~~  $g_i$  form a group iff

1)  $g_i g_j \in G$  if  $g_i$  and  $g_j$  in  $G$

2)  $g_i (g_j g_k) = (g_i g_j) g_k = g_i g_j g_k$   
(associative)

3)  $\mathbb{I} \in G \quad g_i \mathbb{I} = \mathbb{I} g_i = g_i$

4)  $g_i^{-1} \in G \quad g_i^{-1} g_i = \mathbb{I}$

$\Rightarrow$  Symmetry operators  $\hat{U}_i$   
form a group.

The theory of groups  $\Leftrightarrow$  Theory of Symmetry.

## Examples of groups

i) overall translation  $\vec{x} \rightarrow T \vec{x} = \vec{x} + a$

$$\hat{T}_a \psi(T_a x) \equiv \psi(x)$$

$\hat{T}_a \psi$ : ~~rotated~~ <sup>transl</sup> function  
translated function in ~~rotated~~  
translated point has value of  
original function in original point

or  $\hat{T}_a^{-1} \hat{T}_a \psi(T_a x) = \hat{T}_a^{-1} \psi(x)$

$$\psi(T_a x) = \hat{T}_a^{-1} \psi(x)$$

$$\boxed{\hat{T}_a \psi(x) = \psi(T_a^{-1} x)}$$

↓

This is general definition of  
operator on a function, it one  
knows the operation in coordinates.

ii) Overall Rotation (nuclei + electrons)

$$R\psi(x) = \psi(R^{-1}x)$$

iii) Multiplication by a phase

$$|\psi\rangle \rightarrow e^{i\phi} |\psi\rangle$$

(same phase for every state)

- iv) Permutations of electronic coordinates

$$\hat{P}_x \psi(x_1, x_2, \dots, x_N) = \psi(\hat{P}_x^{-1}(x_1, \dots, x_N))$$

- v) Overall rotation of electron spin, for example definition of the z-axis for  $S_z$  operator.

- vi) Point group symmetry in Chemistry

If one rotates nuclei + electrons Hamiltonian is invariant

$$U^\dagger H U = H \quad H U = U H$$

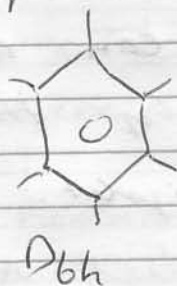
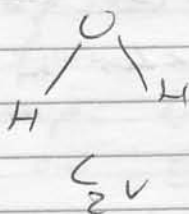
Now rotate only electronic part of the wave function.

Equivalently, rotate nuclei in opposite direction

$$\hat{R} \psi(\vec{r}; Q) = \psi(\vec{r}, R Q)$$

Hamiltonian is invariant under operations: It means nuclei map onto one another.

$\Rightarrow$  point group of molecule



{
   
 rotations
   
 reflections
   
 screw-axis



What are consequences of Symmetry?

Consider a <sup>complete</sup> multiplet of eigenstates of Hamiltonian,  $|\phi_k\rangle$ , all with same energy  $E$ .

They span a space  $\sum_{k \in E} |\phi_k\rangle \langle \phi_k| = \hat{P}_E$

is projector on this space.

Then for any symmetry generator

$$\hat{H} \hat{U}^a |\phi_k\rangle = \hat{U}^a |\phi_k\rangle E$$

hence  $\hat{U}^a |\phi_k\rangle$  is a linear combination of states in the multiplet

$$\begin{aligned} \hat{U}^a |\phi_k\rangle &= \sum_{l \in P_E} |\phi_l\rangle \langle \phi_l | \hat{U}^a | \phi_k \rangle \\ &= \sum_{l \in P_E} |\phi_l\rangle U_{lk}^{(a)} \end{aligned}$$

Like wise

$$\hat{U}^b |\phi_l\rangle = \sum_{m \in P_E} |\phi_m\rangle U_{lm}^{(b)}$$

The important point is that

$\hat{U} |\phi_k\rangle$  can always be expressed in terms of the states in the

Multiplet.

Then  $\hat{U}^b \hat{U}^a |\phi_k\rangle =$

$$\begin{aligned} & \sum_{\substack{m, l \\ \in P_E}} |\phi_m\rangle \langle \phi_m | \hat{U}^b | \phi_l \rangle \langle \phi_l | \hat{U}^a | \phi_k \rangle \\ &= \sum_{\substack{m, l \\ \in P_E}} |\phi_m\rangle U_{ml}^{(b)} U_{lk}^{(a)} \\ &= |\phi_m\rangle U_{mk}^{(ba)} \end{aligned}$$

It follows that the matrix-elements of the symmetry operators follow the same multiplication law as the group

$$\hat{U}^{ba} = \hat{U}^b \hat{U}^a$$

$$U^{ba} = U^b U^a \quad \forall a, b$$

$\Rightarrow$  group multiplication  $\Leftrightarrow$  matrix multiplication.

The dimension of the matrices is the same as degeneracy of Hamiltonian.

Group Theory: The Matrices  $U^a$  form a representation of the group. ~~same~~

If one cannot reduce the set of functions further, i.e. one cannot find a new basis in which

Hilroy

all Matrices  $U^a$  ~~are~~ have  
a block form

$$\left( \begin{array}{c|c} 1 & 0 \\ \hline 0 & 2 \end{array} \right)$$

then the representation is  
called irreducible.

The functions  $|\phi_i\rangle$  are said  
to "carry the representation".

With a little more work one can  
show: The eigenstates of the  
Hamiltonian can always be  
chosen to transform as  
irreducible representations  
of the symmetry group of  $H$ .

$$|\phi_i\rangle |n, \Gamma, i\rangle$$

$\Gamma$  : irreducible representation

$i$  : "column of irrep"

$n$  : Labels different multiplets,  
different  $E_n$ .

Examples: For H-atom orbitals  
are irreps of the rotation group  
 $s, p, d, f$  orbitals

$Y_l^m(\theta, \varphi)$  spherical harmonics

$l$  : label of irrep

$m$  : different columns of irrep.



For many electron atoms, we use the same angular momentum labels

$S, P, D, F$   
and can label functions as  $(L, m)$

$\Rightarrow$  irreducible representations  
(same as orbitals)

For molecules: Orbitals and many-electron wave functions transform as irreducible representations:  $A_1, B_1, B_2, A_2$  for  $C_{2v}$  etc.

The irreducible representations are determined by the symmetry group, independent of Hamiltonian

One can show

$$\langle \phi_k, \Gamma_1, i_1 | \hat{H} | \phi_l, \Gamma_2, i_2 \rangle = 0$$

Unless  $\Gamma_1 = \Gamma_2$  Same irrep  
 $i_1 = i_2$  : Same column  
of irrep

$k$  labels different functions  
all transforming as  $\Gamma_1, i_1$

$\Rightarrow$  The Hamiltonian is block diagonal in a Symmetry - adapted basis.

Only functions of same Symmetry can mix.

Symmetry: a) Can be very important to use to make calculation more efficient

b) States can be labelled according to Symmetry  $\Rightarrow$  qualitative understanding; Degeneracy pattern.

The use of irreducible representations is the most elaborate use of Symmetry, in Quantum chemistry.

An alternate way to think of  
Symmetry: Complete set of  
commuting operators.

Let  $\hat{A}, \hat{B}$  be Hermitian  
operators that commute with  
 $H$ , and also with each other.

$$[\hat{H}, \hat{A}] = [\hat{H}, \hat{B}] = [\hat{A}, \hat{B}] = 0$$

(example  $\hat{H}, \hat{L}^2, \hat{L}_z$ ).

Then we can define a complete  
set of common eigenstates  $|\bar{E}_n, a_i, b_j\rangle$

$$\hat{H} |\bar{E}_n, a_i, b_j\rangle = E_n |\bar{E}_n, a_i, b_j\rangle$$

$$\hat{A} |\bar{E}_n, a_i, b_j\rangle = a_i |\bar{E}_n, a_i, b_j\rangle$$

$$\hat{B} |\bar{E}_n, a_i, b_j\rangle = b_j |\bar{E}_n, a_i, b_j\rangle$$

$\Rightarrow$  Simultaneous  
eigenstates of  $\hat{H}, \hat{A}, \hat{B}$ .

If  $\hat{A}, \hat{B}$  have complete  
set of common eigenstates then  
 $[\hat{A}, \hat{B}] = 0$ .

Proof: Complete:  $|\psi\rangle = \sum_{i,j} |a_i, b_j\rangle C_{ij}$

Any  $\psi$  can be expanded in  $|a_i, b_j\rangle$



$$(\hat{A}\hat{B} - \hat{B}\hat{A})|\psi\rangle =$$

$$(\hat{A}\hat{B} - \hat{B}\hat{A}) \sum_{i,j} |a_i, b_j\rangle c_{ij}$$

$$= \sum_{i,j} (a_i b_j - b_j a_i) c_{ij} = 0 \quad \forall \psi$$

The converse part: if  $[\hat{A}, \hat{B}] = 0$   
they have a complete set of  
common eigenstates is more  
involved, but instructive:

First diagonalize the operator

$$\hat{B} : \hat{B} |b_k\rangle = b_k |b_k\rangle$$

$$\text{Then: } \langle b_i | [\hat{A}, \hat{B}] | b_j \rangle = 0 =$$

$$\langle b_i | (\hat{B}\hat{A} - \hat{A}\hat{B}) | b_j \rangle =$$

$$(b_i - b_j) \langle b_i | \hat{A} | b_j \rangle = 0$$

$\Rightarrow$  if  $b_i \neq b_j$  then

$$\langle b_i | \hat{A} | b_j \rangle = 0$$

$\Rightarrow \hat{A}$  is block diagonal in  
 $\hat{B}$  basis.

Diagonalize  $\hat{A}$ :

$\hat{A}$	$b_1$	$b_2$	$b_3$
$b_1$	X	0	0
$b_2$	0	X	0
$b_3$	0	0	X

$\hat{A}$  is block-diagonal.

$\Rightarrow$  I can diagonalize each block by itself. This does not change eigenvalue of  $\hat{B}$  (all states in a  $b_i$  block have same eigenvalues).

$$\Rightarrow \hat{A} |a_i, b_j\rangle = a_i |a_i, b_j\rangle$$

$$\hat{B} |a_i, b_j\rangle = b_j |a_i, b_j\rangle$$

This procedure can be repeated, including additional commuting generators.

$\Rightarrow$  These all represent good quantum numbers.

$\Rightarrow$  Labels for the states.

Because  $\hat{A}$ ,  $\hat{B}$  are Hermitian, they represent observables.

In a time-dependent formulation  $\langle \hat{A} \rangle$  and  $\langle \hat{B} \rangle$  would not depend on time.

$$\begin{aligned} \langle \psi(t) | \hat{A} | \psi(t) \rangle &= \\ \langle \psi(t=0) | e^{iHt} \hat{A} e^{-iHt} | \psi(t=0) \rangle \\ &= \langle \psi(t=0) | \hat{A} | \psi(t=0) \rangle \end{aligned}$$

$H$  independent of time

$$[H, A] = 0$$

$$\Rightarrow \frac{d\langle A \rangle}{dt} = 0$$

Such operators represent conserved quantities.

Any Hermitian operator that has  $[H, A] = 0$  is a conserved quantity.

$$e^{i\hat{A}} \cdot (e^{iA})^\dagger = e^{i\hat{A}} e^{-i\hat{A}} = \mathbb{I}$$

$\hat{A}$ : hermitian  $e^{i\hat{A}}$  is a symmetry operator; or even  $e^{iA}$  is symmetry generator.

Here  $\alpha$  would be a real parameter.

This is a way to make the connection between symmetries and conserved quantities.

Example:  $\hat{L}_x, \hat{L}_y, \hat{L}_z$  are hermitean, commute with  $H$ .  
 $e^{i(\alpha \hat{L}_x + \beta \hat{L}_y + \gamma \hat{L}_z)}$  is an operator that defines wfn's in a rotated frame.

These symmetries are continuous symmetries. group described by Lie algebra.