

So what is varied in the Hartree Fock method to minimize  $E_0$ ?

The spin orbitals which are used in the  $N$ -electron Slater det. Namely, you give the Hartree Fock method more than  $N$  spin orbitals, and it decides which ones should be occupied and which ones should be unoccupied to best approximate the ground state  $\Phi_0$ .

This minimization procedure can be written as an eigenvalue equation  $f(i)\chi(x_i) = \epsilon\chi(x_i)$

where  $f(i)$  is the one-electron Fock operator

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + V^{\text{HF}}(i)$$

electron kinetic energy

electron-nuclei attraction

average potential felt by  $i$ th electron due to other electrons

The key idea is to replace the many-electron problem ~~with~~ with  $N$  one-electron problems.

Each one-electron problem depends on already having the solution for the other electrons. This means the equations are implicit: they all depend on each other so where do you start?

The procedure to solve the HF equations is called the self-consistent-field method (SCF).

The idea is to start with an initial guess and iterate.

We label the occupied spin orbitals with  $a, b, c, \dots = \chi_a, \chi_b, \chi_c, \dots$   
Also called hole orbitals.

Label the unoccupied, a virtual, a particle spin orbitals  
with  $r, s, t, \dots = \chi_r, \chi_s, \chi_t, \dots$

Given  $K$  spatial basis functions  $\phi_1(r), \phi_2(r), \dots, \phi_K(r)$   
we can form  $2K$  spin orbitals. ( $\alpha, \beta$  spin).

$N$  of these are occupied and  $2K - N$  are unoccupied

The Slater det. formed from the  $N$  occupied spin orbitals  
is the HF ground state  $|\Psi_0\rangle$ .

In the limit of  $K \rightarrow \infty$  we approach the best solution possible  
in the HF theory, called the Hartree Fock limit.

### Excited State Det.

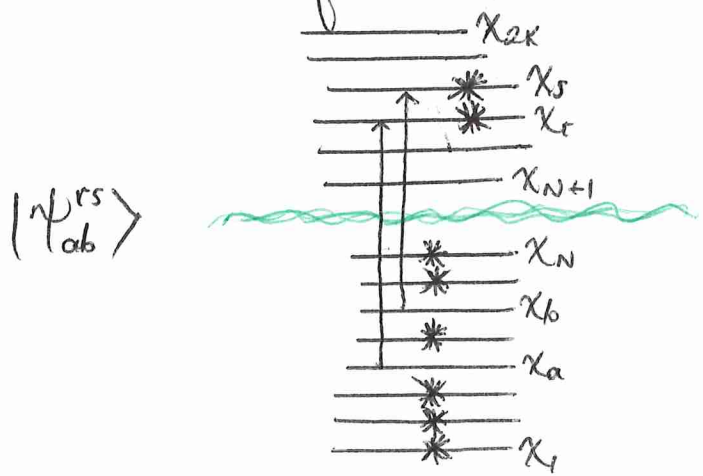
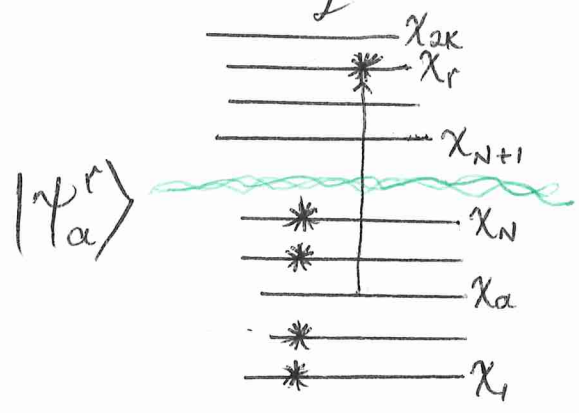
We write the HF ground state as  $|\Psi_0\rangle = |\chi_1 \chi_2 \dots \chi_a \chi_b \dots \chi_N\rangle$

We can also form other Slater det. using the unoccupied orbitals  
in  $\binom{2K}{N} = \frac{(2K)!}{N!(2K-N)!}$  different ways.

We will keep track of these by how they differ from  $|\Psi_0\rangle$ .

In a singly excited det one electron moves from  $\chi_a$  to  $\chi_r$ .

In a doubly excited det two electrons move from  $\chi_a, \chi_b$  to  $\chi_r, \chi_s$ .



# Exact Wavefunction and CI

(22)

Suppose we have a basis for one-electron wavefunctions  $\{\chi_i(x)\}$ . This could happen if  $K \rightarrow \infty$  in the orbitals we use for HF.

Then, any one-electron wavefunction  $\Phi(x_1)$  can be written  $\Phi(x_1) = \sum_i \alpha_i \chi_i(x_1)$  where  $\alpha_i = \langle \chi_i | \Phi \rangle$

What about a function of two-electrons  $\Phi(x_1, x_2)$ ?

If we imagine fixing  $x_2$  we have  $\Phi(x_1, x_2) = \sum_i \alpha_i(x_2) \chi_i(x_1)$  since for each different (fixed) value of  $x_2$  the expansion coefficients change.

But then  $\alpha_i(x_2) = \sum_j b_{ij} \chi_j(x_2)$  so  $\Phi(x_1, x_2) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2)$ .

We also need  $\Phi(x_1, x_2) = -\Phi(x_2, x_1) \Rightarrow b_{ij} = -b_{ji}$  and  $b_{ii} = 0$ ,

$$\text{so that } \Phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij} [\chi_i(x_1) \chi_j(x_2) - \chi_j(x_1) \chi_i(x_2)] \\ = \sum_{i<j} \sqrt{2} b_{ij} |\chi_i \chi_j \rangle$$

Hence any antisymmetric function of two electrons can be written in terms of all possible det. formed from one-electron wavefunctions. This argument extends to  $N$ -electron wavefunctions.

Since any  $N$ -electron Slater det. can be expressed by how it differs from the HF ground state, we can express the exact  $N$ -electron wavefunction as

$$|\Phi\rangle = c_0 |\Psi_0\rangle + \sum_{r, \alpha} C_{\alpha}^r |\Psi_{\alpha}^r\rangle + \sum_{\substack{\alpha < \beta \\ r < s}} C_{\alpha\beta}^{rs} |\Psi_{\alpha\beta}^{rs}\rangle + \sum_{\substack{\alpha < \beta < \gamma \\ r < s < t}} C_{\alpha\beta\gamma}^{rst} |\Psi_{\alpha\beta\gamma}^{rst}\rangle + \dots$$

This procedure is called CI "configuration interaction".

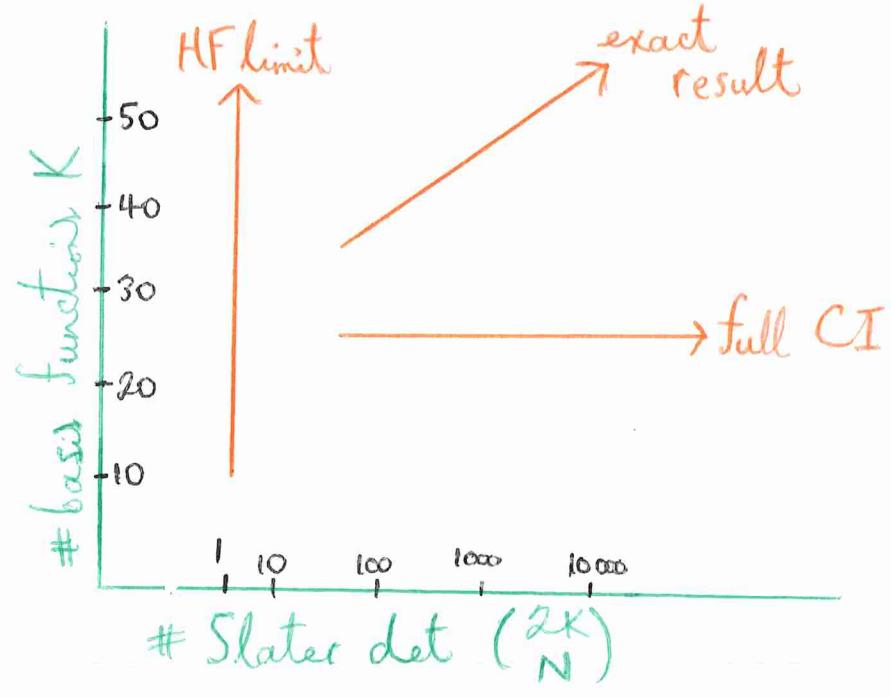
In principle it gives the exact nonrelativistic ground state of the electronic Hamiltonian in the Born - Appenheimer approx.

The difference between this exact energy  $E_0$ , and the HF limit  $E_0$  is called the correlation energy

$$E_{corr} = E_0 - E_0$$

since the motion of electrons with opposite spin is not correlated at the HF level.

Fig 2.9 of Szabo



# The HF theory

Given a set of spin orbitals  $\{\chi_i\}$ , we want to find the best  $N$ -electron det  $|\Psi_0\rangle = |\chi_1 \chi_2 \dots \chi_a \chi_b \dots \chi_N\rangle$  to approximate the ground state of  $H$ , the electronic Hamiltonian

The variational principle says the best det is the one that minimizes the energy  $E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_{ab} \langle ab || ab \rangle$

This is a calculus problem: we want to find a minimum.

But it is not the "usual" problem:

Normally in calculus you are given a function  $f(x)$  and you are asked what values of  $x$  minimize the value of the function  $f(x)$ . So your "search space" is the real numbers: you should decide which real number  $x$  to use.

Here the "search space" is wavefunctions. Which function  $\Psi_0$  minimizes  $E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$ ?

The calculus needed for this kind of minimization problem is called "calculus of variations" and its history is linked to the brachistochrone problem.

The brachistochrone problem was posed by Johann Bernoulli in *Acta Eruditorum* in June 1696. He introduced the problem as follows:

I, Johann Bernoulli, address the most brilliant mathematicians in the world. Nothing is more attractive to intelligent people than an honest, challenging problem, whose possible solution will bestow fame and remain as a lasting monument. Following the example set by Pascal, Fermat, etc., I hope to gain the gratitude of the whole scientific community by placing before the finest mathematicians of our time a problem which will test their methods and the strength of their intellect. If someone communicates to me the solution of the proposed problem, I shall publicly declare him worthy of praise.

*The problem he posed was the following:*

Given two points  $A = (x_1, z_1)$  and  $B = (x_2, z_2)$  with  $x_1 < x_2, z_1 > z_2$ , what is the curve traced out by a point acted on only by gravity, which starts at A and reaches B in the shortest time.

Answer: cycloid

For the HF problem, the solution to this calculus problem is given by the integro-differential equation

$$h^{(1)}\chi_{\alpha}^{(1)} + \sum_{b \neq \alpha} \left[ \int dx_2 |\chi_b^{(2)}|^2 r_{12}^{-1} \right] \chi_{\alpha}^{(1)} - \sum_{b \neq \alpha} \left[ \int dx_2 \chi_b^{*(2)} \chi_{\alpha}^{(2)} r_{12}^{-1} \right] \chi_b^{(1)} = \epsilon_{\alpha} \chi_{\alpha}^{(1)}$$

one-electron term

Coulomb

electron-electron terms

exchange

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} = \text{kinetic} + \text{nuclear attraction energy for each electron.}$$

Define Coulomb operator  $J_b(i)\chi_\alpha(i) = \left[ \int dx_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \right] \chi_\alpha(i)$

and exchange operator  $K_b(i)\chi_\alpha(i) = \left[ \int dx_2 \chi_b^*(2) r_{12}^{-1} \chi_\alpha(2) \right] \chi_b(i)$

exchange operator is non-local.

This lets us write the HF equation as

$$\left[ h(i) + \sum_{b \neq \alpha} J_b(i) - \sum_{b \neq \alpha} K_b(i) \right] \chi_\alpha(i) = \epsilon_\alpha \chi_\alpha(i)$$

The operator in [ ] is different for each orbital because of  $b \neq \alpha$ .

However,  $[J_\alpha(i) - K_\alpha(i)] \chi_\alpha(i) = 0$  so we can add this in to obtain the same operator for each electron,

$$f|\chi_\alpha\rangle = \epsilon_\alpha|\chi_\alpha\rangle$$

with  $f = f(i) = h(i) + \sum_b J_b(i) - \sum_b K_b(i)$ .

To proceed, we now want to turn this integro-differential eigenvalue equation into a linear algebra problem by choosing a basis.