

or if symmetrization magically [5-263]
~~magically~~ ~~magically~~

turns on when systems get close enough to each other.

Nature is very clever at hiding the truth about QM from us.

11) Hartree Method
& Hartree-Fock Method
(ER-319, Baym 443, 498)

These methods are the traditional way to solve for the ground state of atoms.

I think they are still in use, but how higher

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accuracy one needs
advanced many-body
methods (Lindmilla)

Their limitation is that
they are both mean field
theories in which the
actual complex interactions
between electrons are replaced
by a mean field.

— one electron instead
of feeling the individual
potentials of the others
~~part b~~

Instead of each electron sensing
the individual fields of
the others,

it senses only the average field created by the others.

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— there are other limitations too. (It's non-relativistic, it doesn't include spin interactions and nuclear interactions, other things)

— Also H & HF methods have many variations. We only look at one version of each.

— for HF method, I'm only go to sketch a ~~pseudo~~ ^{heuristic} version.

The real version (e.g., Baym 448) is just a bit ^{too} intricate to discuss.

→ the ~~pseudo~~ ^{heuristic} version would work too, but probably no better than the H method.

The heuristic version works too in principle I think, but utterly impractical as I discovered.

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Let's start with HF method
and the H method is a
simplification.

HF Method (the ~~pseudo~~ ^{heuristic}
version)

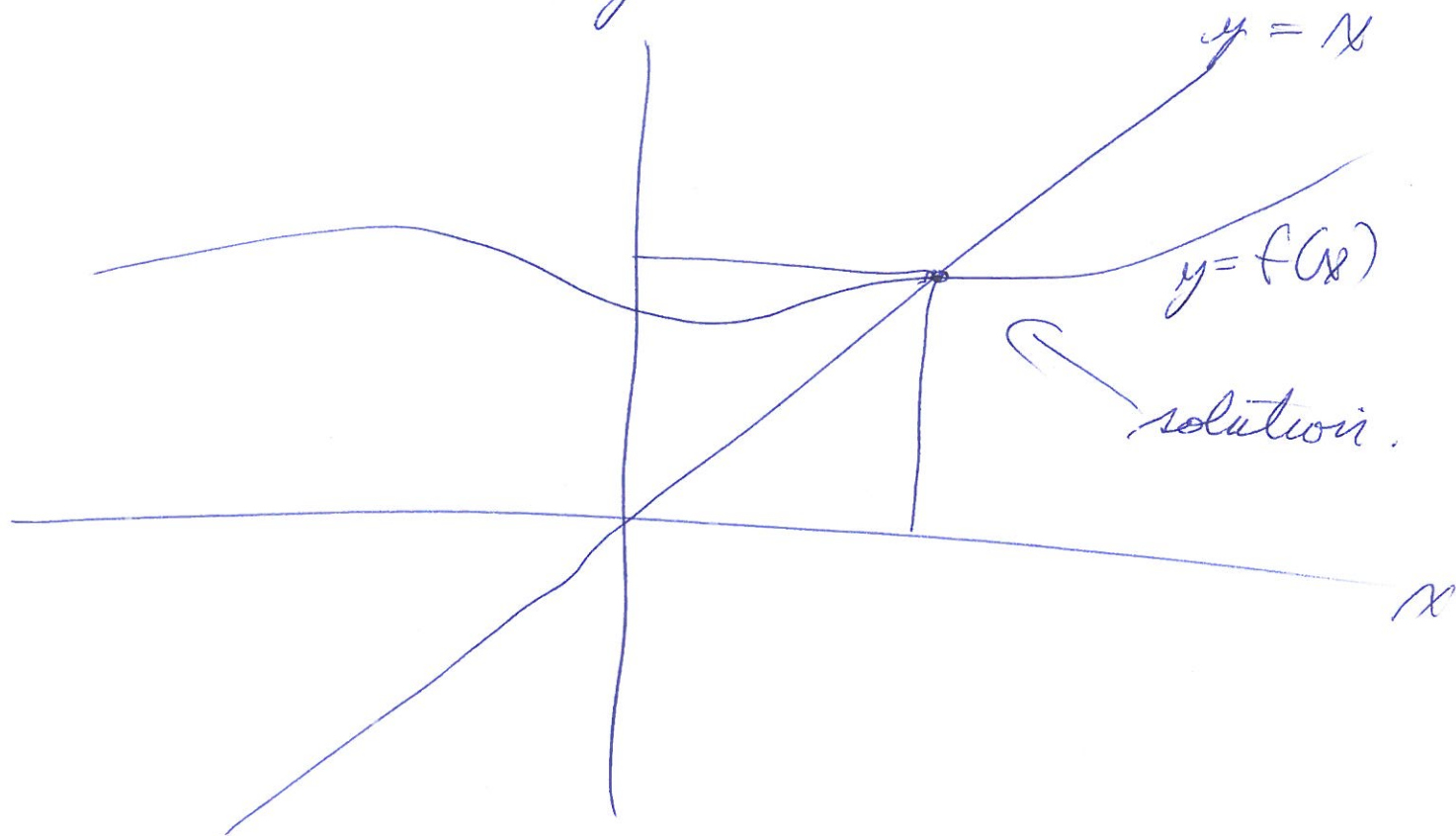
— it's an iteration to
a self-consistent solution.

↳ such approaches are essential
in solving highly non-linear
problems → ones that
can't be reduced to
solving a matrix equation
once.

~~A one variable iteration~~ A one ~~variable~~ variable
iteration, would be a case where
one has a function $g(x) = 0$
in which g is rather complex,
and one wants to solve for x .

The ^{equation} can be rearranged 5-267
to $x = f(x)$

or $y = x$ and $y = f(x)$



One takes an initial value x_0
and finds

$$x_1 = f(x_0)$$

$$x_2 = f(x_1)$$

\vdots

$$x_i = f(x_{i-1})$$

} an
iteration
to a
solution.

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But does one get convergence
or divergence or oscillation?

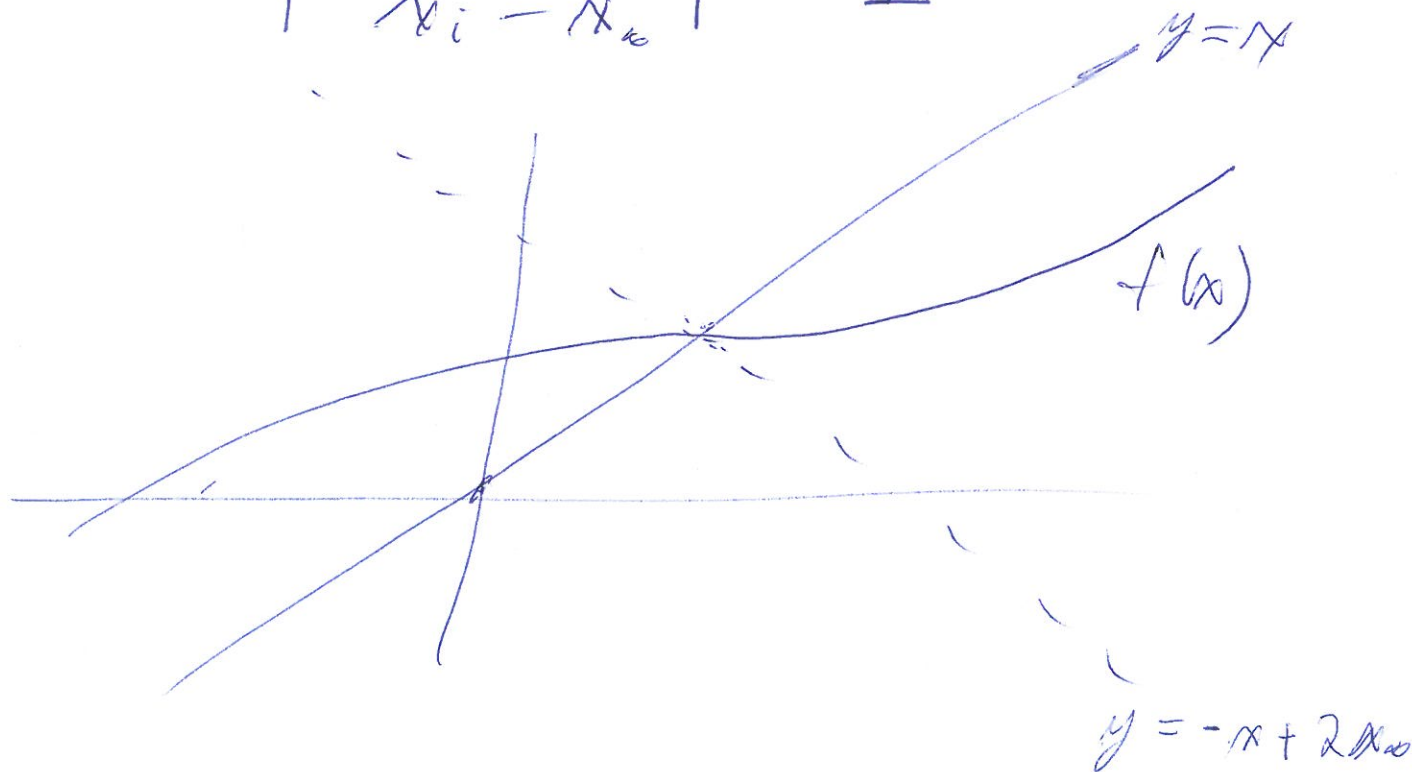
Say x_{∞} is the solution: $x_{\infty} = f(x_{\infty})$

An iteration step ~~it converges~~
is convergent if

$$|x_{i+1} - x_{\infty}| < |x_i - x_{\infty}|$$

or $|f(x_i) - f(x_{\infty})| < |x_i - x_{\infty}|$

or $\left| \frac{f(x_i) - f(x_{\infty})}{x_i - x_{\infty}} \right| < 1$



So as long as $f(x)$

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is between the $y = x$

$$y = -x + 2x_0$$

lines, there is convergence,
(maybe not fast)

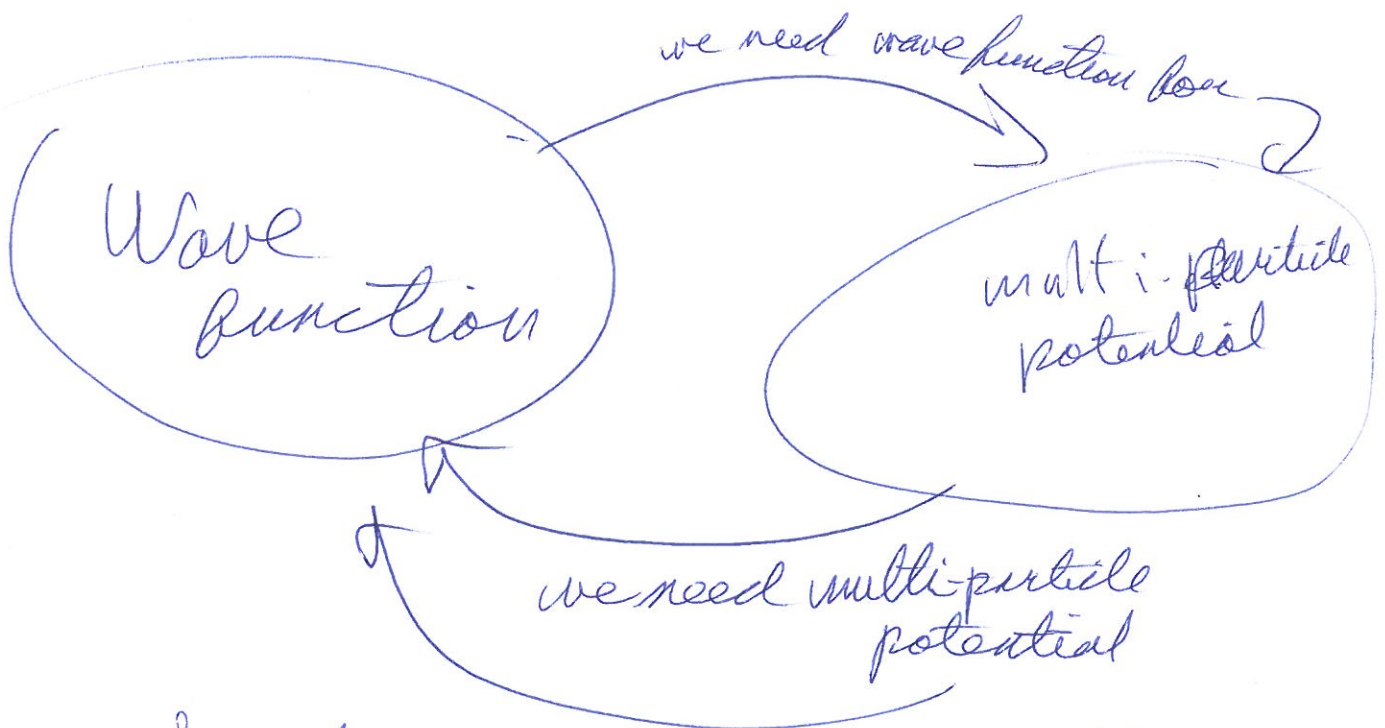
The flatter $f(x)$, the faster
the convergence.

For multi-variable iteration
problems, nothing is so simple,
but still a good convergence
"function" (which may be
a complex evaluation) and
good starting values speeds
convergence.

For the HF method, the
solution is the multi-electron
wave function.

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— If we have that, we know everything QM allows us to know about the atom.
Of course, we with HF we only get an approximate wave function and only get approximate information.



— Sort of chicken & egg problem
— Such problems are very common.

We need a guessed initial wave function

and a guessed multiparticle potential

and iterate and hope for convergence — No one

comments that convergence is tricky but it is a computationally heavy problem.

Nowadays with big computers ~~the~~ HF is probably pretty easy, but ~~more~~ the more accurate the ~~without~~ without the heavier the computation in general.

In old days — more than 30 years ago — HF was pretty hard.

But even the initial guesses, the faster convergence in general.

Real HF, not my heuristic version which we'll see is usually impossible.

5-272

To start we guess
hydrogenic ~~was~~
single-particle
~~wave~~ stationary states.

These also form our
complete basis for the whole
calculation.

Nucleus has charge Z .

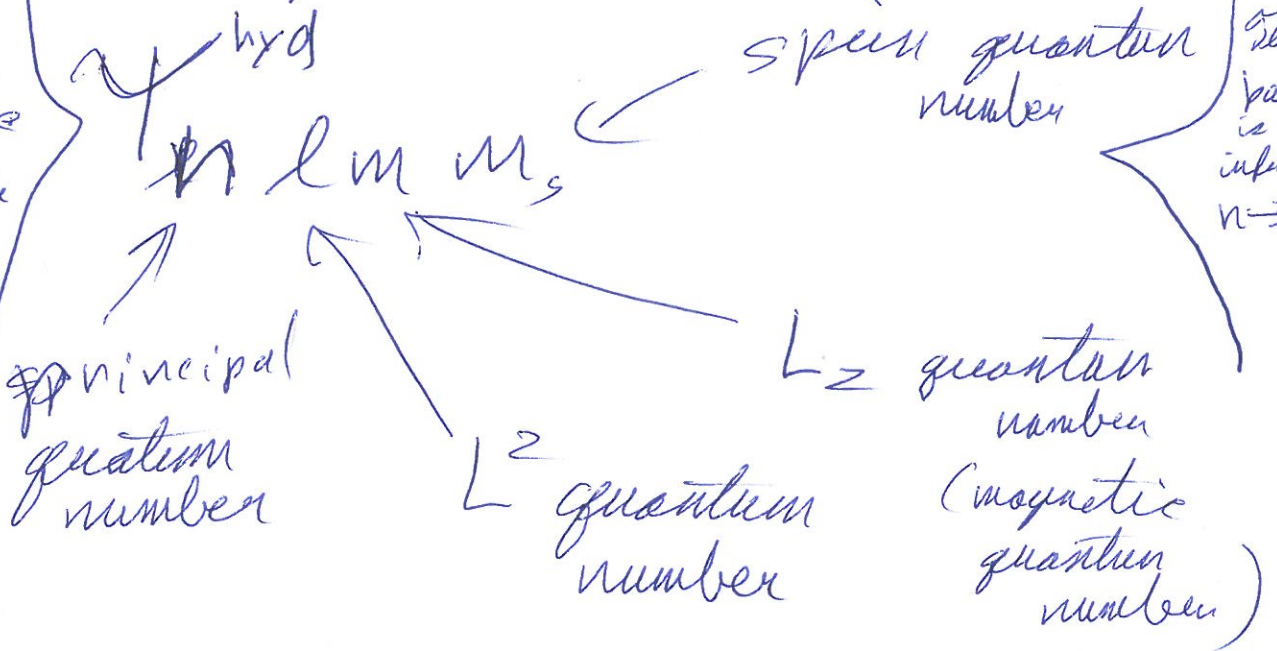
Electron close to nucleus will see Ze
Those at edge maybe e .

So Z_{eff} is $\approx \frac{1}{2}Z$
as a guess

$$\mu = \frac{1}{m_{\text{nuc}}}$$

$\frac{1}{m_e}$

could be a good guess.



For initial potential?

Will the nucleus

has $-\frac{Ze^2}{4\pi\epsilon_0 r}$ for every electron.

that part is exact [5-273]
~~is often~~ assuming a
point nucleus.

The inter-electron potential
for
electron i

$$\sum_{j \neq i} \frac{e^2}{4\pi\epsilon_0 |\underline{r}_j - \underline{r}_i|}$$

But this is too tough for us.
We will assume ~~this~~ ^{the total potential} can be
replaced by a mean field.
Our initial guess, maybe

$$V = \begin{cases} -\frac{e^2}{4\pi\epsilon_0 r} f(r), & \text{in general} \\ -\frac{Ze^2}{4\pi\epsilon_0 r} & ? \quad r \rightarrow 0 \\ & \text{near the nucleus} \\ -\frac{e^2}{4\pi\epsilon_0 V} & ? \quad \text{near outer} \\ & \text{edge where} \\ & \text{all the} \end{cases}$$

$f(r)$ is some
interpolation
formula.

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other electrons
screen the
the nucleus from
~~the~~ electron i .

This screened potential is
spherically symmetric

and

in our development

we always assume

a spherically symmetric
potential at every step.

(Neither HF nor H methods
have to make this assumption,
but it's a lot easier to
do so especially in
a heuristic discussion.)

We ~~have~~ ^{include} no spin interaction (5-279)

but still have spin ~~states~~
stationary states: χ_{\pm}

In ~~reality~~ reality,
there will be spin

$$\chi_{+} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\chi_{-} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

interactions that will
probably make these eigenstates
favored or least
a good basis for favored
states.

(Actually the electrons in
the ~~unfilled~~ ^{unfilled} subshell
at the outer edge need
special care for their
spin states as we'll
see.)

Note the stationary states are NOT
going to be spherically symmetric even
if the potential is. This is no
different from classical central force
systems where all states are NOT sph. sym. — particle
in orbit, etc.

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Step 1

Given our basis states
and our initial potential

how do we solve for
a better set of ~~states~~
single-particle stationary states?

We diagonalize the Hamiltonian.
— general idea.

~~We are solving for a new set~~

All electrons are identical and
the potential for each is the
same and just depends on r .

~~So all the~~

— So the full ~~Hamiltonian~~ Sch. eqn.
can be separated into

Z such equation

— all the same since the electrons are identical

$$H\psi = E\psi$$

We know
this

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r)$$

from
p. 5-273

ψ and E are unknowns.

But we expand ψ in our complete set (from p. 5-272)

$$\psi = \sum_j c_j \psi_j$$

and pre multiply ψ_i^*

$$\sum_j c_j \psi_i^* H \psi_j = E \sum_j c_j \psi_i^* \psi_j$$

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Now integrate over all space.

$$\int \psi_i^* H \psi_j dx$$

$$= \langle \psi_i | H | \psi_j \rangle$$

$$= H_{ij}$$

is the matrix element.

$$\int \psi_i^* \psi_j dx = \delta_{ij}$$

$$\therefore \sum_j H_{ij} c_j = E c_i$$

which we recognize as a matrix eigen equation

$$H \underline{c} = E \underline{c}$$

— and we hand this over to a computer for a solution.

- computers like matrix equation
- there are standard routines (e.g., in LAPACK) for diagonalization (i.e., solution of eigenvalues and eigenvectors.)

Note we've established the connection between Schrödinger's wave mechanics & Heisenberg's matrix mechanics ~~and~~ that was noticed pretty early on in QM circa 1926 or so.

But there is a problem — the basis is infinite. — So an exact ~~solution~~ ~~is~~ matrix problem is $\infty \times \infty$.

9-280

which presents some difficulty.

This is a common problem
in diagonalization.

Typically one just
truncates to the N lowest
energy basis states.

~~One assumes that~~

The solutions of interest are
the low energy ones often
and as long as the low energy
basis states are included, those
solutions will be approximately
good.

One has to test ~~in general~~.

One tries N and then
say $3N$ and if the
lowest states $\ll N$ of interest

stay constant nearly
within tolerance

5-281

then N was good enough.

Now in our particular case?

Will we have to go high enough
at least to include all
single particle states needed
for the ground state and
maybe a bit higher

Shell number and principal quantum number	n	$g = 2n^2$	g_{cum}	g_r (see p. 5-284)
	1	2	2	1
	2	8	10	3
	3	18	28	6
	4	32	60	10
	5	50	110	15
	6	72	182	21
	7	98	280	28

5-282

A lot of going ~~away~~
to high z .

But there is some simplification.

The angular and spin solutions
are already known

no
angular
or spin
dependence

$$Y_{lm}(\theta, \phi) \text{ and } \chi_{\pm}$$

So we only have to solve
for radial part of Sch. eqn.
and the radial solutions.

$$\left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + V(r) \right] R = ER$$

(Gr-134)

Acts
Like
repulsive
potential
in a
1-d
problem

$$+ \frac{\hbar^2}{2mr^2} l(l+1)] R = ER$$

The radial solutions
depend on $l(l+1)$ which
was the constant of separation

for the angular part.

5-283

Recall l is the L^2 quantum number. It must be an integer

For hydrogenic atoms,

l is limited $l = 0, 1, \dots, n-1$.

Must be a general proof.

It seems to be "unspeakable", but this limit seems to be general for a spherically symmetric potential.

For hydrogenic atoms

(i.e., for inverse-square law forces), E is independent of l

(i.e. of angular momentum)

Radial wave function does depend on l though.

Gr -152

But this is not true of other spherically symmetric potentials so our ~~solutions~~ ~~will be~~ E values will depend on n and l .

5-284

So if one ~~you~~ need to go up
to n_f

$$g_r = \sum_{n=1}^{n_f} n = \frac{n_f(n_f+1)}{2}$$

states

Wiki:
sums
of powers
Faulhaber
formula

Say one had $Z = 21$

then $g_{\text{cm}} = 28$ for all

the states in ~~the~~ up to
the $n=3$ shell are at
least needed, I'd guess.

So the number of R_{nl} states
needed is 6.

So you'd need a 6×6 matrix
with matrix elements

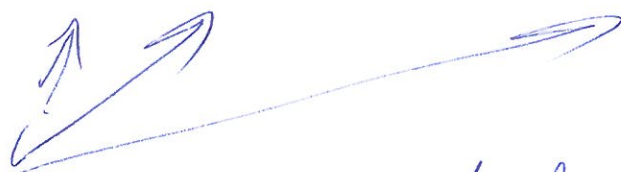
$$\langle R_i | H_r | R_j \rangle$$

7-286)

Step 2

Create the product
ground state
for ~~2~~ electrons

$$\Psi_{\text{pro}} = \Psi_1(1) \Psi_2(2') \dots \Psi_z(z')$$



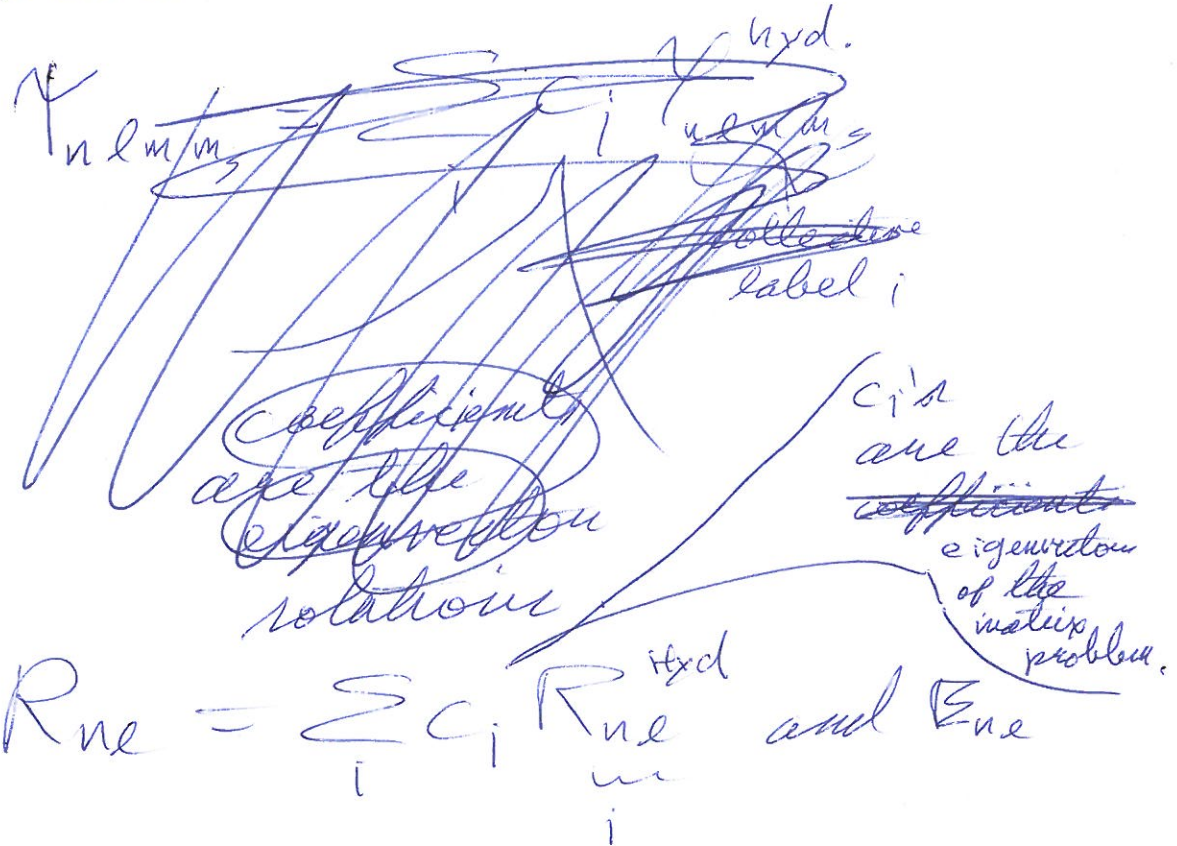
stands for
space spin
coordinates
of

all states must be distinct
or else the product
state cannot be
symmetrized for fermion.
zth electron

→ one chooses the lowest
energy states for ground
state.

↳ but there is some choice
because of degeneracy with
the m and m_s quantum
numbers.

So you solve
 the matrix and
 get the radial states R_{nl}
 up to n_l
 and construct
 the single particle
 states



$\Psi_i = \Psi_{nlm m_s} = R_{nl} Y_{lm} \chi_{m_s}$
 Now what?

So some freedom to choose. It doesn't matter which one choose since we will average - average the probability density anyway.

$$\Psi_{sym} = \frac{1}{\sqrt{Z!}} \begin{vmatrix} \psi_1(1') & \dots & \psi_1(1') \\ \psi_1(2') & & \vdots \\ \psi_1(3') & & \vdots \\ \vdots & & \vdots \\ \psi_1(z') & \dots & \psi_2(z') \end{vmatrix}$$

explicit Slater determinant construction of the ~~orthonormal~~ ~~state~~ symmetrized state.

What we need it for is the probability density for $Z-2$ electrons.

In real HF, we don't explicitly construct this.

Note this determinant is NOT trivial if Z is big.

Example $Z=21$

There will be $21!$ terms $\approx 5.10909422 \times 10^{19}$

- even in modern computers this is inverting on impossible.

5-288

$$P_1(\underline{r}_1) = \int |\Psi_{\text{sym}}|^2 \underbrace{d\underline{r}'_2 d\underline{r}'_3 \dots d\underline{r}'_N}_{d\underline{r}_2 d\underline{r}_3 \dots d\underline{r}_N}$$

Recall all cross terms vanish except those where

$$\Psi_i^*(\underline{r}_1) \Psi_j(\underline{r}_1)$$

is the only ~~summed over~~ factor with

$$i \neq j.$$

$$\int \Psi_i^*(\underline{r}_2) \Psi_j(\underline{r}_2) d\underline{r}_2$$

$$= \delta_{ij} \text{ recall.}$$

all spin sums including for particles 1 summed by spinors

$$\chi_i^\dagger \chi_i = \begin{cases} 1 \\ 0 \end{cases}$$

integrals over all ~~coordinates~~ ~~except~~ space coordinates except

$$\underline{r}_1$$

as we proved on p. 5-271

$$P_1(\underline{r}) = P_2(\underline{r}) = \dots = P_N(\underline{r})$$

identical particles.

(5-289)

The charge density for
($Z-1$) electrons is then

$$\rho_q(\underline{r}) = -e(Z-1)\rho(\underline{r})$$

$Z-1$ is needed
not Z .

- electrons may be identical to us, but each electron knows itself.
- It ~~may~~ does it exist in a superposition of position, but ~~it doesn't~~ the electron at one place doesn't feel the force of itself at another.

5-290

the Hydrogenic atom would be impossible to solve if this were not true.

~~From~~

$\rho_q(r)$ will NOT

Probably pretty close with all those ~~complete~~ full subshells with all spherical Harmonics.

have spherical symmetry in general.

— we want a spherical potential

So we $\rho_{\text{angle average}} = \int \rho(r, \theta, \phi) d\Omega$

then $\rho_q(r) = -e(z-1) \rho_{\text{angle averaged}}(r)$

From $\rho_q(r)$, we can with a tedious process find the electrical potential $\phi(r)$ for $z-1$ electrons.

Then our new
potential (i.e., potential
energy)

is

$$V(r) = -\frac{Z_0^2}{4\pi\epsilon_0 r} \quad \underbrace{-e\phi(r)}$$

from
nucleus
— a negative
term

overall
positive
since $\phi(r) < 0$
for the
cloud
of
negative
electrons.

So now
go back to step 1
replacing our
initial $V(r)$ with our
new $V(r)$
and then iterate until
convergence.

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i.e., until the single-particle states and energies stop changing to within some tolerance.

— So that is a heuristic HF

→ not the way it is actually done

But computationally it is arduous

→ and perhaps surprisingly the ~~anti~~ symmetrization is awful: e.g., $Z = 2!$

$$\approx 5 \times 10^{19}$$

all those terms which ~~are~~ each have complex ~~ster~~ functional behaviors.

Real HF avoids the problem of explicitly constructing the full ~~anti~~ symmetrized states.

it is almost impossible to imagine doing that now let alone in 1928 (ER-370) or so when Douglas Hartree (1897-1958) started calculating atoms with — pen and paper I guess.

He had a famous Ph.D. student Charlotte Fisker (1929 —) who was at Vanderbilt Univ. but somehow I failed to meet her when I was there — she was in the com. Sci department not the Phy. & Astr. one.

So there are simplifications

→ the biggie is NOT symmetrizing the product state.
of p. 5-286

→ The product state already is partially symmetrized in that it obeys the Pauli-exclusion principle for the stationary state but not

5-294

the space-spin Pauli exclusion principle.

→ the full symmetrization
it seems just creates
minor modifications
in the probability density
(ER-332)
and these leave average
charge density
little affected.

Maybe
some
~~strategy~~
good
proof of this

→ and in HF we
angle average anyway.

~~Leaves~~

So we don't symmetrize
the product state
reducing $Z!$ terms
to 1 term.

often
called
the Pauli
exclusion
principle
but not
symmetrization

But only Pauli exclusion
principle in one
sense of the term

and this is what ^{starting}

Hartree did in 1928.

So no full symmetrization in the Hartree method

(and never got the Nobel prize)

probably with a lot of other simplifications.

(he did eventually meet up with ENIAC)

Both H & HF (real one, not my homework one)

methods don't meet the accuracy of modern multi-body method,

but they probably still get use — I don't really know.

HF is a bit more accurate than H method, but much more painful

But they did give the QM understanding of ground state structure of atoms.

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— they give the electron configuration

↳ the set of single-particle states that make up the atom ground state

They make it up in an approximate sense.

— One usually says there is one electron in each of these states — but really each electron is really in a ~~superposition~~ superposition of all of them — but that's just too fussy to say

and it is true that the probability of collapsing the wave function and finding 2 electrons in one single particle state is zero.

Correct
superposition
think,

I think this is the correct interpretation of the fact that ~~Φ~~

for example $\Psi_a(v_1) \Psi_a(v_2)$

just isn't in the symmetrized wave function.

↳ but maybe other argument is needed. No, it seems right.

