12) As discussed on pp. ip 13-15 above, a fruitful attack on the <u>N-electron problem</u>, viz:

$$\mathcal{H}\Psi = E\Psi, \quad \text{w/} \quad \Psi = \Psi(1,2,...,N) \text{ and } \mathcal{H} \text{ the } N\text{-electron Hamiltonian, i.e....}$$

$$\rightarrow \mathcal{H}(1,2,...,N) = \sum_{k=1}^{N}\left[-\left(\frac{\hbar^2}{2m}\right)\nabla_k^2 - \frac{Ze^2}{r_k}\right] + \sum_{k>j}^{N}\sum_{j=1}^{N}(e^2/r_{jk})$$

$\mathbf{r}_k = k^{th}$ electron position,
$r_{jk} = |\mathbf{r}_j - \mathbf{r}_k| =$ separation of electrons j & k,
$\nabla_k = \partial/\partial \mathbf{r}_k$;   (44)

Coulomb attraction   electron repulsion

was to split the problem into <u>N one-electron problems</u>: $\mathcal{H} = \sum_{k=1}^{N} H_k$, $\Psi = \phi(1)\phi(2)\cdots\phi(N)$,

so: $H_k\phi(k) = \mathcal{E}\phi(k)$, $k = 1$ to N, w/ $H_k = -(\hbar^2/2m)\nabla_k^2 + U(k)$. The chief prob-

lem in this attack is to find "reasonable" forms for the <u>one-electron potentials U(k)</u>.

We have seen how the Thomas-Fermi approx^n <u>fixes</u> the U(k) by a semi-classical

(statistical) approach, and yields acceptable eigenenergies for heavy atoms (Z >> 1).

Now we look at a different method of getting at the U(k), due to <u>Hartree</u>,[*]

which allows the U(k) to be <u>adjusted</u> to fit the actual eigenenergies to an arbi-

trary degree of accuracy. Hartree's method is computational, not calculational.

<u>1:</u> Hartree's key idea was this: the potential U(k) in which the kth electron moves

can be calculated reasonably by including the nuclear potential $-Ze^2/r_k$ plus a

central field generated by all electron <u>distributions</u> for $j \neq k$. That is, if electron

#j is in the eigenstate $\phi_{n_j}(\mathbf{r}_j)$, then its charge distribution is $-e|\phi_{n_j}(\mathbf{r}_j)|^2$,

and the interaction between it and the kth electron -- <u>considered as a point</u> -- is:

$$\rightarrow W_k(\mathbf{r}_k) = \int_\infty d^3x_j |\phi_{n_j}(\mathbf{r}_j)|^2 \frac{e^2}{r_{jk}}$$

potential for k^{th} point electron in QM distribution of jth electron.   (45)

Summed over all electrons with $j \neq k$, this should (approximately) account for

the e-e repulsion terms acting on electron #k. Thus, Hartree wrote the potential:

$$U(k) = -(Ze^2/r_k) + \sum_{j\neq k}^{N}\int_\infty d^3x_j |\phi_{n_j}(\mathbf{r}_j)|^2 \frac{e^2}{r_{jk}},$$ (46)

and took the $\mathcal{H}(N\text{-electron}) \rightarrow \sum_k H_k(\text{one-electron})$ split to be...

[*] D. R. Hartree, Proc. Cambridge Phil. Soc. <u>24</u>, 111 (1928).

The Hartree "one-electron" equations. Iterative (numerical) solution.   ip 121

H'TREE 2
(47)

$$\rightarrow \mathscr{H}(1,2,\dots,N) = \sum_{k=1}^{N} H_k \; , \; \text{w/} \; H_k = -(\hbar^2/2m)\nabla_k^2 + U(k).$$

Neglecting exchange symmetry for the time being, we assume simple product states of the form (as above): $\underline{\Psi(1,2,\dots,N) = \phi_{n_1}(\vec{v}_1)\phi_{n_2}(\vec{v}_2)\cdots\phi_{n_N}(\vec{v}_N)}$. Then the N-electron problem $\mathscr{H}\Psi = E\Psi$ splits into N one-electron problems of the form:

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla_k^2 - \frac{Ze^2}{r_k} + \sum_{j\neq k}\int_\infty |\phi_{n_j}(\vec{v}_j)|^2 \frac{e^2}{r_{jk}} d^3x_j\right]\phi_{n_k}(\vec{v}_k) = \mathcal{E}_{n_k}\phi_{n_k}(\vec{v}_k)} \; , \quad (48)$$

Coulomb attraction   e-e repulsion

HARTREE'S EQTN

with total system energy : $E = \sum_{k=1}^{N} \mathcal{E}_{n_k}$.

The "splitting" is more apparent than real : $\phi(k)$ is <u>coupled</u> to all the other $\phi(j\neq k)$. In fact what we've done is to convert $\mathscr{H}\Psi = E\Psi$ into <u>N coupled</u> <u>non-linear integro-differential eqtns for the single electron eigenfcns ϕ_{n_k}</u> <u>and eigenvalues</u> $\mathcal{E}_{n_k}$. Is this progress? Clearly Eq.(48) cannot be solved "by hand"; numerical methods must be used. Hartree hung tough (ca.1930).

<u>2.</u> The numerical attack on (48) is straightforward in principle. <u>Iterate as follows</u>:

a) Choose a "reasonable" set of $\{\phi_{n_\ell}(\vec{v}_\ell)\}$, $\ell=1$ to N, and calculate $U(k)$ as it appears in Eq.(46), and in H_k in (48) above. Then, numerically solve (48), i.e. $H_k\phi'_{n_k} = \mathcal{E}_{n_k}\phi'_{n_k}$, to produce a <u>new</u> set of eigenfcns $\{\phi'_{n_\ell}(\vec{v}_\ell)\}$. If the trial fcns $\{\phi_{n_\ell}(\vec{v}_\ell)\}$ were a reasonably good guess, then the $\{\phi'_{n_\ell}(\vec{v}_\ell)\}$ will differ only "slightly" from the original trial fcns.

b) Now use the <u>new</u> set $\{\phi'_{n_\ell}(\vec{v}_\ell)\}$ to calculate an <u>improved</u> version $U'(k)$ of the one-electron potentials. Numerically solve : $H'_k\phi''_{n_k} = \mathcal{E}'_{n_k}\phi''_{n_k}$, to give a <u>newer</u> set of eigenfcns $\{\phi''_{n_\ell}(\vec{v}_\ell)\}$. These <u>newer</u> $\{\phi''_{n_\ell}(\vec{v}_\ell)\}$ can be used to find an <u>even</u> <u>better</u> version $U''(k)$ of the one-electron potential. Etc.

c) The iteration is repeated: $\{\phi(\ell)\} \rightarrow \{\phi'(\ell)\} \rightarrow \{\phi''(\ell)\} \rightarrow \cdots \Rightarrow U(k) \rightarrow U'(k) \rightarrow$

Comments on Hartree's Eqtn. Variational Aspects. ip 22

H'TREE 3

$U''(k) \to \cdots$, until there is only a <u>negligible difference</u> (a judgement call !) between an input $U^{(\lambda)}(k)$ and an output $U^{(\lambda+1)}(k)$, or between the eigenenergy $\mathcal{E}_{n_k}^{(\lambda)}$ after λ iterations and its improved version $\mathcal{E}_{n_k}^{(\lambda+1)}$. At this point, one <u>stops</u> the iteration, and declares : <u>(1)</u> $U^{(\lambda)}(k)$ is a "<u>self-consistent</u>" central potential for the $k^{\underline{th}}$ electron [i.e., it is consistent with the set $\{\phi_{n_\ell}^{(\lambda-1)}(\vec{r}_\ell)\}$ that generated it], <u>(2)</u> the eigenenergies $\mathcal{E}_{n_k}^{(\lambda)}$ & eigenfcns $\phi_{n_k}^{(\lambda)}$ after λ iterations are "good" enough to be compiled.

d) Hartree's method allows for <u>readjusting</u> $U(k)$ at each iteration (in contrast to Thomas-Fermi) and should work equally well for $N=1$ or $N \to \infty$ electrons. While there is the question of whether the iteration procedure actually <u>converges</u> to anything definite (it does -- in a variational sense), the method does provide a comprehensive -- if tedious -- way of dealing systematically with <u>all</u> atoms & ions, and (in modified form) molecules, surface states, etc.

<u>3.</u> We will not deal with Hartree's method in great detail, but we will remark on the following points...

A Connexion of Hartree's Equation, Eq. (48), with a variational principle.

B Interpretation of the energy $E = \sum_{k=1}^{N} \mathcal{E}_{n_k}$ in Eq. (48).

C Application of Hartree's method to a two-electron atom [e.g. $He(1^1S_0)$].

D Corrections due to imposing electron exchange symmetry (Hartree-Fock Eq.).

A Hartree's Eqtn, viz. Eq. (48) : $H_k \phi_{n_k}(\vec{r}_k) = \mathcal{E}_{n_k} \phi_{n_k}(\vec{r}_k)$, with :

$$\to H_k = -(\hbar^2/2m)\nabla_k^2 - (Ze^2/r_k) + \sum_{j \neq k} \int_\infty |\phi_{n_j}(\vec{r}_j)|^2 \frac{e^2}{r_{jk}} d^3x_j , \qquad (49)$$

ensures that the variation : $\underline{\delta \langle \Psi | \mathcal{H} | \Psi \rangle = 0}$, for the N-electron problem, where $\mathcal{H}$ is the full Hamiltonian [Eq. (44)], and $\Psi = \phi(1)\phi(2)\cdots\phi(N)$ is the product state we have used [e.g. above Eq. (48)]. For, we calculate...

Comments on Hartree's Eqtn: Variational Aspects (cont'd).

p 23

H'TREE 4

$$\langle\Psi|\mathcal{H}|\Psi\rangle = \int_\infty d^3x_N \cdots \int_\infty d^3x_1 [\Psi^* \mathcal{H} \Psi]$$

$$= \sum_{k=1}^{N} \int_\infty d^3x_k \, \phi_{n_k}^*(\vec{r}_k)\left[-\frac{\hbar^2}{2m}\nabla_k^2 - \frac{Ze^2}{r_k}\right]\phi_{n_k}(\vec{r}_k) + \tag{50}$$

$$+ \sum_{k>j}^{N}\sum_{j=1}^{N}\int d^3x_j \int_\infty d^3x_k \, \phi_{n_j}^*(\vec{r}_j)\phi_{n_k}^*(\vec{r}_k)\left[\frac{e^2}{r_{jk}}\right]\phi_{n_j}(\vec{r}_j)\phi_{n_k}(\vec{r}_k).$$

This assumes the $\phi_{n_k}(\vec{r}_k)$ are orthonormal.[*] The optimum Ψ which ensures that $\delta\langle\Psi|\mathcal{H}|\Psi\rangle = 0$ is obtained by varying each of the single-electron wavefcns ϕ_{n_k} **separately**, in order to minimize the energy $\langle\Psi|\mathcal{H}|\Psi\rangle$. Now the only variation of $\langle\Psi|\mathcal{H}|\Psi\rangle$ on a particular ϕ_{n_k} is through those terms in (50) which involve ϕ_{n_k} **explicitly**, viz.

$$\rightarrow \int_\infty d^3x_k \, \phi_{n_k}^*(\vec{r}_k)\left[-\frac{\hbar^2}{2m}\nabla_k^2 - \frac{Ze^2}{r_k}\right]\phi_{n_k}(\vec{r}_k) + \tag{51}$$

$$+ \int_\infty d^3x_k \, \phi_{n_k}^*(\vec{r}_k)\left[\sum_{j\neq k}^{N}\int_\infty d^3x_j |\phi_{n_j}(\vec{r}_j)|^2 \frac{e^2}{r_{jk}}\right]\phi_{n_k}(\vec{r}_k) = \underline{\langle\phi_{n_k}|H_k|\phi_{n_k}\rangle}.$$

In other words, in Hartree's formulation: $\underline{\langle\Psi|\mathcal{H}|\Psi\rangle = \sum_{k=1}^{N}\langle\phi_{n_k}|H_k|\phi_{n_k}\rangle}$. Then, since ϕ_{n_k} is an eigenfcn of H_k in Eq.(48), i.e. $H_k\phi_{n_k} = \mathcal{E}_{n_k}\phi_{n_k}$, we have: $\langle\phi_{n_k}|H_k|\phi_{n_k}\rangle = \mathcal{E}_{n_k} = $ cnst, so: $\underline{\delta\langle\Psi|\mathcal{H}|\psi\rangle = \delta(\sum_k \mathcal{E}_{n_k}) = 0.}$ As advertised, Hartree's Eqtn.(48) ensures that $\langle\Psi|\mathcal{H}|\Psi\rangle$ is stationary.

NOTE: this connexion with a variational principle suggests (but does not prove) that successive choices of the set $\{\phi_{n_k}(\vec{r}_k)\} \rightarrow \{\phi'_{n_k}(\vec{r}_k)\} \rightarrow$ etc. will converge(from above) on the true eigenenergies $\{\mathcal{E}_{n_k}\}$. This will certainly be true in the system ground state (by the Rule of Ritz), and it can be made to happen in excited system states by proper choice of $\Psi(\text{exc.}) \perp \Psi(\text{gnd})$.

B By writing the total Ham^n: $\mathcal{H} = \sum_k H_k$, as in (47), we get the total system energy: $E = \sum_k \mathcal{E}_{n_k}$ $(^w\!/\langle\phi_{n_k}|H_k|\phi_{n_k}\rangle)$, per Eq.(48). If, more reasonably,

[*] This is always true for electrons (fermions): no two electrons can be in same state.