$$\frac{\mathrm{d}^2(rV(r))}{\mathrm{d}r^2} = -\frac{r\rho(r)}{\epsilon_0} \tag{1}$$

$$V_{ee}^{exch}(r) = -\frac{3e}{4\pi\epsilon_0}\left(\frac{3\rho(r)}{8\pi e}\right)^{1/3} \tag{2}$$

Each triplet (n, ℓ, m) can be occupied by zero, one or two electrons. The total charge distribution is then the sum of the contributions from each electron:

$$\rho(r,\theta,\varphi) = \sum_{n=1}^{N}\sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell} g_{n\ell m}\rho_{n\ell m}(r,\theta,\varphi) \tag{3}$$

where $g_{n\ell m}$ takes the value zero, one or two which is the number of electrons occupying the (n, ℓ, m) state, and

$$\begin{aligned}\rho_{n\ell m}(r,\theta,\varphi) &= -e\left|\psi_{n\ell m}(r,\theta,\varphi)\right|^2 \\ &= -eR_{n\ell}^2(r)\left|Y_{\ell m}(\theta,\varphi)\right|^2.\end{aligned} \tag{4}$$

We'll replace the spherical harmonic with its average

$$\begin{aligned}&\left|Y_{\ell m}(\theta,\varphi)\right|^2 \\ &\to \frac{1}{4\pi}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\left|Y_{\ell m}(\theta,\varphi)\right|^2 r^2\sin\theta\mathrm{d}\theta\mathrm{d}\varphi = \frac{1}{4\pi}\end{aligned} \tag{5}$$

so that $\rho_{n\ell m} \to eR_{n\ell}^2/4\pi$. We notice that different m give the same charge distribution for fixed n and ℓ, i.e. $\rho_{n\ell m} = \rho_{n\ell m'}$. Thus, we define $g_{n\ell}$ to be the number electrons being in a state with principal and azimuthal quantum number (n, ℓ) so that we can write

$$\rho(r) = -\frac{e}{4\pi}\sum_{n=1}^{N}\sum_{\ell=0}^{n-1} g_{n\ell}R_{n\ell}^2(r) \tag{6}$$

where $\rho(r)$ is to be understood as the approximation of $\rho(r, \theta, \varphi)$ in which we have averaged over the spherical harmonics.

The radial functions are solutions to

$$\begin{aligned}&-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\left(rR_{n\ell}\right)}{\mathrm{d}r^2} \\ &+\left[\frac{\hbar^2\ell(\ell+1)}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} - eV_{ee}(r)\right](rR_{n\ell}) = E(rR_{n\ell})\end{aligned} \tag{7}$$

where $P_{n\ell} = rR_{n\ell}$ is the reduced radial wavefunction and $V_{ee}(r)$ is a yet unknown electric potential.

1. Set $V_{ee} = 0$.
2. Calculate $\rho(r)$ by solving (7) for the different n and ℓ and calculating the sum in (6).
3. Use $\rho(r)$ to solve Poisson's equation (1) and obtain from it the potential V_{ee}^{dir}.
4. Calculate the exchange potential V_{ee}^{exch} using equation (2) and set $V_{ee} = V_{ee}^{dir} + V_{ee}^{exch}$.
5. Repeat from 2. until convergence of energy $E_{n\ell}$.

Notes

With $V_{ee} = 0$, we get a numerical solution on $(0, 1)$, $u(\xi)$, where $\xi = r/a_0D$. Then,

$$rR_{n\ell}(r) = \frac{u_{n\ell}(r/a_0D)}{\sqrt{a_0D}} \tag{8}$$

The distribution is then

$$\rho(r) = -e\sum_{n,\ell} g_{n\ell}R_{n\ell}^2. \tag{9}$$

Insert this into

$$\begin{aligned}0 &= \frac{\mathrm{d}(rV_{ee}^{dir})}{\mathrm{d}r^2} + r\rho(r)/\epsilon_0 \\ &= \frac{1}{(a_0D)^2}\frac{\mathrm{d}^2(\alpha\lambda)}{\mathrm{d}\xi^2} - \frac{e}{\epsilon_0}\sum_{n,\ell} g_{n\ell}\frac{u_{n\ell}^2(\xi)}{(a_0D)^2\xi}\end{aligned} \tag{10}$$

so set $\alpha = -e/\epsilon_0$ such that

$$\frac{\mathrm{d}^2\lambda}{\mathrm{d}\xi^2} + \sum_{n,\ell} g_{n\ell}\frac{u_{n\ell}^2(\xi)}{\xi} = 0 \tag{11}$$

Which becomes

$$\lambda'' + \xi\sigma(\xi) = 0 \tag{12}$$

where

$$\sigma(\xi) = \sum_{n,\ell} g_{n\ell}\frac{u_{n\ell}^2}{\xi^2} \tag{13}$$

The boundary conditions are $\lambda(0) = 0$ and $\lambda(1) = N/4\pi$ (check). From this we have

$$rV_{ee}^{dir} = \alpha\lambda(r/a_0D) \tag{14}$$

or

$$V_{ee}(r) = -\frac{e}{\epsilon_0 r}\lambda(r/a_0D) \tag{15}$$

which should be negative.

The new radial wavefunction is then given by

$$\begin{aligned}&-\beta^2\left[u'' - \frac{\ell(\ell+1)}{\xi^2}u + \frac{2}{\beta}\left(\frac{1}{\xi} - \frac{4\pi\lambda(\xi)}{Z\xi}\right)u\right] \\ &= E'u\end{aligned} \tag{16}$$

Defining $u_{n\ell}$ to be the numerical solution to $rR_{n\ell}$ and making the substitutions

$$\xi = r/a_0, \quad E' = E/(\hbar^2/a_0^2 m), \tag{17}$$

the radial function becomes

$$-\frac{1}{2}u'' + \left[\frac{\ell(\ell+1)}{2\xi^2} - \frac{mea_0^2}{\hbar^2}(\varphi_C + \varphi_{ee})\right] u = E'u \tag{18}$$

The electric potential φ_{ee} is the solution to the Poisson equation:

$$(r\varphi_{ee})'' + r\rho(r)/\epsilon_0 = 0 \tag{19}$$

Now, we define

$$\hat{\varphi}_{ee} = \frac{\varphi_{ee}}{\hbar^2/(ma_0^2 e)} \tag{20}$$

and set $\sigma = \rho/B$ where B is to be determined. Making these substituions, and setting $r = a_0\xi$, we get

$$(\xi\hat{\varphi}_{ee})'' + \frac{4\pi a_0^3}{e}B\sigma(\xi)\xi = 0 \tag{21}$$

So if we let $B = e/(4\pi a_0^3)$, we get

$$(\xi\hat{\varphi}_{ee})'' + \xi\sigma(\xi) = 0 \tag{22}$$

The Coulomb part is always the same:

$$\hat{\varphi}_C = \frac{\varphi_C}{\hbar^2/(ma_0^2 e)} = \frac{Z}{\xi} \tag{23}$$