1)

3(B):

HARTREE POTENTIAL AND SUGGESTED NUMERICAL CROSS CHECKS

Start with the definitions:

$$\underline{E} = -\underline{\nabla}\phi + \underline{\omega}\phi \quad -(1)$$

$$\underline{\nabla}\cdot\underline{E} = \rho/\epsilon_0 \quad -(2)$$

then:

$$\nabla^2\phi - \underline{\nabla}\cdot(\underline{\omega}\phi) = -\rho/\epsilon_0 \quad -(3)$$

i.e.

$$\nabla^2\phi - \underline{\omega}\cdot\underline{\nabla}\phi - (\underline{\nabla}\cdot\underline{\omega})\phi = -\rho/\epsilon_0 \quad -(4)$$

a) Define:

$$\underline{\omega} = -\frac{1}{Z}\underline{k} \quad -(5)$$

to obtain:

$$\nabla^2\phi + \frac{1}{Z}\underline{\nabla}\phi\cdot\underline{k} - \frac{1}{Z^2}\phi = -\rho/\epsilon_0 \quad -(6)$$

Let:

$$\rho = \rho_0\cos(\underline{\kappa}\cdot\underline{r}). \quad -(6a)$$

In one dimension:

$$\boxed{\frac{\partial^2\phi}{\partial Z^2} + \frac{1}{Z}\frac{\partial\phi}{\partial Z} - \frac{1}{Z^2}\phi = -\frac{\rho_0}{\epsilon_0}\cos(\kappa Z)} \quad -(6b)$$

Solve this numerically for ϕ.

a)

Eq. (6b) is equivalent to:

$$\frac{\partial^2 \phi}{\partial Z^2} + k^2 \phi = \frac{f_0}{\epsilon_0} \text{Real}\left(e^{2ikz} \cos\left(e^{ikz}\right)\right) \quad -(6$$

Solve eq. (6c) for ϕ and the solution should be the same as for eq. (6b). The numerical solution of eq. (6b) cross-checks the numerical solution of eq (6c).

b) Define:

$$\underline{\omega} = \frac{1}{Z} \underline{k} \quad -(7)$$

to obtain:

$$\frac{\partial^2 \phi}{\partial Z^2} - \frac{1}{Z} \frac{\partial \phi}{\partial Z} + \frac{1}{Z^2} \phi = -\frac{f_0}{\epsilon_0} \cos(kZ). \quad -(8)$$

Solve this numerically for ϕ. Determine whether there is any difference between the numerical solutions of eq. (6b) and eq. (8). The latter is equivalent to:

$$\frac{\partial^2 \phi}{\partial Z^2} - k^2 \phi = \frac{f_0}{\epsilon_0} \text{Real}\left(e^{2ikz} \cos\left(e^{ikz}\right)\right) \quad -(8a)$$

Check that the numerical solutions of eqs. (8) and (8a) are the same.

When these checks have been completed the potential ϕ (in volts) can be used to build up the Hartree term for density functional code. In three dimensions the Hartree term is defined in density functional code through the Schrödinger equation:

$$H\phi = (T + V + U)\phi. \quad -(9)$$

The Hartree term describes the electron - electron Coulomb interaction. In S.I. units it is the energy:

$$V = \frac{1}{4\pi\epsilon_0}\int \frac{e^2 n_s(\underline{r})}{|\underline{r} - \underline{r}'|} d^3r'. \quad -(10)$$

Units Checks

a) $4\pi\epsilon_0 = 1.112650 \times 10^{-10} J^{-1} C^2 m^{-1}$

$V = J C^{-2} m \, C^2 m^2 m^{-3} = J$ ✓

The number density $n_s(\underline{r})$ must have the units of m^{-3}, the energy V has the units of joules.

b) The units of ϕ are volts $= J C^{-1}$

so $e\phi$ = joules (J) ✓

So the Hartree potential is:

$$V = e\phi \quad -(11)$$

Therefore ϕ from the 3-D equivalents of eqs. (6b) etc. may be expressed as:

$$\boxed{\phi_H = \frac{e}{4\pi\epsilon_0}\int n_s(\underline{r})\, d^3r'} \quad -(12)$$

At resonance the $n_s(\underline{r})$ is greatly amplified. This means that the electron - electron repulsion is greatly amplified.

The 3-D equations needed to build up eq. (12) are dependent on the sign chosen for the spin connection. The equivalent of eq. (6b) in 3-D is:

$$\nabla^2\phi + \frac{(\underline{r}-\underline{r}_i)}{|\underline{r}-\underline{r}_i|^2}\cdot\underline{\nabla}\phi - \frac{1}{|\underline{r}-\underline{r}_i|^2}\phi = -\frac{1}{\epsilon_0}\sum_{i=1}^{n} e_i\,\delta(\underline{r}-\underline{r}_i) \quad -(13)$$

and the equivalent of eq. (8) in 3-D is:

$$\nabla^2\phi - \frac{(\underline{r}-\underline{r}_i)}{|\underline{r}-\underline{r}_i|^2}\cdot\underline{\nabla}\phi + \frac{1}{|\underline{r}-\underline{r}_i|^2}\phi = -\frac{1}{\epsilon_0}\sum_{i=1}^{n} e_i\,\delta(\underline{r}-\underline{r}_i) \quad -(14)$$

The experience gained from solving eqs. (6b) and (8) numerically is used to solve eqs. (13) & (14) numerically. Finally ϕ is expressed in terms of $n_s(\underline{r})$ using eq. (12), ϕ having been obtained from