Nonlinear Formulation of DFT

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1 Introduction

In this text, we explore the mathematical structure of the DFT self-consistency cycle and show that it is nothing else than a standard nonlinear problem, only the Jacobian matrix is dense, so we need to use nonlinear solvers that can handle that.

2 Problem

The task is to find such a charge density n, so that all the equations below hold (e.g. are self-consistent):

$$V = -\frac{Z}{r} + V_H + V_{xc}$$

$$\left(-\nabla^2 + V\right)\phi_m = \epsilon_m\phi_m, \qquad m = 1, 2, \dots, 4$$

$$n = \sum_{m=1}^{4} \phi_m^2$$

$$V_{xc} = f(n)$$

$$\nabla^2 V_H = n$$

3 Reformulation

Let's write everything in terms of $\phi_m(x)$ explicitly:

$$n(x) = \sum_{m=1}^{4} \phi_m^2(x)$$

$$V_{xc}(x) = f(n(x)) = f\left(\sum_{m=1}^{4} \phi_m^2(x)\right)$$

$$V_H(x) = \tfrac{1}{2}\int_\Omega \frac{n(x')}{|x'-x|}\d{x}' = \tfrac{1}{2}\int_\Omega \frac{\sum_{m=1}^{4}\phi_m^2(x')}{|x'-x|}\d{x}'$$

$$V(x) = -\frac{Z}{r} + V_H(x) + V_{xc}(x) =$$

$$= -\frac{Z}{r} + \tfrac{1}{2}\int_\Omega \frac{\sum_{m=1}^{4}\phi_m^2(x')}{|x'-x|}\d{x}' + f\left(\sum_{m=1}^{4} \phi_m^2(x)\right)$$

Now we can write everything as just one (nonlinear) equation:

$$\left(-\nabla^2 - \frac{Z}{r} + \tfrac{1}{2}\int_\Omega \frac{\sum_{m=1}^{4}\phi_m^2(x')}{|x'-x|}\d{x}' + f\left(\sum_{m=1}^{4} \phi_m^2(x)\right)\right)\phi_n = \epsilon_n\phi_n, \qquad n = 1, 2, \ldots, 4$$

4 FE Discretization

The correspondig discrete problem has the form

$$\int_\Omega \nabla\phi_n(x)\cdot\nabla v_i(x) + \left[-\frac{Z}{r} + \tfrac{1}{2}\int_\Omega \frac{\sum_{m=1}^{4}\phi_m^2(x')}{|x'-x|}\d{x}' + f\left(\sum_{m=1}^{4} \phi_m^2(x)\right)\right]\phi_n(x)v_i(x)\d{x} =$$

$$= \int_\Omega \epsilon_n\phi_n(x)v_i(x)\d{x}, \qquad n = 1, 2, \ldots, 4; \quad i = 1, 2, \ldots, N$$

where

$$\phi_n = \phi_n(\mathbf{Y}^{(n)}) = \sum_{j=1}^{N} y_j^{(n)} v_j(x)$$

Here $\mathbf{Y}^{(n)} = (y_1^{(n)}, y_2^{(n)}, \ldots, y_N^{(n)})^T$ is the vector of unknown coefficients for the nth wavefunction $\phi_n(x)$. Our equation can then be written in the compact form

$$\mathbf{F}(\mathbf{Y}^{(n)}) = \mathbf{0}, \qquad n = 1, 2, \ldots, 4$$

where $\mathbf{F} = (F_1, F_2, \ldots, F_N)^T$ with

$$F_i(\mathbf{Y}^{(n)}) = \int_\Omega \nabla\phi_n(x)\cdot\nabla v_i(x) + \left[-\frac{Z}{r} + \tfrac{1}{2}\int_\Omega \frac{\sum_{m=1}^{4}\phi_m^2(x')}{|x'-x|}\d{x}' + f\left(\sum_{m=1}^{4} \phi_m^2(x)\right)\right]\phi_n(x)v_i(x)\d{x} -$$

$$- \int_\Omega \epsilon_n\phi_n(x)v_i(x)\d{x}$$

5 Jacobian

The Jacobi matrix has the elements:

$$J_{ik} = \frac{\partial F_i}{\partial y_k^{(s)}}$$

The only possible dense term is:

$$\frac{\partial}{\partial y_k^{(s)}} \int_\Omega \int_\Omega \frac{\sum_{m=1}^4 \phi_m^2(x')}{|x'-x|} \underset{\cdot}{\mathrm{x}}' \, \phi_n(x) v_i(x) \underset{\cdot}{\mathrm{x}} =$$

$$= \frac{\partial}{\partial y_k^{(s)}} \int_\Omega \int_\Omega \frac{\sum_{m=1}^4 \left(\sum_{j=1}^N y_j^{(m)} v_j(x')\right)^2}{|x'-x|} \underset{\cdot}{\mathrm{x}}' \left(\sum_{j=1}^N y_j^{(n)} v_j(x) \right) v_i(x) \underset{\cdot}{\mathrm{x}} =$$

$$= \int_\Omega \int_\Omega \frac{2\left(\sum_{j=1}^N y_j^{(s)} v_j(x')\right) v_k(x')}{|x'-x|} \underset{\cdot}{\mathrm{x}}' \left(\sum_{j=1}^N y_j^{(n)} v_j(x) \right) v_i(x) \underset{\cdot}{\mathrm{x}} +$$

$$+ \int_\Omega \int_\Omega \frac{\sum_{m=1}^4 \left(\sum_{j=1}^N y_j^{(m)} v_j(x')\right)^2}{|x'-x|} \underset{\cdot}{\mathrm{x}}' \, \delta_{ns} v_k(x) v_i(x) \underset{\cdot}{\mathrm{x}}$$

Now we can see that we have in there the following term:

$$\int_\Omega \int_\Omega \frac{v_k(x') v_i(x)}{|x'-x|} \underset{\cdot}{\mathrm{x}}' \underset{\cdot}{\mathrm{x}}$$

which is dense in (ki), as can be easily seen be fixing i and writing

$$\int_\Omega \int_\Omega \frac{v_k(x')}{|x'-x|} \underset{\cdot}{\mathrm{x}}' v_i(x) \underset{\cdot}{\mathrm{x}}$$

so for each k there is some contribution from the integral $\int_\Omega \frac{v_k(x')}{|x'-x|} \underset{\cdot}{\mathrm{x}}'$ for such x where $v_i(x)$ is nonzero, thus making the Jacobian J_{ik} dense.