How to fit the Fermi-Amaldi model

Shu-Yang Ye

University of British Columbia

Fermi-Amaldi Model

The Fermi-Amaldi term $E_x^{FA}[n]$,

$$E_x^{FA} = -\frac{1}{N} E_J \tag{1}$$

$$v_x^{FA} = -\frac{1}{N} v_J \tag{2}$$

$$E_J[n] = -\frac{1}{2} \int \int \frac{n(\mathrm{r}) n(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|} d\mathrm{r} d\mathrm{r}' \tag{3}$$

$$v_J[n] = -\int \frac{n(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|} d\mathrm{r}' \tag{4}$$

where N is the total electron number of the system.

Our Idea

Hybrid the Fermi-Amaldi term with some well-known XC functionals.

$$v_{\mathrm{xc}}^{\mathrm{exact}} \approx a_0 v_{\mathrm{xc}}^{\mathrm{other}} + a_1 v_{\mathrm{x}}^{\mathrm{FA}} \tag{5}$$

Here, "other" can be LDA, GGA or any existed functionals. a_0 and a_1 are the unknown coefficients to be fitted.

Our Idea

Let's be more specific, "other" = LDA.

$$v_{xc}^{exact} \approx a_0 v_x^{slater} + a_1 v_c^{vwn} + a_2 v_x^{FA} \tag{6}$$

Now, our question is how to fit the coefficient? A set of parameters can yield the best total energy, atomization energy, ionization energy, proton affinity, etc.

The Self-Consistent Minimization

The true global minimization can be found by doing all the calculations self-consistently.
Recall the Kohn-Sham equation,

$$\left[-\frac{1}{2}\nabla^2 + v(\mathrm{r}) + \int d\mathrm{r}' \frac{n(\mathrm{r}')}{|\mathrm{r}' - \mathrm{r}|} + v_{\mathrm{xc}}(\mathrm{r}; n)\right] \phi_\alpha(\mathrm{r}) = \epsilon_\alpha \phi_\alpha(\mathrm{r}) \tag{7}$$

$$n(\mathrm{r}) = \sum_{\alpha}^{occ.} |\phi_\alpha(\mathrm{r})|^2 \tag{8}$$

$$\begin{aligned} E = &\int d\mathrm{r}\tau(\mathrm{r}) + \int d\mathrm{r} n(\mathrm{r}) v(\mathrm{r}) \\ &+ \frac{1}{2}\int d\mathrm{r} \int d\mathrm{r}' \frac{n(\mathrm{r}) n(\mathrm{r}')}{|\mathrm{r}' - \mathrm{r}|} + E_{\mathrm{xc}}[n] \end{aligned} \tag{9}$$

The Loss Function

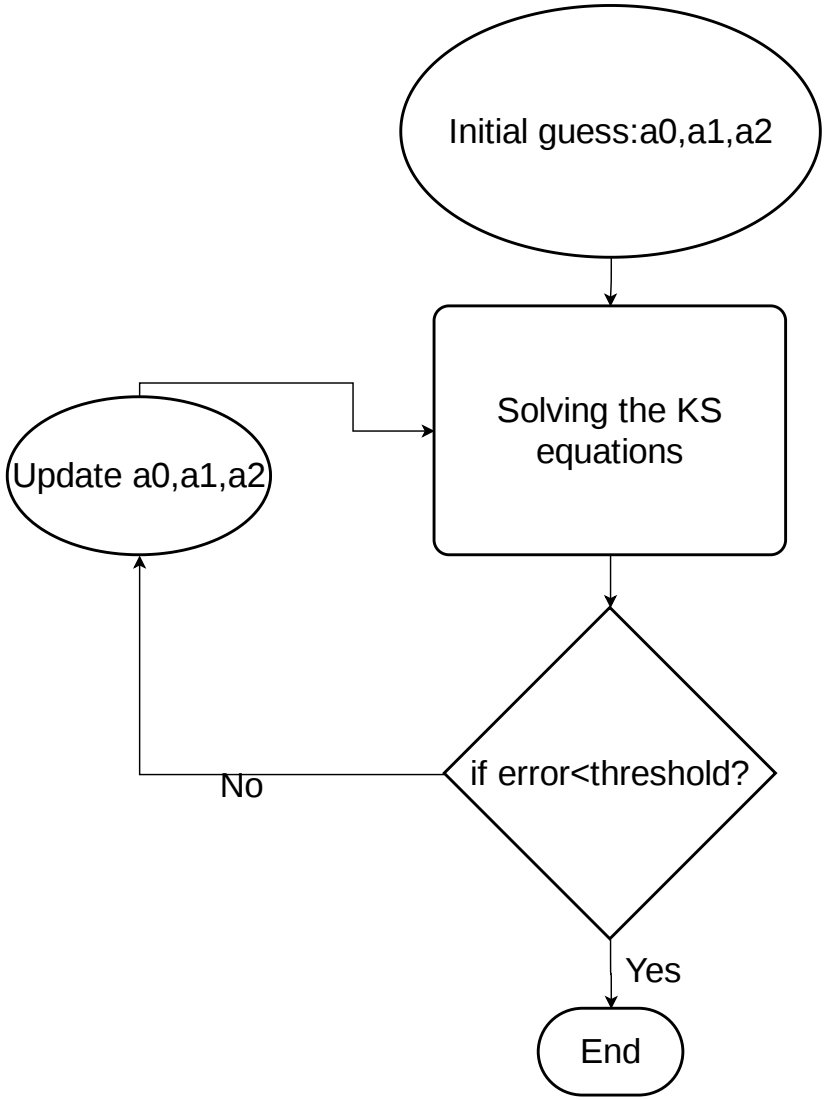
Take total energy as an example.

$$\hat{E}_{\text{tot}}^{a_0,a_1,a_2} = T + V_{\text{ext}} + V_{nn} + E_J + E_{\text{XC}} \tag{10}$$

Define the loss function $f(a_0, a_1, a_2)$ as

$$f(a_0, a_1, a_2) = \sum_{\text{all systems}} (\hat{E}_{\text{tot}}^{a_0,a_1,a_2} - E_{\text{tot}}^{\text{Exp}})^2 \tag{11}$$

The Self-Consistent Minimization



Visual Paradigm Online Diagrams Express Edition

The Self-Consistent Minimization

- Naive search requires huge amount of time. Suppose the parameter space has 10000 points (will be much larger than this in reality), and solving KS equations for all systems in training set takes 24 hours. Then we need 10000 day to finish this project!
- Modern machine learning techniques can handle this kind of optimization. Bayesian optimization can help us update the parameters wisely.

Non Self-Consistent Minimization

The traditional wisdom is to do the fitting process in a non self-consistent manner. Naively assuming that the total energy depends on the parameter linearly.

$$\hat{E}_{\text{tot}} = T + V_{\text{ext}} + V_{nn} + E_J + a_0 E_{\text{x}}^{\text{slater}} + a_1 E_{\text{c}}^{\text{vwn}} + a_2 E_{\text{x}}^{\text{FA}} \tag{12}$$

Our target is still to find the best set of parameters,

$$(a_0, a_1, a_2)^* = \underset{a_0, a_1, a_2}{\operatorname{argmin}} f(a_0, a_1, a_2) \tag{13}$$

Non Self-Consistent Minimization

Take H atom as an example.

- Step1: set XC functional to be LDA, do the scf calculation.
  - Total DFT energy = -0.499475547937
  - One electron energy = -0.499111883754
  - Coulomb energy = 0.301216478089
  - Exchange energy = -0.279620939075
  - Correlation energy = -0.021959203196
  - Nuclear repulsion energy = 0.000000000000
- Step2: Establish the loss function and solve for the best parameters.

$$\begin{aligned} f(a_0, a_1, a_2) =& (-0.499111883754 + 0.301216478089 \\ &+ a_0 * -0.279620939075 + a_1 * -0.021959203196 \\ &+ a_2 * 0.301216478089/1 - 0.5)^2 \end{aligned} \tag{14}$$

Non Self-Consistent Minimization

- Step3: Replace the XC functional with our fitted one, and redo all the calculation self-consistently.
- Step4: Compute the error (usually use the root mean square error).

Non Self-Consistent Minimization

Famous G1/G2/G3 database provide hundreds of reliable data for us to do the fitting. Just like B3LYP, I also focused on four major types: total energy, atomization energy, ionization energy, proton affinity.

- Atomization energy: 54 systems
- Ionization energy: 40 systems
- Total energy: 189 systems
- Proton affinity: 8 systems

In total, there are 291 systems in my training set so far (may add more in the future).

Result

The parameters

- $a_0 = 1.035686$
- $a_1 = 1.002274$
- $a_2 = 0.0216025$

The root mean square error

- Atomization energy(Kcal/mol): Our Model = 25.25, LDA = 51.99
- Ionization energy(eV): Our Model = 1.49, LDA = 1.30
- Proton affinity(Kcal/mol): Our Model = 4.22, LDA = 5.766
- Total energy(Hartree): Our Model = 0.20, LDA = 0.99

Future work

- Keep expanding the training set.
- Try to mix with GGA (what I am doing right now)
- If we successfully improve the performence of GGA hybriding with Ferimi-Amaldi term, we can further use Bayesian optimization(BO) to search for the true global minimization.

End

Thank you!
Questions?

When can we use BO?

Suppose solving the problem

$$\max_{x \in A} f(x) \tag{15}$$

- The input x is in $\mathbb{R}^d$ (Typically $d < 20$).
- The feasible A is a simple set.
- The objective function f is continuous.
- f is "expensive to evaluate".
- f is a "black box".
- we observe only $f(x)$ and no first- or second-order derivatives.
- Our focus is on finding a *global* rather than local optimum.