Density Functional Theory

I. INTRODUCTION

What is Density Functional Theory (DFT)?

DFT is a method which provides a way to obtain the pair correlation function (and through the pair correlation function, thermodynamic properties) using the calculus of variations and functional derivatives. As such, it belongs in a list of methods with which one can obtain the pair correlation function, $g(r, r')$, including

- Molecular Dynamics
- Monte Carlo
- Integral Equations (Ornstein-Zernike, YGB Hierarchy)
- Perturbation Theories
- Density Functional Theory

Molecular DFT vs Electronic DFT

DFT can be used to obtain the distributions of both molecular species and electrons. In the former case, we call the method molecular DFT and in the latter case electronic DFT. The conceptual idea of using the calculus of variations and functional derivatives to obtain the distribution of particles, be they molecules or electrons, is the same. The difference is in the constitutive equations. In molecular DFT, which is in the realm of classical physics, the constitutive equations are Newton's equations of motion. In electronic DFT, which is in the realm of quantum physics, the constitutive equations are the Schrödinger equations for each electron. Frequently, both types of DFT are just called DFT. When a solid state physicist says she is using DFT, she means electronic DFT. When a chemical engineering molecular modeler says he is using DFT, he typically, though not always, means molecular DFT.

II. CALCULUS OF VARIATIONS AND FUNCTIONAL DERIVATIVES

Before applying the calculus of variations to the statistical mechanical problems which DFT addresses, we must first learn the mathematics of the calculus of variations.   In ordinary calculus, we have functions of variables, y(x), in which the function provides a mathematical rule for obtaining a number, y, for a given number x. In the calculus of variations, we have functions of functions, $F(\{y\})$, which returns a number F, for a given function, y(x). $F(\{y\})$ is called a functional.

Example 1.

Consider the functional

$$F(\{y\}) = \int_0^1 \left\{ \frac{1}{2} y(x)^2 - y(x)e^{-x} \right\} dx \tag{1}$$

In this case $F(\{y\})$ is a functional. Another functional is the configurational partition function of classical fluids, $Z_N(\{U\})$, where U is the potential energy, which is a function of the 3N coordinates of the atomic positions.

We will want to find the function $y_s(x)$ that minimizes $F(\{y\})$. If we consider the functional in equation (1), the solution can be obtained by evaluating the $F(\{y\})$ at $F(\{y + \varepsilon v\})$ where ε is a small number and $v(x)$ is a arbitrary, square-integrable function.

$$F(\{y_s + \varepsilon v\}) = \int_0^1 \left\{ \frac{1}{2} [y_s(x) + \varepsilon v(x)]^2 - [y_s(x) + \varepsilon v(x)]e^{-x} \right\} dx \tag{2}$$

$$F(\{y_s + \varepsilon v\}) = \int_0^1 \left\{ \frac{1}{2} [y_s(x)^2 + 2y_s(x)\varepsilon v(x) + \varepsilon^2 v(x)^2] - [y_s(x) + \varepsilon v(x)]e^{-x} \right\} dx \tag{3}$$

Taking the ordinary derivative with respect to epsilon we find

$$\frac{dF(\{y_s + \varepsilon v\})}{d\varepsilon} = \int_0^1 \left\{ \frac{1}{2} [2y_s(x)v(x) + 2\varepsilon v(x)^2] - [v(x)]e^{-x} \right\} dx \tag{4}$$

At $\varepsilon = 0$, the derivative is 0, since $y_s(x)$ is the solution to $F(\{y\})$.

$$\left. \frac{dF(\{y_s + \varepsilon v\})}{d\varepsilon} \right|_{\varepsilon=0} = \int_0^1 \left\{ [y_s(x) - e^{-x}]v(x) \right\} dx = 0 \tag{5}$$

This equation holds for arbitrary $v(x)$, so we define $v(x) = y_s(x) - e^{-x}$, so that we have

$$\left. \frac{dF(\{y_s + \varepsilon v\})}{d\varepsilon} \right|_{\varepsilon=0} = \int_0^1 \left\{ [y_s(x) - e^{-x}]^2 \right\} dx = 0 \tag{6}$$

This equation is only satisfied when $y_s(x) - e^{-x} = 0$ so $y_s(x) = e^{-x}$. In this way, we have obtained the solution; we have found the found the function $y_s(x)$ that minimizes $F(\{y\})$. This was an easy example because obtaining $y_s(x)$ involved the solution of an algebraic equation. Things get harder.

Example 2.

Consider the functional

$$F(\{y\}) = \int_0^1\int_0^1\left\{\frac{1}{2}e^{-x-x'}y(x)y(x')\right\}dxdx' - \int_0^1\left\{\frac{1}{2}y(x)^2 + 2y(x)\right\}dx \qquad (7)$$

Performing the same differentiation as done in Example 1, yields (skipping steps)

$$\left.\frac{dF(\{y_s + \varepsilon v\})}{d\varepsilon}\right|_{\varepsilon=0} = \int_0^1\left\{\int_0^1 e^{-x-x'}y_s(x')dx' - y_s(x) - 1\right\}dx = 0 \qquad (8)$$

which is only satisfied when

$$\int_0^1 e^{-x-x'}y_s(x')dx' - y_s(x) = 1 \qquad (9)$$

This is an integral equation that we must solve for y(x). Of course, since we have taken ChE 505, we recognize equation (9) as a Fredholm integral equation (the limits of integration are fixed) of the second kind (y(x) appears both inside and outside the integral).

$$\phi(x) = f(x) + \lambda\int_a^b N(x, y)\phi(y)dy \qquad (10)$$

We know how to obtain the analytical solution to this sort of integral equation. The solution to equation (9) is (skipping steps)

$$y_s(x) = -\left[1 + 2\left(\frac{1 - e^{-1}}{1 + e^{-2}}\right)e^{-x}\right] \qquad (11)$$

More on Functionals

With functions, the argument x can be a D-dimensional vector, $\mathbf{x}$. With functionals, the same is true; $\mathbf{x}$ can be a D-dimensional vector, and $\mathbf{y}(\mathbf{x})$ can be an n-dimensional vector.

Functionals can contain functions of y(x), integrals of y(x), and derivatives of y(x), y'(x).

Example 3. Using the calculus of variations to demonstrate the equivalency of Lagrangian and Newtonian formulations of the classical equations of motion

Consider the functional

$$F(\{r\}) = \int_{t_1}^{t_2} \left\{ \frac{1}{2} m \left(\frac{dr}{dt} \right)^2 - V(r) \right\} dt \tag{12}$$

where m, r, t, and V(r) are the mass, position, time, and potential energy of a particle in a classical system, i.e. the functional is the Lagrangian. We want to find the function $r_s(t)$ which minimizes the functional.

$$\left. \frac{dF(\{r_s + \varepsilon v\})}{d\varepsilon} \right|_{\varepsilon=0} = \int_{t_1}^{t_2} \left\{ m \left(\frac{dr_s}{dt} \right) \frac{dv}{dt} - \frac{dV(r_s)}{dr_s} v \right\} dt = 0 \tag{13}$$

This equation can be rearranged as

$$\left. \frac{dF(\{r_s + \varepsilon v\})}{d\varepsilon} \right|_{\varepsilon=0} = \int_{t_1}^{t_2} \left\{ -m \frac{d^2 r_s}{dt^2} - \frac{dV(r_s)}{dr_s} \right\} v \, dt = 0 \tag{14}$$

A trick was involved in obtaining equation (14), involving integration by parts

$$\int u \, dv = uv - \int v \, du \tag{15}$$

$$\int_{t_1}^{t_2} \left(\frac{dr_s}{dt} \right) \frac{dv}{dt} dt = \int_{v(t_1)}^{v(t_2)} \left(\frac{dr_s}{dt} \right) dv = \left[\left(\frac{dr_s}{dt} \right) v \right]_{t_1}^{t_2} - \int_{t_1}^{t_2} \left(\frac{d^2 r_s}{dt^2} \right) v \, dt = -\int_{t_1}^{t_2} \left(\frac{d^2 r_s}{dt^2} \right) v \, dt \tag{16}$$

where we have used the boundary conditions $v(t_1) = 0$ and $v(t_2) = 0$. In order for equation (14) to be true for arbitrary v,

$$m \frac{d^2 r_s}{dt^2} = -\frac{dV(r_s)}{dr_s} \tag{17}$$

This is Newton's equation of motion for a particle in a conservative force field. Therefore, we have shown that Newton's equations of motion provide the minimum function (the solution to a functional which is the classical Langrangian).

Functional Differentiation

$$\left[\frac{dF}{d\varepsilon}(\{y+\varepsilon\,v\})\right]_{\varepsilon=0} \equiv \int \frac{\delta F(\{y\})}{\delta y(\underline{x})} v(\underline{x}) d^D x \tag{18}$$

$\dfrac{\delta F(\{y\})}{\delta y(\underline{x})}$ is a functional derivative. It is itself a functional, completely defined by the original

functional $F(\{y\})$. Equation (18) is the definition of the functional derivative. For the functional given in Example 1, equation (1), we see that the functional derivative is given by equation (5),

$$\frac{\delta F(\{y\})}{\delta y(\underline{x})} = y_s(x) - e^{-x} \tag{19}$$

This gives us a general method for obtaining the functional derivative, given the functional. If the functional is a function, i.e. F evaluated at a single point i does not depend upon y at every point but only y at point i, then we can write the functional as

$$F(\{y\}) = f(y(x),x) = \int f(y(x'),x')\delta(x'-x)dx' \tag{20}$$

The functional derivative of a function generates a function times the Dirac delta function.

$$\frac{\delta F(\{y\})}{\delta y(\underline{x})} = \frac{\delta f(y(x),x)}{\delta y(\underline{x})} = \frac{\partial f(y(x),x)}{\partial y(\underline{x})}\delta(x'-x) \tag{21}$$

Functional Taylor Series

Functional Taylor series can be derived and yield for the case of a single function, y, and single variable, x:

$$F(\{y+v\}) = \sum_{k=0}^{\infty} \frac{1}{k!}\int\ldots\int \frac{\delta^k F(\{y\})}{\delta y(x_1)\ldots\delta y(x_k)} v(x_1)\ldots v(x_k)dx_1\ldots dx_k \tag{22}$$

For the case where we have a single function, y, which is a function of the vector, $\underline{x}$:

$$F(\{y+v\}) = \sum_{k=0}^{\infty} \frac{1}{k!}\int\ldots\int \frac{\delta^k F(\{y\})}{\delta y(\underline{x}_1)\ldots\delta y(\underline{x}_k)} v(\underline{x}_1)\ldots v(\underline{x}_k)d^D\underline{x}_1\ldots d^D\underline{x}_k \tag{23}$$

For the case where we have many functions, $\underline{y}$, which are functions of the vector, $\underline{x}$:

$$F(\{\underline{y}+\underline{v}\}) = \sum_{k=0}^{\infty} \frac{1}{k!}\sum_{\alpha_1}\ldots\sum_{\alpha_k}\int\ldots\int \frac{\delta^k F(\{\underline{y}\})}{\delta y_{\alpha_1}(\underline{x}_1)\ldots\delta y_{\alpha_k}(\underline{x}_k)} v_{\alpha_1}(\underline{x}_1)\ldots v_{\alpha_k}(\underline{x}_k)d^D\underline{x}_1\ldots d^D\underline{x}_k \tag{24}$$

Additional Rules of Functional Differentiation

The chain rule of differential calculus is also valid for functional differentiation.

$$\frac{\delta F(\{y\})}{\delta\eta(x)} = \int \frac{\delta F(\{y\})}{\delta y(x')} \frac{\delta y(x')}{\delta\eta(x)} dx' \tag{25}$$

If $F(\{y\}) = \delta\eta(x'')$

$$\frac{\delta F(\{y\})}{\delta\eta(x)} = \int \frac{\delta\eta(x'')}{\delta y(x')} \frac{\delta y(x')}{\delta\eta(x)} dx' = \delta(x - x') \tag{26}$$

The rules of implicit differentiation for differential calculus can also be extended to functional calculus.

Functionals can also be integrated. (see "Statistical Mechanics of Phases, Interfaces, and Thin Films", H.T. Davis, p. 434-435.)