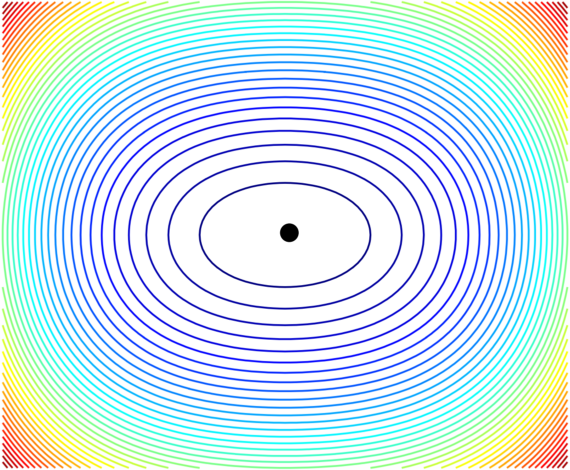
Solving Response-Type Problems with Automatic Differentiation

January 26, 2010

The Response Problem

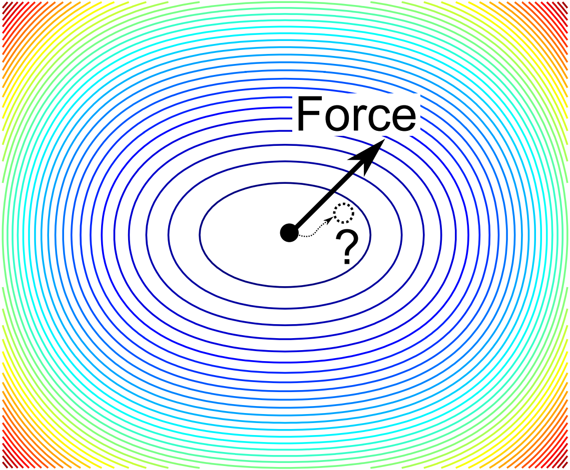
Perturbation Theory



Start in equilibrium (bottom of potential well)

The Response Problem

Perturbation Theory



Turn up force slowly

How does the system respond?

The Response Problem

Formal statement

1. Given a variationally optimized system (equilibrium)
2. Assuming the perturbed system stays variational

- How does the system respond to infinitesmal perturbations?
- How does the energy change with respect to the perturbation strengths?
- What if the perturbations are time dependent?

Applications in Quantum Chemistry

- Geometric gradients, Hessians. Geometry optimization and dynamics.
- Electromagnetic interactions — Absorption, Emission, Optics.
- Electron correlation (Møller–Plesset perturbation theory)
- Nuclear Magnetic Resonance (NMR)
- Relativity

We often go to high orders (nonlinear optics, combined geometric–electronic perturbations, excited state properties,..) Response theory only feasible way to calculate time dependent properties in many cases.

Our Cast

The infinitesmal perturbation strengths

$$\epsilon = (\epsilon_1, \epsilon_2, \ldots \epsilon_K)^T$$

K is a small number ($\sim 1 - 10$)

The model parameters

$$x = x(\epsilon) = (x_1, x_2, \ldots x_N)^T$$

N is a large number ($\sim 10^6$–10^8).

The energy functional which determines the dynamics

$$L(x(\epsilon), \epsilon)$$

The Response Problem

Observable properties can be calculated as derivatives of the "energy"; *Response Functions*:

$$\langle\langle \hat{A}; \hat{B} \rangle\rangle = \frac{\partial^2}{\partial \epsilon_A \partial \epsilon_B} L(x(\epsilon), \epsilon)$$

But, the energy must be variational for all perturbation strengths

$$\nabla_x L(x(\epsilon), \epsilon) = 0$$

We have to determine the Taylor expansion of $x(\epsilon)$

$$x = x(\epsilon) = 0 + x_1\epsilon_1 + x_2\epsilon_2 + x_{12}\epsilon_1\epsilon_2 + \dots$$

Some Notation

With a *multi index* $m = (m_1, m_2, \ldots m_K)$ we mean

$$x^m = x_1^{m_1} x_2^{m_2} \ldots x_K^{m_K}$$

and if N is an integer:

$$c_N x^N = \sum_{|m|=N} c_m x^m.$$

We write (slightly non-standard but following Brent)

$$f(x) = p(x) \mod x^{N+1}$$

when the *Taylor expansions* in x are equal up to order N.

Response Algorithm

Algorithm 1 Determine the Taylor expansion $L(x(\epsilon), \epsilon) \mod \epsilon^{2N+2}$, with the constraint $\nabla_x L(x(\epsilon), \epsilon) = 0$.

Require: $\nabla_x L(x, 0)\big|_{x=0} = 0$

$x^{(0)} \leftarrow 0$

for $k = 1$ **to** N **do**

  $g^{(k)} \leftarrow \nabla_x L(x^{(k-1)}, \epsilon) \mod \epsilon^{k+1}$ {Order k forces}

  Solve $\nabla_x L(x_k \epsilon^k, 0) = -g^{(k)} \mod \epsilon^{k+1}$ {Linear in x_k}

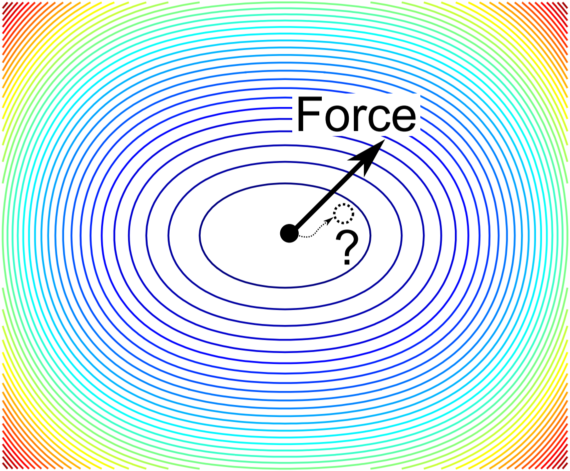
  $x^{(k)} \leftarrow x^{(k-1)} + x_k \epsilon^k$ {Build polynomial solution}

end for

Ensure: $\nabla_x L(x^{(N)}(\epsilon), \epsilon) = 0 \mod \epsilon^{N+1}$

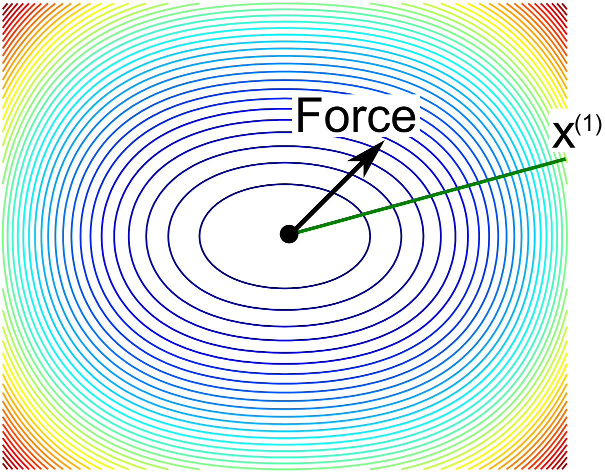
return $L(x^{(N)}(\epsilon), \epsilon) \mod \epsilon^{2N+2}$ {Wigner $2N + 1$ rule}

An example: Harmonic well with x^4 confinement



Apply the algorithm..

An example: Harmonic well with x^4 confinement



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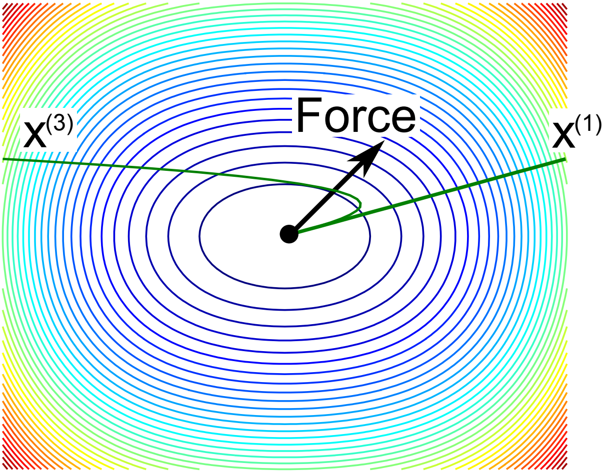

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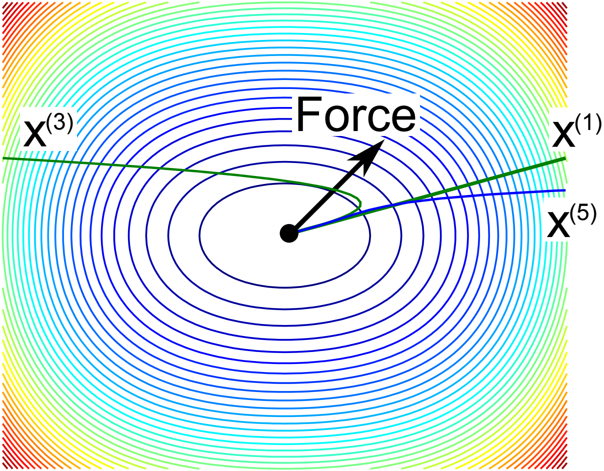

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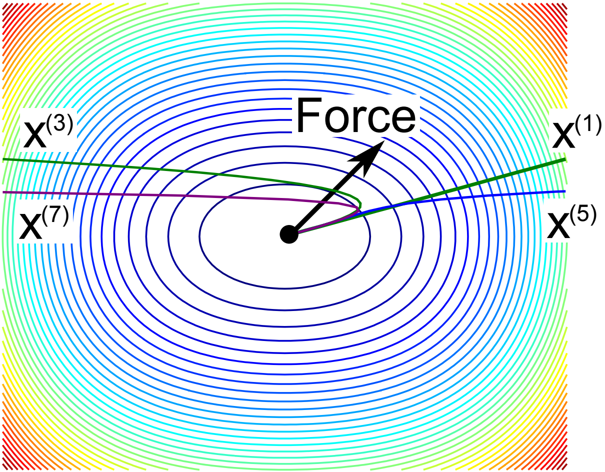

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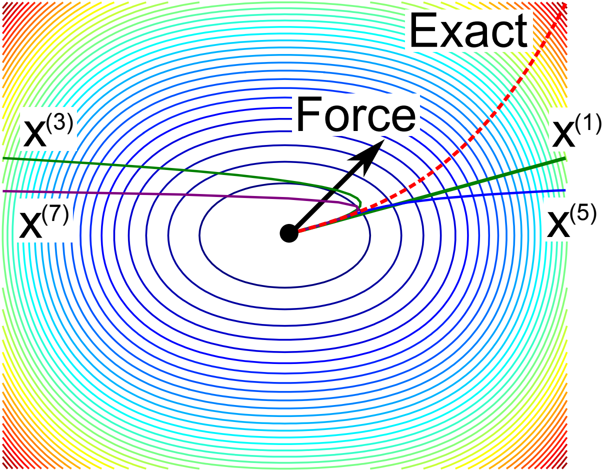


Solution only improved for small forces (radius of convergence)
Usually we don't know the exact solution..
(Can try Padé or *better parameterization*)

Response from Automatic Differentiation

What do you have to program yourself?

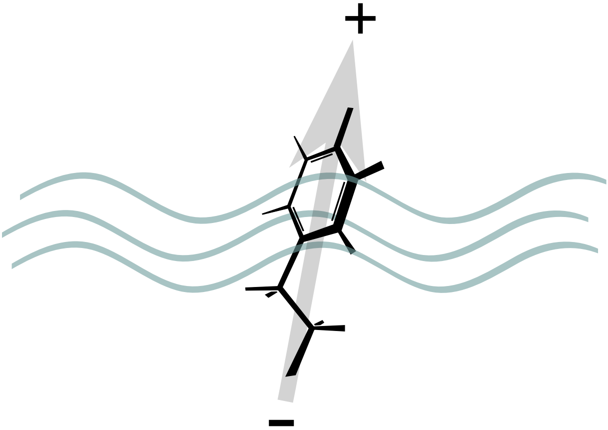
1. Implement the energy $L(x, \epsilon)$
2. (Optimize the reference state)
3. (Implement an *efficient* Hessian solver $Hx = g$)

What is done for you:

1. Arbitrary order gradient $\nabla_x L(x^{(k-1)}, \epsilon)$
2. Arbitrary order properties $L(x^{(N)}(\epsilon), \epsilon)$

- Useful for all nonlinear energy expressions!

Time Dependent Perturbation Theory



Light pushes and pulls electrons back and forth

Time Dependent Case

Many physical perturbations are time-periodic (EM fields etc). Look at the quasi-energy

$$Q(t) = \langle \Psi(t) | \hat{H}(t) - i \frac{\partial}{\partial t} | \Psi(t) \rangle$$

We have a variational principle for $Q(t)$. But we don't want to make a super long Taylor expansion in t!

The Adiabatic Approximation

- Periodic perturbation
- No memory between cycles
- *No absorption*, instead divergences
- Response is *in phase* (0° or 180°) with the perturbation
- Fourier series solution! (Floquet theory)

Time dependent Taylor variables

Let's turn our Taylor polynomial into a Fourier expansion:

$$\epsilon = Fe^{i\omega_\epsilon t}.$$

We can treat it with AD if we program

$$\frac{\partial \epsilon^n}{\partial t} = in\omega_\epsilon \epsilon.$$

Taylor expand

$$Q(\epsilon, \epsilon^*)$$

and use the response algorithm.

Density Functional Theory: A case for AD

In Density Functional Theory the energy ϵ_{XC} is extremely complicated

$$\ldots$$

$$d = 1/12\,\frac{\sqrt{\sigma}3^{5/6}}{u(\rho(a),\rho(b))\sqrt[6]{\pi^{-1}}\rho^{7/6}}, \tag{115}$$

$$u(\alpha,\beta) = 1/2\,(1+\zeta(\alpha,\beta))^{2/3} + 1/2\,(1-\zeta(\alpha,\beta))^{2/3}, \tag{116}$$

$$H(d,\alpha,\beta) = 1/2\,(u(\rho(a),\rho(b)))^3\lambda^2\ln\left(1+2\frac{\iota\,(d^2+A(\alpha,\beta)d^4)}{\lambda\,(1+A(\alpha,\beta)d^2+(A(\alpha,\beta))^2d^4)}\right)\iota^{-1}, \tag{117}$$

$$A(\alpha,\beta) = 2\iota\lambda^{-1}\left(e^{-2\frac{\iota\varepsilon(\alpha,\beta)}{(u(\rho(a),\rho(b)))^3\lambda^2}}-1\right)^{-1}, \tag{118}$$

$$\ldots$$

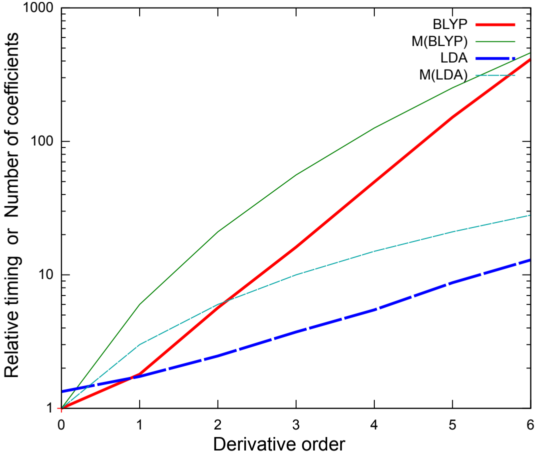
But for the algorithm we need k:th order derivatives:

$$g^{(k)} \leftarrow \nabla_x L(x^{(k-1)},\epsilon) \mod \epsilon^{k+1}$$

Hopeless to differentiate by hand, easy with AD. No explosion of partial derivatives.

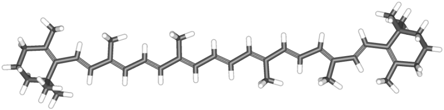
Benchmark

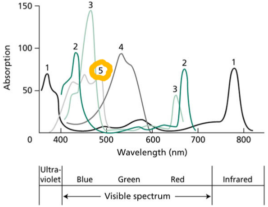
Exchange-correlation Derivatives



Not so bad, but don't compute so many partials..

So what can we use it for?





Response theory connects Caroten ↑ and Carrots ↓