Lecture Wednesday 19. September 2007

Topics:

Hartree-Fock Method, Variational method

Lagrange Multipliers special addition

Comments

The missing last slide corrected (after the lecture, 20.09.2007)

Lagrange formalism in Class. Mechanics

(d'Alembert etc. ....) virtual work $\bullet x', t'$ $\bullet x, t$

Lagrange → field theory → continuous systems

$\vec{x} \cdot \vec{x}$ (quadratic; $\frac{d}{dx_i}(\vec{x} \cdot \vec{x}) \longrightarrow x_i^2 \to 2x_i \ldots\ldots$

Linear algebra → dual spaces

Operator $\left[\; M \;\right]$ vector $\begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix}$

$[x_1 x_2 \ldots\ldots x_n]$ $\begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix}$ dual vector

bi-linear function(al)

of $\begin{bmatrix} x \\ \vdots \end{bmatrix} \ldots$ $[x \ldots]$

Space of "functions" or "states"

covered by Dirac notation

<bra| states

|ket> states

scaler pr. $\langle \alpha | \beta \rangle \ldots\ldots \langle \alpha | \alpha \rangle$

$\langle \beta | \left(M | \alpha \rangle \right) \longrightarrow \langle \beta | M | \alpha \rangle$

$M|\beta\rangle \longrightarrow \langle \beta M | ? \longrightarrow \langle \beta | M^{+}$

[for matrices it is easy; Hermite]

Lagrange Formalism; Virtual Work; Linear ALgebra and all that

Dirac Notation

$\int \psi_\alpha^*(\tau)\, O\, \psi_\beta(\tau)\, d\tau \longrightarrow \langle \psi_\alpha | O | \psi_\beta \rangle$ Dirac formulation

$|\psi_\alpha\rangle$ ..... $|\tau\rangle$ ..... $\psi_\alpha(\tau) \equiv \langle \tau | \psi_\alpha \rangle$

[We just mention .... $\int d\tau\, |\tau\rangle\langle\tau| = \mathbb{1}$]

$e^{i\alpha}\, e^{-i\alpha} = 1 \qquad x \cdot \frac{1}{x} \qquad$ (1 and ($\equiv$ 1))

Variational Method → "derivation" of Schrödinger Eq.

$\langle \psi | H | \psi \rangle$ (Helium .... $\psi(z)$)

$\longrightarrow H(z) = \langle \psi(z) | H | \psi(z) \rangle$

But if it is <u>not</u> an explicit parametric function : WHAT TO DO ?

$\boxed{\frac{\partial H}{\partial z}(z) = 0}$

Variational ... How to get general Schr. Eq.

Variational Method → "derivation" of Schrödinger Eq.

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$\longrightarrow H(\alpha) = \langle \psi(\alpha) | H | \psi(\alpha) \rangle$

But if it is <u>not</u> an explicit parametric function : WHAT TO DO ?

$\boxed{\frac{\partial H}{\partial \alpha}(\alpha) = 0}$

Analogy: dx .... df .... $\frac{df}{dx}$ as a derivative

differential

δf ... generalization of diff → variation

$I(f) = \int f(\tau) K(\tau) d\tau$ .... $\delta I \longleftarrow \delta f$

$\longrightarrow$ derivative → functional derivative $\frac{\delta I}{\delta \varphi}$

in the limit $\delta f \to 0 \Leftarrow \int |\delta f|^2 d\tau \to 0$ [δ-ε mechanism]

Start Again – How to get it?

Variational Method → "derivation" of Schrödinger Eq.

$\langle\psi|H|\psi\rangle \equiv I(|\psi\rangle)$ $\qquad (H|\psi\rangle = E|\psi\rangle)$

$\delta|\psi\rangle$ - - - δI

$\delta(\langle\psi|)$ do the variation in the dual space

$\frac{\delta I}{\delta\langle\psi|} \longrightarrow H|\psi\rangle \longrightarrow = 0$

Lagrange multiplier... !!!

invent a constraint and apply Lag. Mul.

How to apply Lagrange multipliers ?

Lagrange multiplier... !!!
invent a constraint and apply Lag. Mul.)

How to apply Lagrange multipliers ?

$F(x,y)$ → find minimum $\frac{\partial F}{\partial x} = 0$ $\frac{\partial F}{\partial y} = 0$ $x_0\, y_0$

in minimum point, the gradient is 0

(local or absolute minimum .... at least local minimum)

minimum on a circle

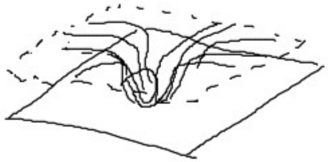
$g(x,y) \equiv (x-a)^2 + (y-b)^2 - r^2 = 0$ circle

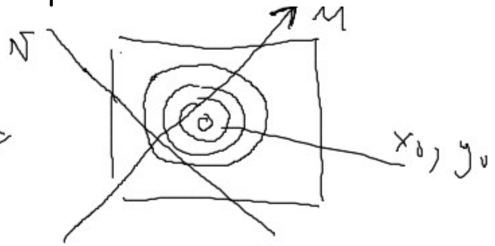
Find a minimum of $F(x,y) - \lambda g(x,y)$

How ... x_0, y_0, .. λ is unknowns

$$\frac{\partial (F - \lambda g)}{\partial x} = 0 \qquad \frac{\partial F - \lambda g}{\partial y} = 0 \qquad g(x,y) = 0$$

Lagrange Multipliers Part 2 – plane and surface

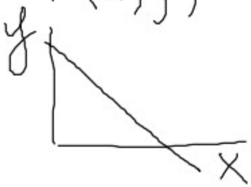




$$\left.\frac{\partial F}{\partial x}\right|_{x_0} = 0$$

etc....

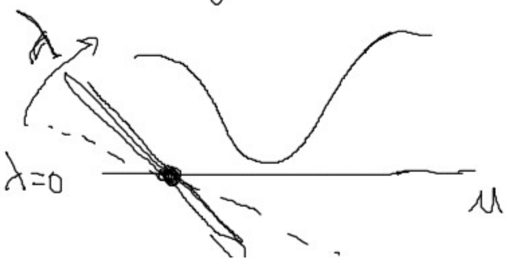
F(x,y) on the line $ax + by + c = 0$



$$\frac{\partial\left(F(x,y) - \lambda(ax+by+c)\right)}{\partial x} \to 0$$

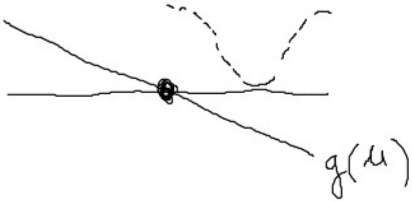
Think like this

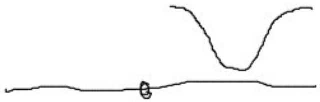
turning arround the plane



$$\lambda(ax + by + c) = \lambda g(x,y)$$

Lagrange Multipliers Part 3





How does he know

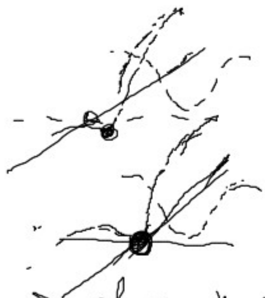
$$\cdot\cdot\, a(u-u_0)^2$$

$$a(u-u_0)^2 + b(u-a)$$

$$\longrightarrow c(u-u_1)^2$$

add linear to quadratic changes the position

$\lambda > 0$



The Lagrange multiplication $\longrightarrow$ changing the "steepness"

Now we know what to put there:

Variational Method → "derivation" of Schrödinger Eq.

$\langle\psi|H|\psi\rangle \equiv I(|\psi\rangle)$ $\qquad$ $(H|\psi\rangle = E|\psi\rangle)$

$\delta|\psi\rangle$ ... δI

$\delta(\langle\psi|)$ do the variation in the dual space

$\frac{\delta I}{\delta\langle\psi|} \longrightarrow H|\psi\rangle \longrightarrow \quad = 0$

Lagrange multiplier ... !!!

invent a constraint and apply Lag. Mul.

How to apply Lagrange multipliers?

The constraint is: $\langle\psi|\psi\rangle - 1 = 0$

$\langle\psi|H|\psi\rangle - \lambda\langle\psi|\psi\rangle$; $(\langle\psi|\psi\rangle - 1 = 0)$

$\delta\left[\langle\psi|H|\psi\rangle - \lambda\langle\psi|\psi\rangle\right] = 0 \rightarrow H|\psi\rangle = \lambda|\psi\rangle$

Comment ... the $e^{i\alpha}$ is an eigenvalue ... αβγδ

And Here we start from Helium energy

$$H = T_1 + V_1 + T_2 + V_2 + V_{12} \quad ; \quad \varphi_1 , \varphi_2$$

$$\mathcal{H}(\varphi_a, \varphi_a) = \langle \varphi_a | T + V | \varphi_a \rangle + \langle \varphi_b | T + V | \varphi_b \rangle$$

$$+ \langle \varphi_a \varphi_b | V_{12} | \varphi_a \varphi_b \rangle \qquad \delta \langle \varphi_a |$$

$$- \langle \varphi_a \varphi_b | V_{12} | \varphi_b \varphi_a \rangle \qquad \delta \langle \varphi_b |$$

$$\frac{\delta \mathcal{H}}{\delta \varphi_a} \qquad \delta\left(\mathcal{H} - \lambda_a \langle \varphi_a | \varphi_a \rangle - \lambda_b \langle \varphi_b | \varphi_b \rangle \right)$$

$$\langle \varphi_a | \quad \left[(T+V) | \varphi_a \rangle + \langle \varphi_b | V_{12} | \varphi_b \rangle \, | \varphi_a \rangle - \langle \varphi_b | V_{12} | \varphi_a \rangle \, | \varphi_b \rangle \right] = \lambda_a | \varphi_a \rangle$$

$$\langle \varphi_b | \quad \left[(T+V) | \varphi_b \rangle + \langle \varphi_a | V_{12} | \varphi_a \rangle | \varphi_b \rangle - \langle \varphi_a | V_{12} | \varphi_b \rangle | \varphi_a \rangle \right] = \lambda_b | \varphi_b \rangle$$

the previous note edited: Helium and variation -> Hartree-Fock equations

$$H = T_1 + V_1 + T_2 + V_2 + V_{12} \qquad \varphi_a ,\ \varphi_b$$

$$\begin{aligned}\mathcal{H}(\varphi_a, \varphi_a) = & \langle \varphi_a | T + V | \varphi_a \rangle + \langle \varphi_b | T + V | \varphi_b \rangle \\ & + \langle \varphi_a \varphi_b | V_{12} | \varphi_a \varphi_b \rangle \\ & - \langle \varphi_a \varphi_b | V_{12} | \varphi_b \varphi_a \rangle\end{aligned}$$

$$\delta\Big(\mathcal{H} - \lambda_a \langle \varphi_a | \varphi_a \rangle - \lambda_b \langle \varphi_b | \varphi_b \rangle\Big) \rightarrow \begin{array}{l} \delta \langle \varphi_a | \\ \delta \langle \varphi_b | \end{array}$$

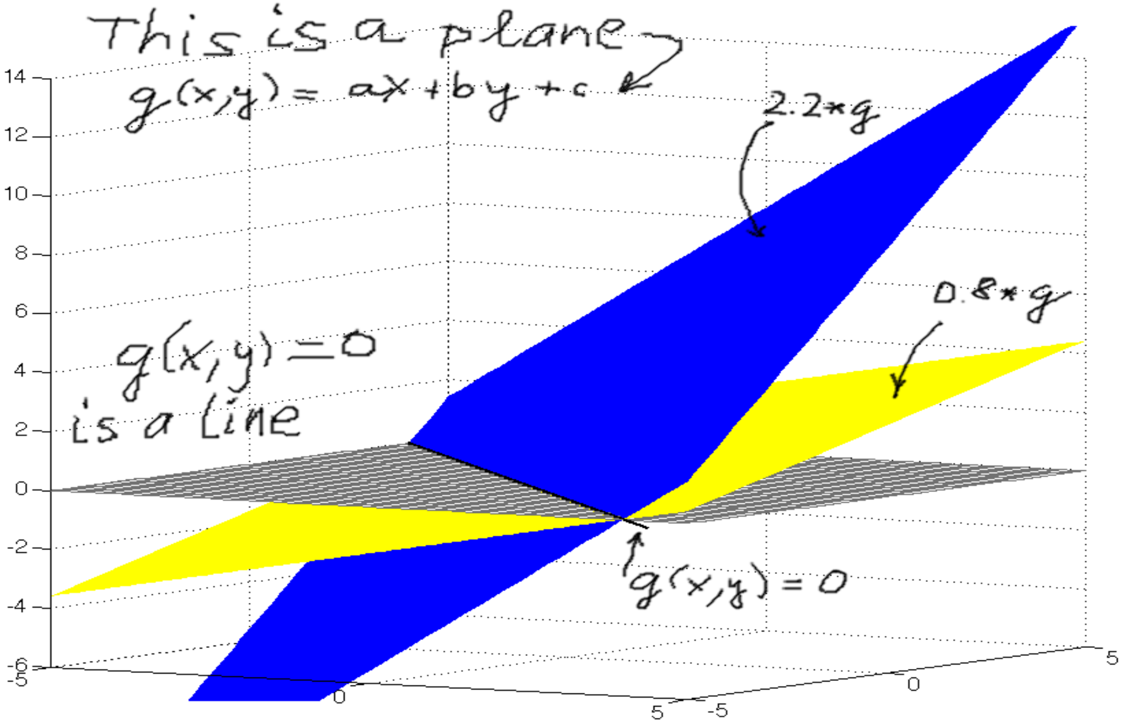
The 2 stationarity conditions

$$\frac{\delta \mathcal{H}}{\delta \langle \varphi_a |} \quad (T + V)|\varphi_a\rangle + \langle \varphi_b | V_{12} | \varphi_b \rangle |\varphi_a\rangle - \langle \varphi_b | V_{12} | \varphi_a \rangle |\varphi_b\rangle - \lambda_a |\varphi_a\rangle = 0$$

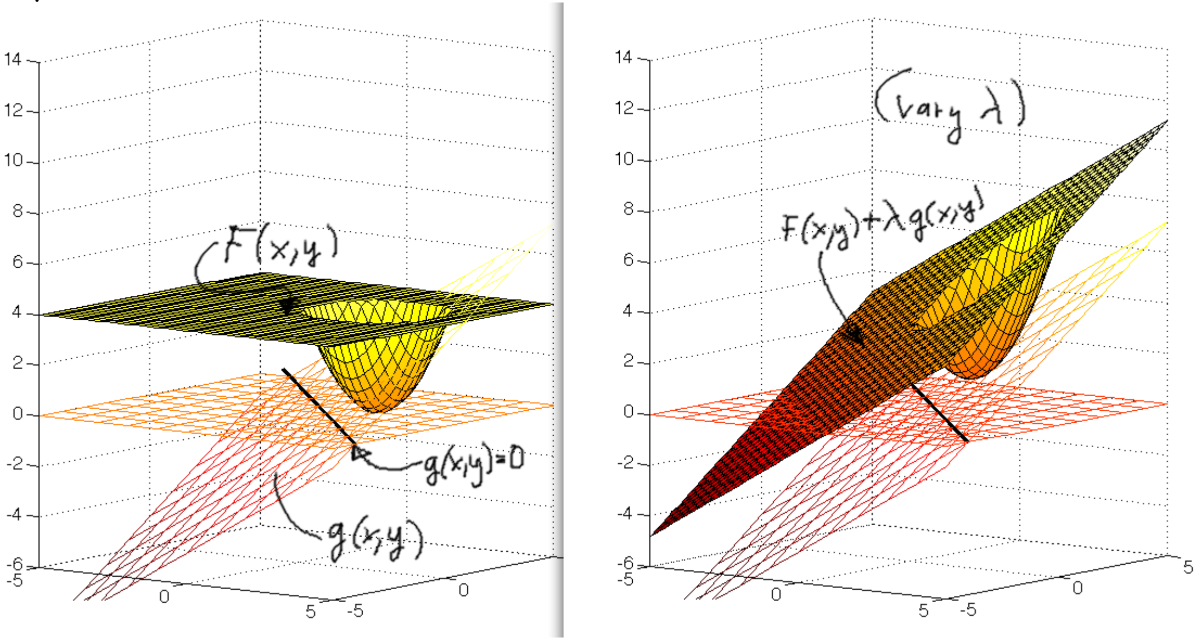
$$\frac{\delta \mathcal{H}}{\delta \langle \varphi_b |} \quad (T + V)|\varphi_b\rangle + \langle \varphi_a | V_{12} | \varphi_a \rangle |\varphi_b\rangle - \langle \varphi_a | V_{12} | \varphi_b \rangle |\varphi_a\rangle - \lambda_b |\varphi_b\rangle = 0$$

(.... Comment ... the $e^{i\alpha}$ is an eigenvalue ... αβγλ ......)

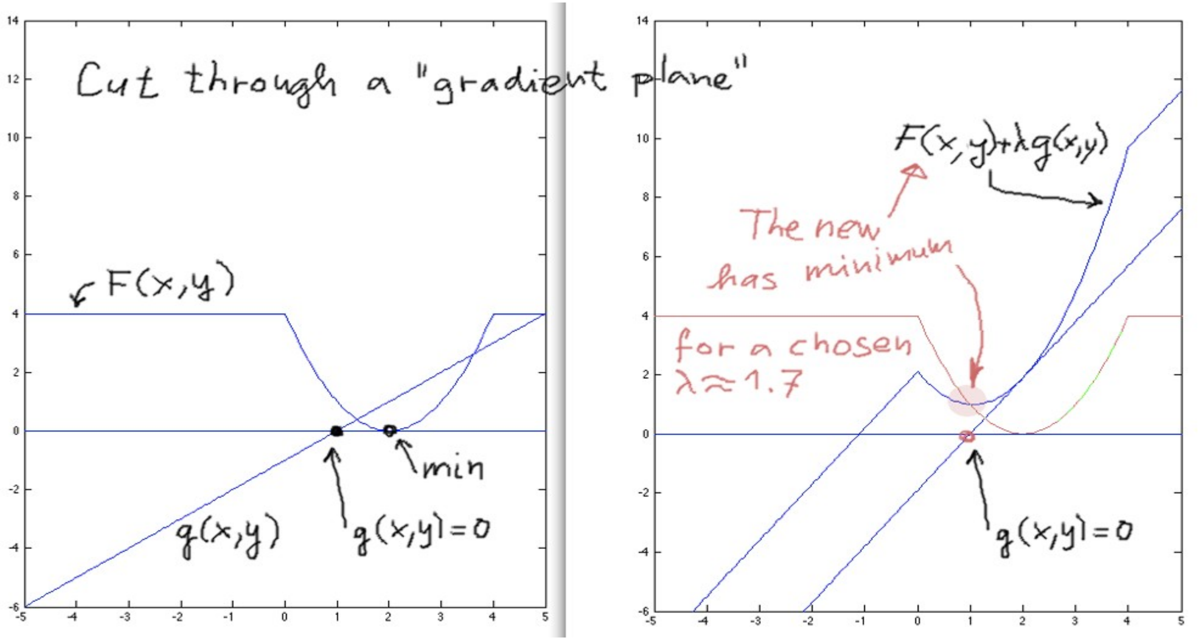
More on Lagrange Multipliers: Minimum of $F(x,y)$ on a curve(line) $g(x,y)=0$
Here we show $g(x,y)=ax+by+c$ A plot is a plane. We see plot of $\lambda g(x,y)$ for $\lambda=2.2$ and $\lambda=0.8$. As we increase λ, we get a steeper plane.



More on Lagrange Multipliers: $F(x,y)$ is here shown – it is a constant mostly with a parabolic hole. The curve(line) $g(x,y)=0$ is shown, as well as mesh plot of $g(x,y)$. To the left we plot $F(x,y) + \lambda g(x,y)$ for about $\lambda = 1$. The point is to vary λ



Now we only show cut by a plane. F(x,y) and g(x,y) shown in the left part with a parabolic hole. The line g(x,y)=0 appearsas a dot To the right we plot F(x,y) + λg(x,y) with the “correct” λ = 1.7. We see that the new function really has a local minimum at (x_0 , y_0) lying on the “curve” g(x,y)=0.
Note that since g(x,y)=0, at the minimum, the F(x,y) and the (F(x,y) + λg(x,y)) have the same value



Lagrange Multipliers Summary

Minimum of

F(x,y) on a curve (line) g(x,y)=0

How to: look for minimum of

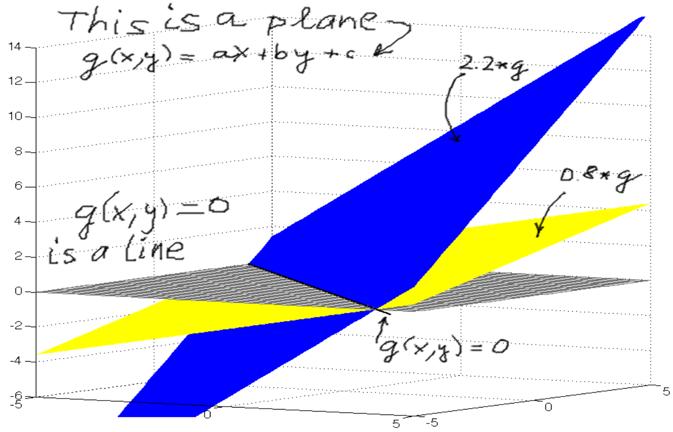
F(x,y) + λg(x,y) with an unknown λ

The three equations

d/dx (F(x,y) + λg(x,y)) = 0

d/dy (F(x,y) + λg(x,y)) = 0

g(x,y) = 0



Are solved to give values of x_0 , y_0 and λ

Forget λ , the point(s) (x_0 , y_0) give you the desired extremum (minimum, or extrema...)

Why does it work for Schrödinger: Remember the theorem about the minimum for the exact solution.

If the straight line is replaced by a circle – a $g(x,y) = x^2 + y^2 - r^2$ would be used

etc, etc.... Generalization to 3,4,5 ... N dimensions ....