Question 1: Undetermined multiplier method of Lagrange (I)

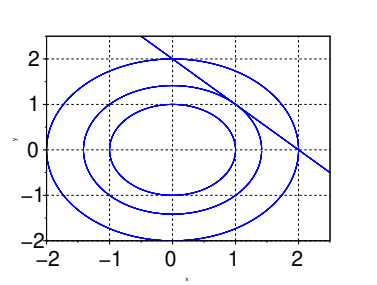
The real functions of two variables, $f(x, y)$ and $g(x, y)$ are given by

$$f(x, y) = x^2 + y^2 \quad (1)$$
$$g(x, y) = x + y - 2 \quad (2)$$

1a. Draw a contour map of $f(x, y)$ with contours $f(x, y) = c$ for $c = 1$, 2, and 4.

1b. In the same figure draw the line $g(x, y) = 0$.

Answer:



1c. Use the undetermined multiplier method of Lagrange to find the minimum of $f(x, y)$ with the constraint that $g(x, y) = 0$, i.e., solve

$$\boldsymbol{\nabla} f(x, y) = \lambda \boldsymbol{\nabla} g(x, y),$$

where λ is the undetermined multiplier and

$$\boldsymbol{\nabla} = \begin{pmatrix} \partial/\partial x \\ \partial/\partial y \end{pmatrix}.$$

After solving the equation, find the value of λ by using the constraint $g(x, y) = 0$.

Answer:

$$\boldsymbol{\nabla} f(x, y) = \begin{pmatrix} 2x \\ 2y \end{pmatrix} = \lambda \boldsymbol{\nabla} g(x, y) = \lambda \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Solution: $x = \lambda/2$, $y = \lambda/2$. *The constraint gives* $x + y - 2 = \lambda - 2 = 0$, *so* $\lambda = 2$ *and* $(x, y) = (1, 1)$.

Question 2: Undetermined multiplier method of Lagrange (II)

The column vector $\boldsymbol{x} \in \mathbb{R}^n$ has components x_i. The real functions $f(\boldsymbol{x})$ and $g(\boldsymbol{x})$ are given by

$$f(\boldsymbol{x}) = \boldsymbol{x}^T \boldsymbol{H} \boldsymbol{x} \quad (3)$$
$$g(\boldsymbol{x}) = \boldsymbol{x}^T \boldsymbol{x} - 1 \quad (4)$$

where $\boldsymbol{H}$ is a real, symmetric, $n \times n$ matrix, i.e. $H_{ij} = H_{ji}$ for $i, j = 1, \ldots, n$.

2a. Show that minimization of $f(\boldsymbol{x})$ with the constraint that $g(\boldsymbol{x}) = 0$ leads to an eigenvalue problem.

Answer: *We need to solve*

$$\boldsymbol{\nabla} f(\boldsymbol{x}) = \lambda \boldsymbol{\nabla} g(\boldsymbol{x}).$$

In components:

$$\frac{\partial}{\partial x_k} \sum_{i,j} x_i H_{i,j} x_j = \lambda \frac{\partial}{\partial x_k} (\sum_i x_i^2 - 1).$$

Use the chain rule and

$$\frac{\partial x_i}{\partial x_k} = \delta_{i,k}.$$

The left hand side:

$$\sum_{i,j} (\delta_{i,k} H_{i,j} x_j + x_i H_{i,j} \delta_{j,k}) = \sum_j H_{k,j} x_j + \sum_i x_i H_{i,k} = 2 \sum_i H_{k,i} x_i.$$

In the last step we used $H_{i,k} = H_{k,i}$. The right hand side gives:

$$\frac{\partial}{\partial x_k} \sum_i x_i^2 = \sum_i \frac{\partial x_i}{\partial x_k} \frac{\partial}{\partial x_i} x_i^2 = \sum_i \delta_{k,i} 2 x_i = 2 x_k.$$

Combining the left and the right hand side:

$$\sum_i H_{k,i} x_i = \lambda x_k$$

In matrix notation

$$\boldsymbol{H}\boldsymbol{x} = \lambda \boldsymbol{x}$$

This is matrix eigenvalue problem.

Question 3: Hartree-Fock equations for a two electron system

A two electron Slater-determinant is given by

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \left| \phi\bar{\phi} \right| . \tag{5}$$

The molecular orbital $\phi(\boldsymbol{r})$, with electron coordinate $\boldsymbol{r} \in \mathbb{R}^3$, is expanded in the m-dimensional AO basis $\{\chi_1(\boldsymbol{r}), \chi_2(\boldsymbol{r}), \ldots, \chi_m(\boldsymbol{r})\}$,

$$\phi(\boldsymbol{r}) = \sum_{\lambda=1}^{m} \chi_\lambda(\boldsymbol{r}) c_\lambda. \tag{6}$$

The electronic Hamiltonian, expressed in one- and two-electron operators $\hat{h}$ and $\hat{g}$ is

$$\hat{H} = \hat{h}(1) + \hat{h}(2) + \hat{g}(1,2). \tag{7}$$

The expectation value of Hamiltonian $\hat{H}$ for wave function Φ is given by

$$E = 2h + J = 2\langle\phi|\hat{h}|\phi\rangle + \langle\phi(1)\phi(2)|\hat{g}(1,2)|\phi(1)\phi(2)\rangle. \tag{8}$$

The overlap and one-electron integrals in the AO basis are given by

$$S_{\lambda,\mu} \equiv \langle\chi_\lambda|\chi_\mu\rangle \tag{9}$$

$$h_{\lambda,\mu} \equiv \langle\chi_\lambda|\hat{h}|\chi_\mu\rangle \tag{10}$$

and the two-electron integrals are given by

$$\langle\lambda\mu||\nu\tau\rangle \equiv \langle\chi_\lambda(1)\chi_\mu(2)|\hat{g}(1,2)|\chi_\nu(1)\chi_\tau(2)\rangle. \tag{11}$$

3a. Where did the exchange integral in Eq. (8) go?

Answer: *There are just 2 electrons, with opposite spins, so the exchange integral $K = 0$. You might object that there could be an artifical self-exchange, see the next question.*

3b. Compare Eq. (8) with the online notes from the lecture.

Answer: *The notes say:*

$$E = \sum_i^2 \langle \psi_i | h_i | \psi_i \rangle + \frac{1}{2} \sum_i^2 \sum_{i \neq j}^2 \langle \psi_i \psi_j | \hat{g}(1,2) | \psi_i \psi_j \rangle$$

with $|\psi_1\rangle = |\phi\rangle|\alpha\rangle$ *and* $|\psi_2\rangle = |\phi\rangle|\beta\rangle$. *The one-electron part is trivial:*

$$\sum_i^2 \langle \psi_i | h_i | \psi_i \rangle = \sum_i^2 \langle \phi | h | \phi \rangle (\langle \alpha | \alpha \rangle + \langle \beta | \beta \rangle) = 2 \langle \phi | h | \phi \rangle = 2h$$

In the two-electron part the double sum yields two identical terms (one with the α*-spin in orbital 1 and* β*-spin in orbital 2 and one with the* β*-spin in orbital 1 and the* α*-spin in orbital 2). This yields a factor 2 that cancels the factor 1/2 before the summation. So we get:*

$$\langle \phi(1)\phi(2) | \hat{g}(1,2) | \phi(1)\phi(2) \rangle = J$$

So in total:

$$E = 2h + J = 2h + 2J - K$$

Here we introduced the self-exchange K *that cancels the self-Coulomb contribution.*

3c. Derive the energy expression (assume that all functions and coefficients are real)

$$E = 2 \sum_{\lambda,\mu} h_{\lambda,\mu} c_\lambda c_\mu + \sum_{\lambda,\mu,\nu,\tau} \langle \lambda, \mu || \nu, \tau \rangle c_\lambda c_\mu c_\nu c_\tau. \tag{12}$$

Answer: *Assume that all functions and coeffients are real. The one-electron term:*

$$2\langle \phi | \hat{h} | \phi \rangle = 2 \langle \sum_\lambda \chi_\lambda(\boldsymbol{r}) c_\lambda | \hat{h} | \sum_\mu \chi_\mu(\boldsymbol{r}) c_\mu \rangle = 2 \sum_{\lambda,\mu} \langle \chi_\lambda | \hat{h} | \chi_\mu \rangle c_\lambda c_\mu = 2 \sum_{\lambda,\mu} h_{\lambda,\mu} c_\lambda c_\mu$$

The two-electron term:

$$\begin{aligned} \langle \phi(1)\phi(2) | \hat{g}(1,2) | \phi(1)\phi(2) \rangle &= \langle \sum_\lambda \chi_\lambda(1) c_\lambda \sum_\mu \chi_\mu(2) c_\mu | \hat{g}(1,2) | \sum_\nu \chi_\nu(1) c_\nu \sum_\tau \chi_\tau(2) c_\tau \rangle \\ &= \sum_{\lambda,\mu,\nu,\tau} \langle \lambda, \mu || \nu, \tau \rangle c_\lambda c_\mu c_\nu c_\tau. \end{aligned}$$

3d. Minimize the energy with the constraint that $\langle \phi | \phi \rangle = 1$ using the undetermined multiplier method of Lagrange.

Answer: *The energy E must be minimized under the constraint that the molecular orbital ϕ is normalized. This gives*

$$\boldsymbol{\nabla} E(\boldsymbol{c}) = \lambda \boldsymbol{\nabla} g(\boldsymbol{c}),$$

with the constraint

$$g(\boldsymbol{c}) = \langle\phi|\phi\rangle - 1 = \langle \sum_{\lambda} \chi_\lambda(\boldsymbol{r}) c_\lambda | \sum_{\mu} \chi_\mu(\boldsymbol{r}) c_\mu \rangle - 1 = \sum_{\lambda,\mu} S_{\lambda,\mu} c_\lambda c_\mu - 1 = 0.$$

When computing the gradient use

$$\frac{\partial c_\lambda}{\partial c_\rho} = \delta_{\lambda\rho}.$$

For the one-electron part of the energy we have

$$\begin{aligned}\frac{\partial h}{\partial c_\rho} &= \frac{\partial}{\partial c_\rho} \sum_{\lambda,\mu} h_{\lambda,\mu} c_\lambda c_\mu = \sum_{\lambda,\mu} h_{\lambda,\mu} \delta_{\lambda\rho} c_\mu + \sum_{\lambda,\mu} h_{\lambda,\mu} c_\lambda \delta_{\mu\rho} \\ &= \sum_{\mu} h_{\rho,\mu} c_\mu + \sum_{\lambda} h_{\lambda,\rho} c_\lambda = 2 \sum_{\mu} h_{\rho,\mu} c_\mu.\end{aligned}$$

In the last step we used that $\hat{h}$ is hermitian and real, $h_{\lambda,\rho} = h_{\rho,\lambda}$.
The gradient of the constraint is derived analogously

$$\frac{\partial g(\boldsymbol{c})}{\partial c_\rho} = 2 \sum_{\mu} S_{\rho,\mu} c_\mu.$$

The gradient of the Coulomb integral

$$\begin{aligned}\frac{\partial J}{\partial c_\rho} &= \frac{\partial}{\partial c_\rho} \sum_{\lambda\mu\nu\tau} \langle \lambda\mu||\nu\tau\rangle c_\lambda c_\mu c_\nu c_\tau \\ &= \sum_{\lambda,\mu,\nu,\tau} \langle \lambda\mu||\nu\tau\rangle (\delta_{\rho\lambda} c_\mu c_\nu c_\tau + c_\lambda \delta_{\rho\mu} c_\nu c_\tau + c_\lambda c_\mu \delta_{\rho\nu} c_\tau + c_\lambda c_\mu c_\nu \delta_{\rho\tau}) \\ &= 4 \sum_{\mu\nu\tau} \langle \rho\mu||\nu\tau\rangle c_\mu c_\nu c_\tau.\end{aligned}$$

Answer: *To show that all four contributions are the same in the last step, use*

$$\langle \lambda\mu||\nu\tau\rangle = \langle \nu\tau||\lambda\mu\rangle$$

and

$$\langle \lambda\mu||\nu\tau\rangle = \langle \mu\lambda||\tau\nu\rangle.$$

3e. Show that the resulting equations can be rewritten as

$$\boldsymbol{F}\boldsymbol{c} = \epsilon \boldsymbol{S}\boldsymbol{c}, \tag{13}$$

where the matrix elements of the so-called Fock matrix $\boldsymbol{F}$ are given by

$$F_{\rho,\nu} = h_{\rho,\nu} + \sum_{\mu,\tau} P_{\tau\mu} \langle \rho\mu || \nu\tau \rangle \tag{14}$$

and the *density matrix* $\boldsymbol{P}$ is defined by

$$\boldsymbol{P} = \boldsymbol{c}\boldsymbol{c}^T, \tag{15}$$

or, in components

$$P_{\tau\mu} = c_\tau c_\mu. \tag{16}$$

Answer: *To introduce the Fock-matrix we first note that indices ρ and ν refer to electron 1 in the expression for the gradient of the Coulomb integral. Therefore, we rewrite the gradient of the one electron term using the same indices:*

$$\frac{\partial h}{\partial c_\rho} = 2 \sum_\nu h_{\rho,\nu} c_\nu$$

and define the Fock-matrix elements by

$$F_{\rho,\nu} = h_{\rho,\nu} + \sum_{\mu,\tau} \langle \rho\mu || \nu\tau \rangle c_\mu c_\tau$$

Thus,

$$\frac{\partial}{\partial c_\rho}(2h + J) = \lambda \frac{\partial}{\partial c_\rho} g(\boldsymbol{c})$$

becomes:

$$4 \sum_\nu F_{\rho,\nu} c_\nu = 2\lambda \sum_\nu S_{\rho,\nu} c_\nu.$$

With $\epsilon = \lambda/2$, in matrix notation:

$$\boldsymbol{F}\boldsymbol{c} = \epsilon \boldsymbol{S}\boldsymbol{c}.$$

Question 4: Symmetric group

The group of all $n!$ permutations of n objects is called the *symmetric group*, denoted by S_n,

$$S_n = \{\hat{P}_i | i = 1, 2, \ldots, n!\}. \tag{17}$$

The set T is defined by

$$T = \{\hat{Q}\hat{P}_i | i = 1, 2, \ldots, n!\}, \tag{18}$$

where $\hat{Q} \in S_n$.

In general, two sets A and B are equal if all elements of A are in B and all elements of B are in A.

4a. Show that $T = S_n$ using the property of a group that each element has an inverse.

Answer: *Sets A and B are equal if $a \in A \leftrightarrow a \in B$. With $\hat{T}_i \equiv \hat{Q}\hat{P}_i$ and $\hat{P}_j \equiv \hat{Q}^{-1}\hat{P}_i$ we see that $\hat{T}_j \equiv \hat{Q}\hat{P}_j = \hat{Q}\hat{Q}^{-1}\hat{P}_i = \hat{P}_i$.*

The antisymmetrizer for n objects is

$$\hat{\mathcal{A}} = \sum_{i=1}^{n!} (-1)^{p_i} \hat{P}_i, \tag{19}$$

where p_i the parity of $\hat{P}$ (p_i is odd or even).

4b. Show that for $\hat{Q} \in S_n$ and $\hat{A}$ the antisymmetrizer

$$\hat{Q}\hat{A} = (-1)^q \hat{A},$$

where q is the parity of $\hat{Q}$.

Answer:

$$\hat{Q}\hat{\mathcal{A}} = \sum_{i=1}^{n!} (-1)^{p_i} \hat{Q}\hat{P}_i = (-1)^q \sum_{i=1}^{n!} (-1)^{p_i+q} \hat{Q}\hat{P}_i = (-1)^q \hat{\mathcal{A}}.$$

In the last step we used that $p_i + q$ is the parity of $\hat{Q}\hat{P}_i$ and that $\hat{Q}\hat{P}_i$ runs through the entire set S_n when $i = 1, \ldots, n!$