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Chapter 4: Density functional theory

1. Introduction
2. Fundamental theorem
3. Functional and variational principle

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Quantitative Calculation

1. Self consistent field method, Hartree, 1928; Symmetry corrected by Fock in 1930, now known as Hartree-Fock method.
2. Perturbation theory, ground state for two-electron systems, Hylleraas, 1930.
3. The cellular method, Na metal, electronic energy and total energy, Wigner and Seitz, 1933; energy band, Wigner and Seitz, 1934; Slater, 1934. Cu bands, Krutter, 1935; NaCl, Shockley, 1936.
4. Augmented plane waves, Slater, 1953.
5. Orthogonalized plane waves (OPW), Herring, 1940.
6. Effective potential (pseudopotentials), Fermi, 1934; Hellman, 1935.
7. Calculation on semiconductors, Ge, Herman and Callaway, 1953
8. Density functional theory, Kohn and Sham, 1964

Hohenberg-Kohn Theorem

An exact theory for many-body systems consisting of interacting particles for electrons and fixed nuclei in an external potential

General Hamiltonian

$$\hat{H} = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

DFT

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_i V_{ext}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\begin{array}{ccc} V_{ext}(\mathbf{r}) & \overset{\text{HK}}{\Leftarrow} & n_0(\mathbf{r}) \\ \Downarrow & & \Uparrow \\ \Psi_i(\{\mathbf{r}\}) & \Rightarrow & \Psi_0(\{\mathbf{r}\}) \end{array}$$

Theorem I:

For any system of interacting particles in an external potential, the potential is determined uniquely, except for a constant, by the ground state particle density.

Theorem II:

A universal functional for the energy E[n] in terms of n(r) can be defined, valid for any external potential V(r). For any V(r), the ground state energy is the global minimum of this functional, and the density n(r) that minimizes the functional is the ground state density.

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Proof of Theorem I

The density of particle

$$n(\mathbf{r}) = \frac{\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle} = N \frac{\int d^3 r_2 ... d^3 r_N \sum_{\sigma_1} |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N)|^2}{\int d^3 r_1 d^3 r_2 ... d^3 r_N |\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N)|^2}$$

density operator

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$$

The total energy may be expressed

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3 r V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{nuclei}$$

Assume

To prove the uniqueness of $V_{ext}(\mathbf{r})$

$$\exists V_{ext}^{(1)}(\mathbf{r}), V_{ext}^{(2)}(\mathbf{r}) \Rightarrow n(\mathbf{r}) \qquad \hat{H}^{(1)}, \hat{H}^{(2)} \Rightarrow \Psi^{(1)}, \Psi^{(2)} \Leftrightarrow n_0(\mathbf{r})$$

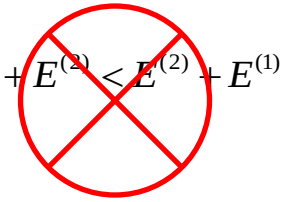
For the state 1, we have

$$\begin{aligned} E^{(1)} &= \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle \\ &= \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle \\ &= E^{(2)} + \int dr^3 \left[V_{ext}^{(1)}(\mathbf{r}) - V_{ext}^{(2)}(\mathbf{r}) \right] n_0(\mathbf{r}) \end{aligned}$$

Similarly for the state 2,

$$E^{(2)} < E^{(1)} + \int dr^3 \left[V_{ext}^{(2)}(\mathbf{r}) - V_{ext}^{(1)}(\mathbf{r}) \right] n_0(\mathbf{r})$$

$$\Rightarrow \quad E^{(1)} + E^{(2)} < E^{(2)} + E^{(1)}$$



Corollary I: Many-body wavefunctions for all states are determined. All properties of the system are determined by the ground state density.

Proof of Theorem II

The space of densities in which functionals of the density can be constructed.

The total energy functional

V-representable

$$E_{HK}[n] = T[n] + E_{\text{int}}[n] + \int d^3 r V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{nuclei}$$

$$\equiv F_{HK}[n] + \int d^3 r V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{nuclei}$$

All internal energies of the interacting electron system

Consider a system with ground state density

$$n^{(1)}(\mathbf{r}) \Leftrightarrow V_{ext}^{(1)}(\mathbf{r}) \qquad E^{(1)} = E_{HK}\left[n^{(1)}\right] = \left\langle \Psi^{(1)} \middle| \hat{H}^{(1)} \middle| \Psi^{(1)} \right\rangle$$

For a different density

$$n^{(2)}(\mathbf{r}) \Leftrightarrow V_{ext}^{(2)}(\mathbf{r}) \qquad E^{(1)} = \left\langle \Psi^{(1)} \middle| \hat{H}^{(1)} \middle| \Psi^{(1)} \right\rangle < \left\langle \Psi^{(2)} \middle| \hat{H}^{(1)} \middle| \Psi^{(2)} \right\rangle = E^{(2)}$$

If the functional is known

$$F_{HK}[n] = T[n] + E_{\text{int}}[n]$$

Corollary II:

The functional E[n] is sufficient to determine the exact ground state density and energy.

Minimizing the total energy functional w.r.t density function

Kohn-Sham approach

Replace many-body problem by an auxiliary independent-particle problem.

Assumptions:

1. Non-interacting V representability. The exact ground state density of the interacting electron system can be represented by the ground state density of an auxiliary system of non-interacting particles.
2. The auxiliary hamiltonian includes the usual kinetic operator and an effective local potential $V_{eff}^{\sigma}(\mathbf{r})$ acting on an electron.

Many-body problem

$$V_{ext}(\mathbf{r}) \overset{\text{HK}}{\Leftarrow} n_0(\mathbf{r})$$
$$\Downarrow \qquad \Uparrow$$
$$\Psi_i(\{\mathbf{r}\}) \Rightarrow \Psi_0(\{\mathbf{r}\})$$

KS

Non-interacting problem

$$n_0(\mathbf{r}) \overset{\text{HK}_0}{\Rightarrow} V_{KS}(\mathbf{r})$$
$$\Uparrow \qquad \Downarrow$$
$$\psi_{i=1,\ldots N_e}(\mathbf{r}) \Leftarrow \psi_i(\mathbf{r})$$

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Kohn-Sham approach

The auxiliary hamiltonian for independent particle system:

$$\hat{H}^{\sigma}_{aux} = -\frac{1}{2}\nabla^2 + V^{\sigma}(\mathbf{r})$$

For a system of N independent electrons

$$n(\mathbf{r}) = \sum_{\sigma} n(\sigma, \mathbf{r}) = \sum_{\sigma}\sum_{i=1}^{N^{\sigma}} \left|\psi_i^{\sigma}(\mathbf{r})\right|^2$$

Kohn-Sham energy functional for ground state:

$$E_{KS}[n] = T_s[n] + E_{Hartree}[n] + \int d^3r V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{nuclei} + E_{xc}[n]$$

$$E_{xc}[n] = F_{HK}[n] - (T_s[n] + E_{Hartree}[n])$$

$$F_{HK}[n] = T[n] + E_{\text{int}}[n]$$

$$T_s = -\frac{1}{2}\sum_{\sigma}\sum_{i=1}^{N^{\sigma}} \left\langle \psi_i^{\sigma} \middle| \nabla^2 \middle| \psi_i^{\sigma} \right\rangle = \frac{1}{2}\sum_{\sigma}\sum_{i=1}^{N^{\sigma}} \int d^3r \left|\nabla \psi_i^{\sigma}(\mathbf{r})\right|^2$$

$$E_{Hartree}[n] = \frac{1}{2}\int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Variation w.r.t wavefunction:

$$\frac{\delta E_{KS}}{\delta \psi^{*\sigma}_i(\mathbf{r})} = \frac{\delta T_s}{\delta \psi^{*\sigma}_i(\mathbf{r})} + \left[\frac{\delta E_{Hartree}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{ext}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r},\sigma)}\right]\frac{\delta n(\mathbf{r},\sigma)}{\delta \psi^{*\sigma}_i(\mathbf{r})} = 0$$

$$\left\langle \psi_i^{\sigma} \middle| \psi_j^{\sigma'} \right\rangle = \delta_{i,j}\delta_{\sigma,\sigma'}$$

$$\frac{\delta T_s}{\delta \psi^{*\sigma}_i(\mathbf{r})} = -\frac{1}{2}\nabla^2 \psi_i^{\sigma}(\mathbf{r}); \frac{\delta n(\mathbf{r},\sigma)}{\delta \psi^{*\sigma}_i(\mathbf{r})} = \psi_i^{\sigma}(\mathbf{r})$$

Kohn-Sham equation:

$$\left(H^{\sigma}_{KS} - \varepsilon_i^{\sigma}\right)\psi_i^{\sigma}(\mathbf{r}) = 0$$

$$H^{\sigma}_{KS}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V^{\sigma}_{KS}(\mathbf{r})$$

$$V^{\sigma}_{KS}(\mathbf{r}) = \frac{\delta E_{Hartree}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{ext}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r},\sigma)} = V_{Hartree}(\mathbf{r}) + V_{ext}(\mathbf{r}) + V^{\sigma}_{xc}(\mathbf{r})$$

Hartree-Fock theory

Hartree Equation

$$\psi(\vec{r}_1,\ldots,\vec{r}_n)=\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\cdots\varphi_n(\vec{r}_n)$$

One particle spin orbitals

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec{R}_I-\vec{r}_i)+\sum_{j\neq i}\int|\varphi_j(\vec{r}_j)|^2\frac{1}{|\vec{r}_j-\vec{r}_i|}d\vec{r}_j\right]\varphi_i(\vec{r}_i)=\varepsilon\varphi_i(\vec{r}_i)$$

Coulomb operator ⟺ Hartree potential

Single Slater determinant for Fermions

$$\phi_i(\boldsymbol{r}_1,\boldsymbol{r}_2,\cdots,\boldsymbol{r}_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(\boldsymbol{r}_1) & \phi_1(\boldsymbol{r}_2) & \cdots & \phi_1(\boldsymbol{r}_N)\\ \phi_2(\boldsymbol{r}_1) & \phi_2(\boldsymbol{r}_2) & \cdots & \phi_2(\boldsymbol{r}_N)\\ \vdots & \vdots & \vdots & \vdots\\ \phi_N(\boldsymbol{r}_1) & \phi_N(\boldsymbol{r}_2) & \cdots & \phi_N(\boldsymbol{r}_N)\end{vmatrix}$$

Coulomb operator

$$J_j(\mathbf{r})\phi_i(\mathbf{r})=\left[\int\phi_j^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_j(\mathbf{r}')d\mathbf{r}'\right]\phi_i(\mathbf{r})$$

Exchange operator

$$K_j(\mathbf{r})\phi_i(\mathbf{r})=\left[\int\phi_j^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r}')d\mathbf{r}'\right]\phi_j(\mathbf{r})$$

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Chapter 8: Functional and variational principles

1. Functional and variation
2. Hamilton's principle
3. Variation with constraints
4. Rayleigh-Ritz method

Functional

Integration over path:

$$J = \int_{x_1}^{x_2} f(y, y_x, x)dx$$

$$y = y(x, \alpha), y_x = \frac{\partial y}{\partial x}$$

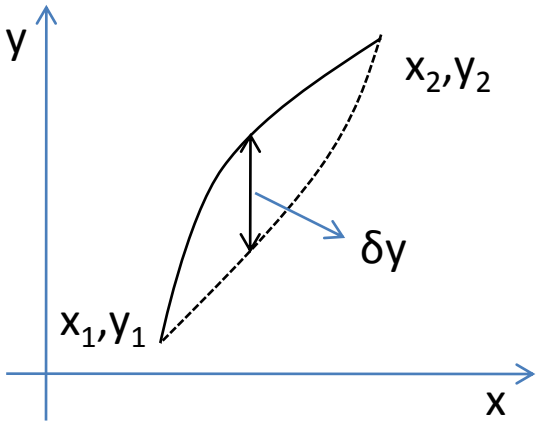
Variation of path:

$$y(x,\alpha) = y(x,0) + \alpha\eta(x)$$
$$\delta y = y(x,\alpha) - y(x,0) = \alpha\eta(x)$$

$$\eta(x_1) = \eta(x_2) = 0$$

$$\frac{\partial y(x,\alpha)}{\partial \alpha} = \eta(x)$$

$$\frac{\partial y_x(x,\alpha)}{\partial \alpha} = \frac{d\eta(x)}{dx}$$



The deformation of the path

Stationary path:

$$y = y(x, \alpha = 0): \left.\frac{\partial J(\alpha)}{\partial \alpha}\right|_{\alpha=0} = 0$$

$$\frac{\partial J(\alpha)}{\partial \alpha} = \int_{x_1}^{x_2} \left[\frac{\partial f}{\partial y}\frac{\partial y}{\partial \alpha} + \frac{\partial f}{\partial y_x}\frac{\partial y_x}{\partial \alpha}\right]dx$$

$$\int_{x_1}^{x_2} \frac{\partial f}{\partial y_x}\frac{d\eta}{dx}dx = \eta(x)\frac{\partial f}{\partial y_x}\Big|_{x_1}^{x_2} - \int_{x_1}^{x_2} \eta(x)\frac{d}{dx}\frac{\partial f}{\partial y_x}dx$$

$$= \int_{x_1}^{x_2} \left[\frac{\partial f}{\partial y}\eta(x) + \frac{\partial f}{\partial y_x}\frac{d\eta}{dx}\right]dx = \int_{x_1}^{x_2} \left[\frac{\partial f}{\partial y} - \frac{d}{dx}\frac{\partial f}{\partial y_x}\right]\eta(x)dx$$

$$\boxed{\frac{\partial f}{\partial y} - \frac{d}{dx}\frac{\partial f}{\partial y_x} = 0}$$

Euler equation

$$\frac{\partial f}{\partial y}-\frac{d}{dx}\frac{\partial f}{\partial y_x}=0$$

Another form:

$$\frac{\partial f}{\partial x}-\frac{d}{dx}\left(f-y_x\frac{\partial f}{\partial y_x}\right)=0$$

$f(y,y_x,x)$ $\quad \frac{df}{dx}=?$

Special case:

$$f=f(y,y_x) \longrightarrow f-y_x\frac{\partial f}{\partial y_x}=const.$$

Necessary but not sufficient to obtain a stationary path

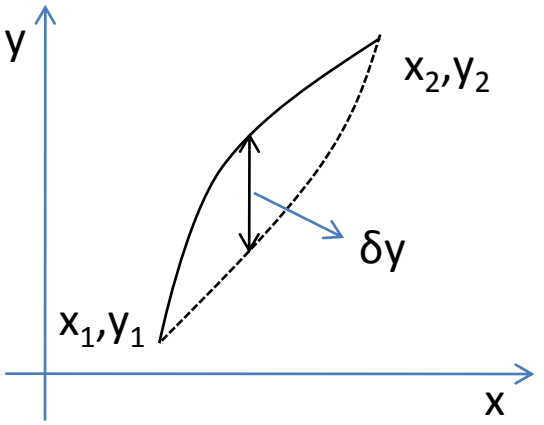
Examples:

$$ds=\sqrt{(dx)^2+(dy)^2}=\sqrt{1+y_x^2}\,dx$$

$$J=\int_{x_1}^{x_2} f(y,y_x,x)dx=\int_{x_1}^{x_2} ds=\int_{x_1}^{x_2}\sqrt{1+y_x^2}\,dx$$

$$f-y_x\frac{\partial f}{\partial y_x}=\sqrt{1+y_x^2}-y_x\frac{y_x}{\sqrt{1+y_x^2}}=\frac{1}{\sqrt{1+y_x^2}}=C$$

$$\Rightarrow y=ax+b$$



Hamilton's principle

Several dependent variables:

$$J=\int_{x_1}^{x_2} f\left(y_1(x), y_2(x),..., y_n(x), y_{1x}(x), y_{2x}(x),..., y_{nx}(x), x\right)dx$$

Define neighboring path:

$$y_i(x,\alpha)=y_i(x,0)+\alpha\eta_i(x)$$

$$\int_{x_1}^{x_2}\sum_i\left(\frac{\partial f}{\partial y_i}-\frac{d}{dx}\frac{\partial f}{\partial y_{ix}}\right)\eta_i(x)dx=0 \longrightarrow \boxed{\frac{\partial f}{\partial y_i}-\frac{d}{dx}\frac{\partial f}{\partial y_{ix}}=0}$$

Euler equation

Lagrangian:

$$L=T-V$$

Stationary value of the action: $\delta\int_{t_1}^{t_2} L\left(x_1, x_2,..., x_n, \dot{x}_1, \dot{x}_2,..., \dot{x}_n, t\right)dt=0$

Lagrangian EOM

$$\frac{\partial L}{\partial x_i}-\frac{d}{dx_i}\frac{\partial L}{\partial \dot{x}_i}=0$$

Example:

$$T=\frac{1}{2}m\dot{x}^2$$

$$\frac{\partial(T-V)}{\partial x_i}-\frac{d}{dx_i}\frac{\partial(T-V)}{\partial \dot{x}_i}=0 \quad \frac{d}{dx}m\dot{x}=F(x)$$

Cylindrical coordinates:

$$T=\frac{1}{2}m\dot{x}^2+\frac{1}{2}m\dot{y}^2=\frac{1}{2}\left(\dot{\rho}^2+\rho^2\dot{\varphi}^2\right)$$

$$\frac{d}{dt}\left(m\dot{\rho}\right)-m\rho\dot{\varphi}^2=0, \quad \frac{d}{dt}\left(m\rho^2\dot{\varphi}\right)=0$$

Laplace equation

Several independent variables:

$$J = \iiint f\left(u, u_x, u_y, u_z, x, y, z\right)dxdydz$$

Variation:

$$u(x,y,z,\alpha) = u(x,y,z,0) + \alpha\eta(x,y,z) \qquad \delta J = \alpha \left.\frac{\partial J(\alpha)}{\partial \alpha}\right|_{\alpha=0} = 0$$

$$\left.\frac{\partial J(\alpha)}{\partial \alpha}\right|_{\alpha=0} = \iiint \left(\frac{\partial f}{\partial u}\eta + \frac{\partial f}{\partial u_x}\eta_x + \frac{\partial f}{\partial u_y}\eta_y + \frac{\partial f}{\partial u_z}\eta_z\right)dxdydz = 0$$

$$\Rightarrow \iiint \left(\frac{\partial f}{\partial u} - \frac{\partial}{\partial x}\frac{\partial f}{\partial u_x} - \frac{\partial}{\partial y}\frac{\partial f}{\partial u_y} - \frac{\partial}{\partial z}\frac{\partial f}{\partial u_z}\right)\eta(x,y,z)dxdydz = 0$$

$$\Rightarrow \quad \frac{\partial f}{\partial u} - \frac{\partial}{\partial x}\frac{\partial f}{\partial u_x} - \frac{\partial}{\partial y}\frac{\partial f}{\partial u_y} - \frac{\partial}{\partial z}\frac{\partial f}{\partial u_z} = 0$$

Euler equation

Example:

Energy density

$$\rho = \frac{1}{2}\varepsilon E^2 = \frac{1}{2}\varepsilon(\nabla\varphi)^2$$

$$J = \iiint (\nabla\varphi)^2 dxdydz = \iiint \left(\varphi_x^2 + \varphi_y^2 + \varphi_z^2\right)dxdydz$$

$$\delta J = 0 \Rightarrow \nabla^2\varphi(x,y,z) = 0$$

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Lagrangian multipliers

For a function to be an extremum:

$$f = f(x,y,z) \qquad df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz = 0$$

Variables are subjected to constraints:

$$\varphi(x,y,z) = 0 \qquad d\varphi = \frac{\partial \varphi}{\partial x}dx + \frac{\partial \varphi}{\partial y}dy + \frac{\partial \varphi}{\partial z}dz = 0$$

$$df + \lambda d\varphi = \left(\frac{\partial f}{\partial x} + \lambda\frac{\partial \varphi}{\partial x}\right)dx + \left(\frac{\partial f}{\partial y} + \lambda\frac{\partial \varphi}{\partial y}\right)dy + \left(\frac{\partial f}{\partial z} + \lambda\frac{\partial \varphi}{\partial z}\right)dz = 0$$

Assuming $\frac{\partial \varphi}{\partial z} \neq 0$ choosing the Lagrangian multiplier to satisfy $\frac{\partial f}{\partial z} + \lambda\frac{\partial \varphi}{\partial z} = 0$

$$\Rightarrow \frac{\partial f}{\partial x} + \lambda\frac{\partial \varphi}{\partial x} = 0, \quad \frac{\partial f}{\partial y} + \lambda\frac{\partial \varphi}{\partial y} = 0$$

In general $\frac{\partial f}{\partial x_i} + \sum_i \lambda_k \frac{\partial \varphi_k}{\partial x_i} = 0, \quad i = 1,2,\ldots,n$

Example:

QM particle in a rectangular parallelepiped

$$E = \frac{h^2}{8m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right) \qquad V = abc = k$$

$$f(a,b,c) = E(a,b,c),\ \varphi(a,b,c) = abc - k = 0$$

To determine the shape of the constant-volume box, which minimize the energy E

$$\lambda abc = \frac{h^2}{4ma^2} = \frac{h^2}{4mb^2} = \frac{h^2}{4mc^2}$$

$$\Rightarrow a = b = c$$

Variation with constraints

Make the action stationary:

$$J = \int f\left(y_i, \frac{\partial y_i}{\partial x_j}, x_j \right) dx_j$$

x_j independent, y_i dependent

Variables are subjected to constraints:

$$\varphi_k\left(y_i, x_j\right) = 0$$

Choosing the Lagrangian multiplier to satisfy

$$\int \lambda_k\left(x_j\right)\varphi_k\left(y_i, x_j\right)dx_j = 0 \Rightarrow \delta\int \lambda_k\left(x_j\right)\varphi_k\left(y_i, x_j\right)dx_j = 0$$

Alternatively

$$\int \varphi_k\left(y_i, \frac{\partial y_i}{\partial x_j}, x_j \right) dx_j = const. \Rightarrow \delta\int \lambda_k\varphi_k\left(y_i, \frac{\partial y_i}{\partial x_j}, x_j \right) dx_j = 0$$

We have

$$\delta J' = \int \left[f\left(y_i, \frac{\partial y_i}{\partial x_j}, x_j \right) + \sum_k \lambda_k\left(x_j\right)\varphi_k\left(y_i, x_j\right) \right] dx_j = 0$$

Define:

$$g\left(y_i, \frac{\partial y_i}{\partial x_j}, x_j \right) = f + \sum_k \lambda_k\varphi_k$$

Euler-Lagrangian equation

$$\frac{\partial g}{\partial y_i} - \sum_j \frac{d}{dx_j}\frac{\partial g}{\partial y_i / \partial x_j} = 0$$

Lagrangian equation

No constraint:

$$\frac{d}{dq_i}\frac{\partial L}{\partial \dot{q}_i}-\frac{\partial L}{\partial q_i}=0$$

With constraints:

$$\delta\int\left[L(q_i,\dot{q}_i,t)+\sum_k \lambda_k(t)\varphi_k(q_i,t)\right]dt=0$$

Constraint Lagrangian EOM

$$\frac{d}{dq_i}\frac{\partial L}{\partial \dot{q}_i}-\frac{\partial L}{\partial q_i}=\sum_k a_{ik}\lambda_k$$

In case of that

$$\varphi_k=\varphi_k(q_i,t)\ \Rightarrow\ a_{ik}=\frac{\partial \varphi_k}{\partial q_i}$$

Example:

Euler equation for a QM problem

$$\delta\iiint \psi^*(x,y,z)H\psi(x,y,z)dxdydz=0$$

$$H=-\frac{\hbar^2}{2m}\nabla^2+V(x,y,z)$$

$$\delta\iiint\left(\frac{\hbar^2}{2m}\nabla\psi^*\cdot\nabla\psi+V\psi^*\psi\right)dxdydz=0$$

$$\frac{\partial g}{\partial \psi^*}-\frac{\partial}{\partial x}\frac{\partial g}{\partial \psi_x^*}-\frac{\partial}{\partial y}\frac{\partial g}{\partial \psi_y^*}-\frac{\partial}{\partial z}\frac{\partial g}{\partial \psi_z^*}=0$$

Constraint:

$$\iiint \psi^*\psi dxdydz=1$$

ψ,ψ^* vanished at the boundary

$$g=\frac{\hbar^2}{2m}\nabla\psi^*\cdot\nabla\psi+V\psi^*\psi-\lambda\psi^*\psi$$

Schrodinger wave equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=\lambda\psi$$

Rayleigh-Ritz

Strum-Liouville equation

$$J=\int_a^b\left[p(x)y_x^2-q(x)y^2\right]dx$$

Normalization condition:

$$\int_a^b y^2w(x)dx=1$$

Variation under the constraint

$$\delta J=0\Rightarrow\frac{d}{dx}\left(p(x)\frac{dy}{dx}\right)+q(x)y+\lambda w(x)y=0$$

Calculus of variations ⇔ eigenfunction/eigenvalues

Define a functional:

$$F[y(x)]=\frac{\int_a^b\left[p(x)y_x^2-q(x)y^2\right]dx}{\int_a^b y^2w(x)dx}=\frac{py_xy\big|_a^b-\int_a^b\left[y\frac{d}{dx}\left(p\frac{dy}{dx}\right)+qy^2\right]dx}{\int_a^b y^2wdx}=\lambda$$

Assuming the ground state eigenfunction and eigenvalue: $F[y_0]=\lambda_0$ The zero order approximation

The guess function takes the form:

$$y=y_0+\sum_{i=1}^{\infty}c_iy_i$$

Small quantities

Orthonormalized eigenfunctions

Rayleigh-Ritz

Note:

$$\int_a^b \left[\frac{d}{dx}\left(p\frac{dy_j}{dx} \right) + qy_i \right] y_i dx = -\lambda_i \delta_{ij} \qquad \frac{d}{dx}\left(p(x)\frac{dy}{dx} \right) + q(x)y + \lambda w(x)y = 0$$

Approximate function:

$$F[y(x)] = \frac{\lambda_0 + \sum_{i=1}^{\infty} c_i^2 \lambda_i}{1 + \sum_{i=1}^{\infty} c_i^2} \approx \lambda_0 + \sum_{i=1}^{\infty} c_i^2 (\lambda_i - \lambda_0)$$

Example:

Vibrating spring fixed at x=0 and x=1

$$\frac{d^2 y}{dx^2} + \lambda y = 0, \;\; y(0) = y(1) = 0$$

Exact solution:

$$y_0(x) = \sin \pi x, \;\; \lambda = \pi^2$$

Rayleigh-Ritz

$$p = 1, w = 1$$

$$y(x) = x(1-x)$$

$$F[y(x)] = \frac{\int_0^1 (1-2x)^2 dx}{\int_0^1 x^2 (1-x)^2 dx} = \frac{1/3}{1/30} = 10$$

2-nd order approximation:

$$y(x) = x(1-x) + a_2 x^2 (1-x)^2$$

$$a_2 = 1.1353, F[y(x)] = 9.8697$$

$$\pi^2 \approx 9.8696$$