UNI KASSEL VERSITÄT
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From Electrons to Materials Properties

Density Functional Theory for Engineers and Materials Scientists

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Chapter I

Theoretical Classical Mechanics: Lagrangians and Hamiltonians

Hamilton‘s Principle and the Lagrangian

Consider a Function $L(\boldsymbol{q}, \dot{\boldsymbol{q}}, t)$ describing the mechanical system in generalized coordinates $\boldsymbol{q} = (q_1, q_2, \cdots, q_N)$ and their temporal derivatives $\dot{q}_i = \frac{dq_i}{dt}$ then the integral

(1) $$S = \int_{t_1}^{t_2} L(\boldsymbol{q}, \dot{\boldsymbol{q}}, t)\, dt$$

is stationary with respect to the coordinates:

(2) $$\frac{\delta S}{\delta \boldsymbol{q}(t)} = 0$$

From the variational principle we obtain

(3) $$\delta S = \delta \int_{t_1}^{t_2} L(\boldsymbol{q}, \dot{\boldsymbol{q}}, t) dt = 0$$

This yields

(4) $$\delta \int_{t_1}^{t_2} L(\boldsymbol{q}, \dot{\boldsymbol{q}}, t) dt = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial \boldsymbol{q}} \delta \boldsymbol{q} + \frac{\partial L}{\partial \dot{\boldsymbol{q}}} \delta \dot{\boldsymbol{q}} \right) dt = 0$$

After partial integration we get

(5) $$\delta S = \frac{\partial L}{\partial \dot{\boldsymbol{q}}} \delta \boldsymbol{q} \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial \boldsymbol{q}} - \frac{d}{dt} \frac{\partial L}{\partial \dot{\boldsymbol{q}}} \right) \delta \boldsymbol{q} dt = 0$$

We obtain the Euler-Lagrange equations

(6) $$\frac{d}{dt}\frac{\partial L}{\partial \dot{\boldsymbol{q}}} - \frac{\partial L}{\partial \boldsymbol{q}} = 0$$

Conservation Laws

Homogeneity of time yields

(7) $$\frac{dL}{dt} = \frac{\partial L}{\partial \boldsymbol{q}}\dot{\boldsymbol{q}} + \frac{\partial L}{\partial \dot{\boldsymbol{q}}}\ddot{\boldsymbol{q}}$$

(8) $$\frac{dL}{dt} = \dot{\boldsymbol{q}}\frac{d}{dt}\frac{\partial L}{\partial \dot{\boldsymbol{q}}} + \frac{\partial L}{\partial \dot{\boldsymbol{q}}}\ddot{\boldsymbol{q}} = \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\boldsymbol{q}}}\dot{\boldsymbol{q}}\right)$$

or

(9) $$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\boldsymbol{q}}}\dot{\boldsymbol{q}} - L\right) = 0$$

This means that the energy of a mechanical system is conserved!

Homogeneity of space yields (for all centers of mass *a*)

(10) $$\delta L = \sum_a \frac{\partial L}{\partial \boldsymbol{r}_a} \delta \boldsymbol{r}_a = \boldsymbol{\varepsilon} \sum_{\boldsymbol{a}} \frac{\partial L}{\partial \boldsymbol{r}_a}$$

(11) $$\sum_{\boldsymbol{a}} \frac{\partial L}{\partial \boldsymbol{r}_a} = 0$$

which holds true for

(12) $$\sum_a \frac{d}{dt} \frac{\partial L}{\partial \dot{\boldsymbol{r}}_a} = \frac{d}{dt} \sum_a \frac{\partial L}{\partial \dot{\boldsymbol{r}}_a} = 0$$

Hence, in an adiabatic system the total momentum is conserved:

(13) $$\boldsymbol{p} = \sum_a \frac{\partial L}{\partial \dot{\boldsymbol{r}}_a} = \text{const.}$$

Isotropy of space yields (for rotations φ)

(14) $$\delta \boldsymbol{r} = \delta \boldsymbol{\varphi} \times \boldsymbol{r}$$

For velocities, we derive

(15) $$\delta \dot{\boldsymbol{r}} = \delta \boldsymbol{\varphi} \times \dot{\boldsymbol{r}}$$

Isotropy of space means that the Lagrangian does not change when the system is rotated, hence

(16) $$\delta L = \frac{\partial L}{\partial \boldsymbol{r}} \delta \boldsymbol{r} + \frac{\partial L}{\partial \dot{\boldsymbol{r}}} \delta \dot{\boldsymbol{r}} = 0$$

With our previously defined momenta this writes as

(17) $$\dot{\boldsymbol{p}}(\delta \boldsymbol{\varphi} \times \boldsymbol{r}) + \boldsymbol{p}(\delta \boldsymbol{\varphi} \times \dot{\boldsymbol{r}}) = 0$$

We can rewrite this as

(18) $$\delta\boldsymbol{\varphi}(\boldsymbol{r} \times \dot{\boldsymbol{p}} + \dot{\boldsymbol{r}} \times \boldsymbol{p}) = \delta\boldsymbol{\varphi}\frac{d}{dt}(\boldsymbol{r} \times \boldsymbol{p})$$

As this holds true for any arbitrary number $\delta\boldsymbol{\varphi}$ we can conclude that

(19) $$\frac{d}{dt}(\boldsymbol{r} \times \boldsymbol{p}) = \frac{d}{dt}\boldsymbol{M} = 0$$

The total angular moment is conserved.

Some fun: A particle facing central force

Consider a particle moving in a central force field, i.e.

(F1) $$\boldsymbol{F} = -\frac{\partial U}{\partial \boldsymbol{r}} = -\frac{dU}{dr}\frac{\boldsymbol{r}}{r}$$

with the radial distance *r* and the distance vector ***r***, with respect to the origin of the force ***F***. As we know that the angular momentum is conserved, we can conclude that the particle can only move in a plane. If we are applying polar coordinates, with the origin of our coordinate system being identical to the origin of the force, we obtain the Lagrangian

(F2) $$L = \frac{\mu}{2}(\dot{r}^2 + r^2\dot{\varphi}^2) - U(r)$$

Actually, this not an explicit function of φ. Such coordinates are called cyclic and it holds true for all cyclic coordinates that

(F3) $$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i} = 0$$

In this case, the generalized momentum is identical to the angular momentum, which is constant

(F4) $$M = \mu r^2 \dot{\varphi} = \text{const.}$$

This yields an expression for $\dot{\varphi}$ which can be inserted into F2. This yields the total energy

(F5) $$E = \frac{\mu \dot{r}^2}{2} + \frac{M^2}{2\mu r^2} + U(r)$$

From there, we obtain

(F6) $$\dot{r} = \frac{dr}{dt} = \sqrt{\frac{2}{\mu}(E - U(r)) - \frac{M^2}{\mu^2 r^2}}$$

Next, we take this result and derive

(F7) $$dt = \frac{1}{\sqrt{\frac{2}{\mu}(E - U(r)) - \frac{M^2}{\mu^2 r^2}}} dr$$

After combination with F4 we obtain

(F8) $$\varphi = \int \frac{M}{r^2\sqrt{2\mu(E - U(r)) - \frac{M^2}{r^2}}} dr + \text{const.}$$

The radial part of the potential yields an effective potential energy

(F9) $$U_{\text{eff}} = U(r) + \frac{M^2}{2\mu r^2}$$

Some more fun: Kepler's problem

Let us assume a particle moving within a potential

(K1) $$U = -\frac{\alpha}{r}$$

According to F9 this gives the effective potential

(K2) $$U_{\text{eff}} = -\frac{\alpha}{r} + \frac{M^2}{2\mu r^2}$$

Inserting K1 into F8 and solving the integral yields

(K3) $$\varphi = \arccos\left(\frac{\frac{M}{r} - \frac{\mu\alpha}{M}}{\sqrt{2\mu E + \frac{\mu^2\alpha^2}{M^2}}}\right)$$

We define

(K4) $$p = \frac{M^2}{\mu\alpha}$$

and

(K5) $$e = \sqrt{1 + \frac{2EM^2}{\mu\alpha^2}}$$

and obtain the equation

(K6) $$\frac{p}{r} = 1 + e\cos\varphi$$

This is the equation of an ellipse with parameter *p* and eccentricity *e.*

The semi-major axis is then

(K7) $$a = \frac{p}{1 - e^2} = \frac{\alpha}{2|E|}$$

and the semi-minor axis is

(K8) $$b = \frac{p}{\sqrt{1 - e^2}} = \frac{M}{\sqrt{2\mu|E|}}$$

Note that *a* only depends on the total energy, whereas *b* also depends on the angular momentum of the particle.

Hamiltonian Mechanics

Consider

(20) $$dL = \frac{\partial L}{\partial \boldsymbol{q}} d\boldsymbol{q} + \frac{\partial L}{\partial \dot{\boldsymbol{q}}} d\dot{\boldsymbol{q}}$$

With the definition of momentum we can rewrite this to

(21) $$dL = \dot{\boldsymbol{p}} d\boldsymbol{q} + \boldsymbol{p} d\dot{\boldsymbol{q}}$$

As

(22) $$\boldsymbol{p} d\dot{\boldsymbol{q}} = \dot{d}(\boldsymbol{p}\dot{\boldsymbol{q}}) - \dot{\boldsymbol{q}} d\boldsymbol{p}$$

equation 21 can be written as

(23) $$d(\boldsymbol{p}\dot{\boldsymbol{q}} - L) = -\dot{\boldsymbol{p}} d\boldsymbol{q} + \dot{\boldsymbol{q}} d\boldsymbol{p}$$

The right side of equation 23 is just the expression of *E*, which we will consider the Hamiltonian *H*. hence, we can always transform our Lagrangian into a Hamiltonian:

(24) $$H(\boldsymbol{p}, \boldsymbol{q}, t) = \boldsymbol{p}\dot{\boldsymbol{q}} - L(\dot{\boldsymbol{q}}, \boldsymbol{q}, t)$$

From equation (23) we can easily derive the equations

(25) $$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

and

(26) $$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

If we consider the addition of a parameter λ we obtain a new Lagrangian

(27) $$dL = \dot{\boldsymbol{p}} d\boldsymbol{q} + \boldsymbol{p} d\dot{\boldsymbol{q}} + \frac{\partial L}{\partial \lambda} d\lambda$$

With the definition of the Hamiltonian (eqs. 23 and 24) we can easily obtain the effect of this parameter on the Hamiltonian:

(28) $$dH = -\dot{\boldsymbol{p}} d\boldsymbol{q} + \boldsymbol{p} d\dot{\boldsymbol{q}} - \frac{\partial L}{\partial \lambda} d\lambda$$

Combining both equations we find

(29) $$\left(\frac{\partial H}{\partial \lambda}\right)_{\boldsymbol{p},\boldsymbol{q}} = -\left(\frac{\partial L}{\partial \lambda}\right)_{\dot{\boldsymbol{q}},\boldsymbol{q}}$$

This holds true for the parameter being time, too. Thus, if the Lagrangian yields conservation of energy, so does the Hamiltonian.