

Preface

This textbook is intended for use by students of physics, physical chemistry, and theoretical chemistry. The reader is presumed to have a basic knowledge of atomic and quantum physics at the level provided, for example, by the first few chapters in our book *The Physics of Atoms and Quanta*. The student of physics will find here material which should be included in the basic education of every physicist. This book should furthermore allow students to acquire an appreciation of the breadth and variety within the field of molecular physics and its future as a fascinating area of research.

For the student of chemistry, the concepts introduced in this book will provide a theoretical framework for that entire field of study. With the help of these concepts, it is at least in principle possible to reduce the enormous body of empirical chemical knowledge to a few basic principles: those of quantum mechanics. In addition, modern physical methods whose fundamentals are introduced here are becoming increasingly important in chemistry and now represent indispensable tools for the chemist. As examples, we might mention the structural analysis of complex organic compounds, spectroscopic investigation of very rapid reaction processes or, as a practical application, the remote detection of pollutants in the air.

April 1995

Walter Olthoff
Program Chair
ECOOP'95

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Table of Contents

Hamiltonian Mechanics unter besonderer Berücksichtigung der höherreren Lehranstalten

Ivar Ekeland¹, Roger Temam² Jeffrey Dean, David Grove, Craig Chambers,
Kim B. Bruce, and Elsa Bertino

¹ Princeton University, Princeton NJ 08544, USA,

I.Ekeland@princeton.edu,

WWW home page: <http://users/~iekeland/web/welcome.html>

² Université de Paris-Sud, Laboratoire d'Analyse Numérique, Bâtiment 425,
F-91405 Orsay Cedex, France

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$$\begin{aligned}\dot{x} &= JH'(t, x) \\ x(0) &= x(T)\end{aligned}$$

with $H(t, \cdot)$ a convex function of x , going to $+\infty$ when $\|x\| \rightarrow \infty$.

1.1 Autonomous Systems

In this section, we will consider the case when the Hamiltonian $H(x)$ is autonomous. For the sake of simplicity, we shall also assume that it is C^1 .

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Theorem ?? tells us that if $\lambda + \gamma < 0$, the boundary-value problem:

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has at least one solution \bar{x} , which is found by minimizing the dual action functional:

$$\psi(u) = \int_0^T \left[\frac{1}{2} (\Lambda_o^{-1} u, u) + N^*(-u) \right] dt \quad (4)$$

on the range of Λ , which is a subspace $R(\Lambda)_L^2$ with finite codimension. Here

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is a convex function, and

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Proposition 1. *Assume $H'(0) = 0$ and $H(0) = 0$. Set:*

$$\delta := \liminf_{x \rightarrow 0} 2N(x) \|x\|^{-2} . \quad (7)$$

If $\gamma < -\lambda < \delta$, the solution \bar{u} is non-zero:

$$\bar{x}(t) \neq 0 \quad \forall t . \quad (8)$$

Proof. Condition (??) means that, for every $\delta' > \delta$, there is some $\varepsilon > 0$ such that

$$\|x\| \leq \varepsilon \Rightarrow N(x) \leq \frac{\delta'}{2} \|x\|^2 . \quad (9)$$

It is an exercise in convex analysis, into which we shall not go, to show that this implies that there is an $\eta > 0$ such that

$$f \|x\| \leq \eta \Rightarrow N^*(y) \leq \frac{1}{2\delta'} \|y\|^2 . \quad (10)$$

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Since u_1 is a smooth function, we will have $\|hu_1\|_\infty \leq \eta$ for h small enough, and inequality (??) will hold, yielding thereby:

$$\psi(hu_1) \leq \frac{h^2}{2} \frac{1}{\lambda} \|u_1\|_2^2 + \frac{h^2}{2} \frac{1}{\delta'} \|u_1\|^2. \quad (11)$$

If we choose δ' close enough to δ , the quantity $(\frac{1}{\lambda} + \frac{1}{\delta'})$ will be negative, and we end up with

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On the other hand, we check directly that $\psi(0) = 0$. This shows that 0 cannot be a minimizer of ψ , not even a local one. So $\bar{u} \neq 0$ and $\bar{u} \neq \Lambda_o^{-1}(0) = 0$. \square

Corollary 1. *Assume H is C^2 and (a_∞, b_∞) -subquadratic at infinity. Let ξ_1, \dots, ξ_N be the equilibria, that is, the solutions of $H'(\xi) = 0$. Denote by ω_k the smallest eigenvalue of $H''(\xi_k)$, and set:*

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If:

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then minimization of ψ yields a non-constant T -periodic solution \bar{x} .

We recall once more that by the integer part $E[\alpha]$ of $\alpha \in \mathbb{R}$, we mean the $a \in \mathbb{Z}$ such that $a < \alpha \leq a + 1$. For instance, if we take $a_\infty = 0$, Corollary 2 tells us that \bar{x} exists and is non-constant provided that:

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Proof. The spectrum of Λ is $\frac{2\pi}{T}\mathbb{Z} + a_\infty$. The largest negative eigenvalue λ is given by $\frac{2\pi}{T}k_o + a_\infty$, where

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Hence:

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The condition $\gamma < -\lambda < \delta$ now becomes:

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Lemma 1. Assume that H is C^2 on $\mathbb{R}^{2n} \setminus \{0\}$ and that $H''(x)$ is non-degenerate for any $x \neq 0$. Then any local minimizer \tilde{x} of ψ has minimal period T .

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$$\dot{x} = JH'(x) . \quad (20)$$

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Notes and Comments. The results in this section are a refined version of [?]; the minimality result of Proposition 14 was the first of its kind.

To understand the nontriviality conditions, such as the one in formula (??), one may think of a one-parameter family x_T , $T \in (2\pi\omega^{-1}, 2\pi b_\infty^{-1})$ of periodic solutions, $x_T(0) = x_T(T)$, with x_T going away to infinity when $T \rightarrow 2\pi\omega^{-1}$, which is the period of the linearized system at 0.

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$$H(t, x) \geq n(\|x\|) \quad \text{with } n(s)s^{-1} \rightarrow \infty \quad \text{as } s \rightarrow \infty \quad (25)$$

$$\forall \varepsilon > 0, \quad \exists c : H(t, x) \leq \frac{\varepsilon}{2} \|x\|^2 + c. \quad (26)$$

Assume also that H is C^2 , and $H''(t, x)$ is positive definite everywhere. Then there is a sequence $x_k, k \in \mathbb{N}$, of kT -periodic solutions of the system

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such that, for every $k \in \mathbb{N}$, there is some $p_o \in \mathbb{N}$ with:

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where the Hamiltonian H is $(0, b_\infty)$ -subquadratic, and the forcing term is a distribution on the circle:

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where $f_o := T^{-1} \int_0^T f(t)dt$. For instance,

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A Borelian function $H : [0, T] \times \mathbb{R}^{2n} \rightarrow \mathbb{R}$ is called (A_∞, B_∞) -subquadratic at infinity if there exists a function $N(t, x)$ such that:

$$H(t, x) = \frac{1}{2} (A_\infty(t)x, x) + N(t, x) \quad (32)$$

$$\forall t, \quad N(t, x) \quad \text{is convex with respect to } x \quad (33)$$

$$N(t, x) \geq n(\|x\|) \quad \text{with } n(s)s^{-1} \rightarrow +\infty \text{ as } s \rightarrow +\infty \quad (34)$$

$$\exists c \in \mathbb{R} : \quad H(t, x) \leq \frac{1}{2} (B_\infty(t)x, x) + c \quad \forall x. \quad (35)$$

If $A_\infty(t) = a_\infty I$ and $B_\infty(t) = b_\infty I$, with $a_\infty \leq b_\infty \in \mathbb{R}$, we shall say that H is (a_∞, b_∞) -subquadratic at infinity. As an example, the function $\|x\|^\alpha$, with $1 \leq \alpha < 2$, is $(0, \varepsilon)$ -subquadratic at infinity for every $\varepsilon > 0$. Similarly, the Hamiltonian

$$H(t, x) = \frac{1}{2}k\|k\|^2 + \|x\|^\alpha \quad (36)$$

is $(k, k + \varepsilon)$ -subquadratic for every $\varepsilon > 0$. Note that, if $k < 0$, it is not convex.

Notes and Comments. The first results on subharmonics were obtained by Rabinowitz in [?], who showed the existence of infinitely many subharmonics both in the subquadratic and superquadratic case, with suitable growth conditions on H' . Again the duality approach enabled Clarke and Ekeland in [?] to treat the same problem in the convex-subquadratic case, with growth conditions on H only.

Recently, Michalek and Tarantello (see [?] and [?]) have obtained lower bound on the number of subharmonics of period kT , based on symmetry considerations and on pinching estimates, as in Sect. 5.2 of this article.

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Hamiltonian Mechanics2

Ivar Ekeland¹ and Roger Temam²

¹ Princeton University, Princeton NJ 08544, USA

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where δ_k is the Dirac mass at $t = k$ and $\xi \in \mathbb{R}^{2n}$ is a constant, fits the prescription. This means that the system $\dot{x} = JH'(x)$ is being excited by a series of identical shocks at interval T .

Definition 1. Let $A_\infty(t)$ and $B_\infty(t)$ be symmetric operators in \mathbb{R}^{2n} , depending continuously on $t \in [0, T]$, such that $A_\infty(t) \leq B_\infty(t)$ for all t .

A Borelian function $H : [0, T] \times \mathbb{R}^{2n} \rightarrow \mathbb{R}$ is called (A_∞, B_∞) -subquadratic at infinity if there exists a function $N(t, x)$ such that:

$$H(t, x) = \frac{1}{2} (A_\infty(t)x, x) + N(t, x) \quad (32)$$

$$\forall t , \quad N(t, x) \quad \text{is convex with respect to } x \quad (33)$$

$$N(t, x) \geq n(\|x\|) \quad \text{with } n(s)s^{-1} \rightarrow +\infty \text{ as } s \rightarrow +\infty \quad (34)$$

$$\exists c \in \mathbb{R} : \quad H(t, x) \leq \frac{1}{2} (B_\infty(t)x, x) + c \quad \forall x . \quad (35)$$

If $A_\infty(t) = a_\infty I$ and $B_\infty(t) = b_\infty I$, with $a_\infty \leq b_\infty \in \mathbb{R}$, we shall say that H is (a_∞, b_∞) -subquadratic at infinity. As an example, the function $\|x\|^\alpha$, with $1 \leq \alpha < 2$, is $(0, \varepsilon)$ -subquadratic at infinity for every $\varepsilon > 0$. Similarly, the Hamiltonian

$$H(t, x) = \frac{1}{2} k \|k\|^2 + \|x\|^\alpha \quad (36)$$

is $(k, k + \varepsilon)$ -subquadratic for every $\varepsilon > 0$. Note that, if $k < 0$, it is not convex.

Notes and Comments. The first results on subharmonics were obtained by Rabinowitz in [1], who showed the existence of infinitely many subharmonics both in the subquadratic and superquadratic case, with suitable growth conditions on H' . Again the duality approach enabled Clarke and Ekeland in [2] to treat the same problem in the convex-subquadratic case, with growth conditions on H only.

Recently, Michalek and Tarantello (see Michalek, R., Tarantello, G. [3] and Tarantello, G. [4]) have obtained lower bound on the number of subharmonics of period kT , based on symmetry considerations and on pinching estimates, as in Sect. 5.2 of this article.

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