

**FIRST PRINCIPLE CALCULATIONS OF DEFECT STRUCTURES  
IN ZINC OXIDE**

By

CHRISTIAN LOER T. LLEMIT

An dissertation submitted in partial fulfillment of  
the requirements for the degree of

DOCTOR OF PHILOSOPHY

NATIONAL INSTITUTE OF PHYSICS  
University of the Philippines - Diliman

MAY 2020

© Copyright by CHRISTIAN LOER T. LLEMIT, 2020  
All Rights Reserved



To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of CHRISTIAN LOER T. LLEMIT find it satisfactory and recommend that it be accepted.

---

Roland V. Sarmago, Ph.D., Chair

---

Donald Trump, Ph.D.

---

Rodrigo Duterte, Ph.D.

## ACKNOWLEDGMENT

Nullam mollis et leo at pharetra. Nulla efficitur molestie euismod. Sed dapibus metus sed tempus varius. Aenean finibus eros ut urna luctus feugiat. Duis turpis risus, viverra vitae porta et, ullamcorper ac est. Proin in eros nec ipsum interdum tempus. Nam fringilla lectus velit, non posuere ex vehicula ut. Mauris tincidunt, dolor sit amet commodo tempor, erat mi egestas dui, at elementum tellus est rhoncus libero. Ut et rutrum lectus, id viverra tortor. Vivamus nec lacus eros. Donec dictum porta nisi et vestibulum. Mauris luctus ligula ut libero aliquet luctus. Quisque malesuada egestas finibus.

Mauris dictum pharetra fermentum. Maecenas ut felis varius, dapibus sapien imperdiet, dictum dui. Proin feugiat viverra metus non laoreet. Integer pulvinar mi id lacus semper commodo. Praesent vel erat interdum purus scelerisque maximus. Sed enim risus, mollis blandit ligula ac, sagittis venenatis augue. Mauris nisi purus, gravida ac aliquam eu, ullamcorper eget nulla. Proin id finibus purus. Vestibulum leo ante, porta in quam sed, eleifend feugiat arcu. Nunc viverra fringilla turpis a iaculis. In condimentum aliquet mauris, quis laoreet eros porta eu. Aenean ut turpis a massa gravida pretium. Phasellus auctor purus quis diam interdum, nec luctus lorem auctor. Pellentesque finibus elit justo, a vulputate diam fermentum lacinia.

FIRST PRINCIPLE CALCULATIONS OF DEFECT STRUCTURES  
IN ZINC OXIDE

Abstract

by Christian Loer T. Llemit, BS  
University of the Philippines - Diliman  
May 2020

: Roland V. Sarmago

Nullam mollis et leo at pharetra. Nulla efficitur molestie euismod. Sed dapibus metus sed tempus varius. Aenean finibus eros ut urna luctus feugiat. Duis turpis risus, viverra vitae porta et, ullamcorper ac est. Proin in eros nec ipsum interdum tempus. Nam fringilla lectus velit, non posuere ex vehicula ut. Mauris tincidunt, dolor sit amet commodo tempor, erat mi egestas dui, at elementum tellus est rhoncus libero. Ut et rutrum lectus, id viverra tortor. Vivamus nec lacus eros. Donec dictum porta nisi et vestibulum. Mauris luctus ligula ut libero aliquet luctus. Quisque malesuada egestas finibus.

Mauris dictum pharetra fermentum. Maecenas ut felis varius, dapibus sapien imperdiet, dictum dui. Proin feugiat viverra metus non laoreet. Integer pulvinar mi id lacus semper commodo. Praesent vel erat interdum purus scelerisque maximus. Sed enim risus, mollis blandit ligula ac, sagittis venenatis augue. Mauris nisi purus, gravida ac aliquam eu, ullamcorper eget nulla. Proin id finibus purus. Vestibulum leo ante, porta in quam sed, eleifend feugiat arcu.

# TABLE OF CONTENTS

	Page
<b>ACKNOWLEDGMENT</b> . . . . .	iii
<b>ABSTRACT</b> . . . . .	iv
<b>LIST OF TABLES</b> . . . . .	x
<b>LIST OF FIGURES</b> . . . . .	xi
<b>CHAPTER</b>	
<b>1 INTRODUCTION</b> . . . . .	1
1.1 Purpose and Motivation . . . . .	1
1.2 Objectives . . . . .	1
1.3 Outline . . . . .	1
<b>2 Review of Related Literature</b> . . . . .	2
2.1 Semiconductors . . . . .	2
2.1.1 Properties . . . . .	2
2.1.2 Applications of Semiconductors . . . . .	2
2.1.3 Defects in Semiconductors . . . . .	2
2.2 Zinc Oxide . . . . .	2
2.2.1 Crystal Structure . . . . .	2
2.2.2 Crystallographic Directions and Planes . . . . .	3
2.2.3 Brillouin Zone Symmetry . . . . .	3
2.2.4 Photoluminescence Properties . . . . .	3
2.2.5 Defects . . . . .	3
<b>3 THEORETICAL FRAMEWORK</b> . . . . .	4
3.1 Electronic Structure . . . . .	4

3.1.1	Electronic Bandstructure . . . . .	4
3.1.1.1	Bloch Wavefunctions . . . . .	4
3.1.2	Density of States . . . . .	4
3.1.3	Projected Density of States . . . . .	4
3.2	Many-body Quantum Mechanics . . . . .	4
3.2.1	Time Independent Schrödinger Equation . . . . .	6
3.2.2	Simplifying Assumptions . . . . .	6
3.2.3	Use of Atomic Units . . . . .	6
3.2.4	Hamiltonian Operator . . . . .	6
3.2.5	Indistinguishability of electrons . . . . .	6
3.3	Early First Principle Calculations . . . . .	6
3.3.1	n-electron problem . . . . .	6
3.3.2	Hartree Method . . . . .	6
3.3.3	Hartree-Fock Method . . . . .	6
3.4	Density Functional Theory . . . . .	6
3.4.1	Electron Density . . . . .	6
3.4.2	Hohenberg-Kohn (HK) Formalism . . . . .	6
3.4.2.1	First HK Theorem . . . . .	6
3.4.2.2	Second HK Theorem . . . . .	6
3.4.3	Kohn Sham (KS) Formalism . . . . .	6
3.4.3.1	KS Equation . . . . .	6
3.4.3.2	Energy Terms . . . . .	6
3.4.4	Self Consistent Field Calculation . . . . .	6
3.5	Exchange-correlation Functional . . . . .	6
3.5.1	Local Density Approximation (LDA) . . . . .	6
3.5.2	Generalized Gradient Approximation (GGA) . . . . .	6
3.6	Corrections to DFT . . . . .	6
3.6.1	GW Method . . . . .	6
3.6.2	Hybrid Functionals . . . . .	6
3.6.3	Hubbard U Correction . . . . .	6
4	<b>DFT Calculation of Solids . . . . .</b>	<b>7</b>
4.1	Basis Sets . . . . .	7
4.1.1	Plane Wave . . . . .	7

4.1.2	Gaussian Orbital . . . . .	7
4.1.3	Slater type orbitals . . . . .	7
4.2	Pseudopotential Approach . . . . .	7
4.2.1	Freezing the core electrons . . . . .	8
4.2.2	Pseudizing the valence electrons . . . . .	8
4.2.3	Common Pseudopotentials . . . . .	8
4.2.3.1	Norm-Conserving PP . . . . .	8
4.2.3.2	Ultrasoft PP . . . . .	8
4.2.3.3	Projector Augmented Wave . . . . .	8
4.3	Choosing the appropriate Calculation Size . . . . .	8
4.3.1	Use of Supercell . . . . .	8
4.3.1.1	Periodic Boundary Conditions (PBC) . . . . .	8
4.3.2	Use of Reciprocal Space . . . . .	8
4.3.2.1	Reciprocal Lattice . . . . .	8
4.3.2.2	First Brillouin Zone . . . . .	8
4.3.2.3	Irreducible Brillouin Zone . . . . .	8
4.3.3	k-point sampling . . . . .	8
4.3.3.1	Monkhorst-Pack method . . . . .	8
4.3.3.2	Gamma Point Sampling . . . . .	8
4.4	Bloch Representations . . . . .	10
4.4.1	Electrons in solid . . . . .	10
4.4.2	Bloch Theorem in periodic systems . . . . .	10
4.4.3	Fourier Expansion of Bloch representations . . . . .	10
4.4.3.1	Fourier Expansions . . . . .	10
4.4.3.2	Fast Fourier Transformation (FFT) . . . . .	10
4.4.3.3	Kohn-Sham Matrix Representations . . . . .	10
4.5	Plane Wave (PW) Expansion . . . . .	10
4.5.1	Basis Set . . . . .	10
4.5.1.1	Local Basis Set . . . . .	10
4.5.1.2	Plane Wave Basis Set . . . . .	10
4.5.2	Plane Wave Expansion for KS quantities . . . . .	10



4.5.2.1	Charge Density . . . . .	10
4.5.2.2	Kinetic Energy . . . . .	10
4.5.2.3	Effective Potential . . . . .	10
4.6	Electronic Structure . . . . .	10
4.6.1	Band Structure of free electrons . . . . .	10
4.6.2	Band Structure of electrons in solids . . . . .	10
4.6.3	Electronic Density of States . . . . .	10
4.7	Practical Aspects . . . . .	10
4.7.1	Energy Cutoffs . . . . .	10
4.7.1.1	Cutoff for Wavefunction . . . . .	10
4.7.1.2	Cutoff for Charge Density . . . . .	10
4.7.2	Smearing . . . . .	10
4.7.2.1	Gaussian Smearing . . . . .	10
4.7.2.2	Fermi Smearing . . . . .	10
4.7.2.3	Methfessel–Paxton Smearing . . . . .	10
<b>5</b>	<b>Software Implementation . . . . .</b>	<b>11</b>
5.1	QUANTUM ESPRESSO . . . . .	11
5.1.1	MKL Libraries . . . . .	11
5.1.2	PWSCF routines . . . . .	11
5.2	Intel Compilers . . . . .	12
5.3	Executables . . . . .	12
5.4	Computational Details . . . . .	12
5.4.1	Convergence Testing . . . . .	12
5.4.2	Hubbard correction parameters . . . . .	12
5.4.3	Supercell creation . . . . .	12
5.4.4	Slab Model . . . . .	12
5.4.5	Structural relaxation . . . . .	12
5.4.6	scf calculation . . . . .	12
5.4.7	bandstructure calculation . . . . .	12
5.4.8	dos calculation . . . . .	12

REFERENCES . . . . .	13
----------------------	----

## APPENDIX

A . . . . .	15
B . . . . .	17
C . . . . .	18
D . . . . .	19
E . . . . .	20

# LIST OF TABLES

# LIST OF FIGURES

A.1	Cost per raw megabase of DNA sequence from 2001 to 2015 . . . . .	15
A.2	Cost per raw megabase of DNA sequence from 2001 to 2015 . . . . .	16
B.1	Cost per raw megabase of DNA sequence from 2001 to 2015 . . . . .	17
C.1	Cost per raw megabase of DNA sequence from 2001 to 2015 . . . . .	18
D.1	Cost per raw megabase of DNA sequence from 2001 to 2015 . . . . .	19
E.1	Cost per raw megabase of DNA sequence from 2001 to 2015 . . . . .	20

## **Dedication**

This dissertation/thesis is dedicated to my mother and father who  
provided both emotional and financial support

# Chapter One

## INTRODUCTION

### 1.1 Purpose and Motivation

Describe the importance of defects in ZnO

### 1.2 Objectives

Study the mechanisms of different defects in ZnO

### 1.3 Outline

This is an example of how to cite [1]

# Chapter Two

## Review of Related Literature

### 2.1 Semiconductors

#### 2.1.1 Properties

#### 2.1.2 Applications of Semiconductors

#### 2.1.3 Defects in Semiconductors

### 2.2 Zinc Oxide

describe ZnO in broad perspective

#### 2.2.1 Crystal Structure

Consider different phases

**2.2.2 Crystallographic Directions and Planes**

**2.2.3 Brillouin Zone Symmetry**

**2.2.4 Photoluminescence Properties**

**2.2.5 Defects**



# Chapter Three

## THEORETICAL FRAMEWORK

### 3.1 Electronic Structure

#### 3.1.1 Electronic Bandstructure

##### 3.1.1.1 Bloch Wavefunctions

insert the symmetry points in IBZ.

#### 3.1.2 Density of States

explains fermi dirac distribution

#### 3.1.3 Projected Density of States

### 3.2 Many-body Quantum Mechanics

insert text here



### 3.2.1 Time Independent Schrödinger Equation

### 3.2.2 Simplifying Assumptions

### 3.2.3 Use of Atomic Units

### 3.2.4 Hamiltonian Operator

### 3.2.5 Indistinguishability of electrons

## 3.3 Early First Principle Calculations

### 3.3.1 n-electron problem

### 3.3.2 Hartree Method

### 3.3.3 Hartree-Fock Method

## 3.4 Density Functional Theory

### 3.4.1 Electron Density

### 3.4.2 Hohenberg-Kohn (HK) Formalism

#### 3.4.2.1 First HK Theorem

#### 3.4.2.2 Second HK Theorem

### 3.4.3 Kohn Sham (KS) Formalism

#### 3.4.3.1 KS Equation

#### 3.4.3.2 Energy Terms

### 3.4.4 Self Consistent Field Calculation

## 3.5 Exchange-correlation Functional

# Chapter Four

## DFT Calculation of Solids

### 4.1 Basis Sets

#### 4.1.1 Plane Wave

#### 4.1.2 Gaussian Orbital

#### 4.1.3 Slater type orbitals

### 4.2 Pseudopotential Approach

This is sample text

4.2.1 Freezing the core electrons

4.2.2 Pseudizing the valence electrons

4.2.3 Common Pseudopotentials

4.2.3.1 Norm-Conserving PP

4.2.3.2 Ultrasoft PP

4.2.3.3 Projector Augmented Wave

## 4.3 Choosing the appropriate Calculation Size

4.3.1 Use of Supercell

4.3.1.1 Periodic Boundary Conditions (PBC)

4.3.2 Use of Reciprocal Space

4.3.2.1 Reciprocal Lattice

4.3.2.2 First Brillouin Zone

4.3.2.3 Irreducible Brillouin Zone

4.3.3 k-point sampling

4.3.3.1 Monkhorst-Pack method

4.3.3.2 Gamma Point Sampling

Example of double quotes “word”. Lore



## 4.4 Bloch Representations

### 4.4.1 Electrons in solid

### 4.4.2 Bloch Theorem in periodic systems

### 4.4.3 Fourier Expansion of Bloch representations

#### 4.4.3.1 Fourier Expansions

#### 4.4.3.2 Fast Fourier Transformation (FFT)

#### 4.4.3.3 Kohn-Sham Matrix Representations

## 4.5 Plane Wave (PW) Expansion

### 4.5.1 Basis Set

#### 4.5.1.1 Local Basis Set

#### 4.5.1.2 Plane Wave Basis Set

### 4.5.2 Plane Wave Expansion for KS quantities

#### 4.5.2.1 Charge Density

#### 4.5.2.2 Kinetic Energy

#### 4.5.2.3 Effective Potential

## 4.6 Electronic Structure

### 4.6.1 Band Structure of free electrons

### 4.6.2 Band Structure of electrons in solids

### 4.6.3 Electronic Density of States

## 4.7 Practical Aspects

# Chapter Five

## Software Implementation

### 5.1 QUANTUM ESPRESSO

#### 5.1.1 MKL Libraries

#### 5.1.2 PWSCF routines

cbands, cegterg, cdiaghg



## 5.2 Intel Compilers

## 5.3 Executables

## 5.4 Computational Details

### 5.4.1 Convergence Testing

### 5.4.2 Hubbard correction parameters

### 5.4.3 Supercell creation

### 5.4.4 Slab Model

### 5.4.5 Structural relaxation

### 5.4.6 scf calculation

### 5.4.7 bandstructure calculation

### 5.4.8 dos calculation

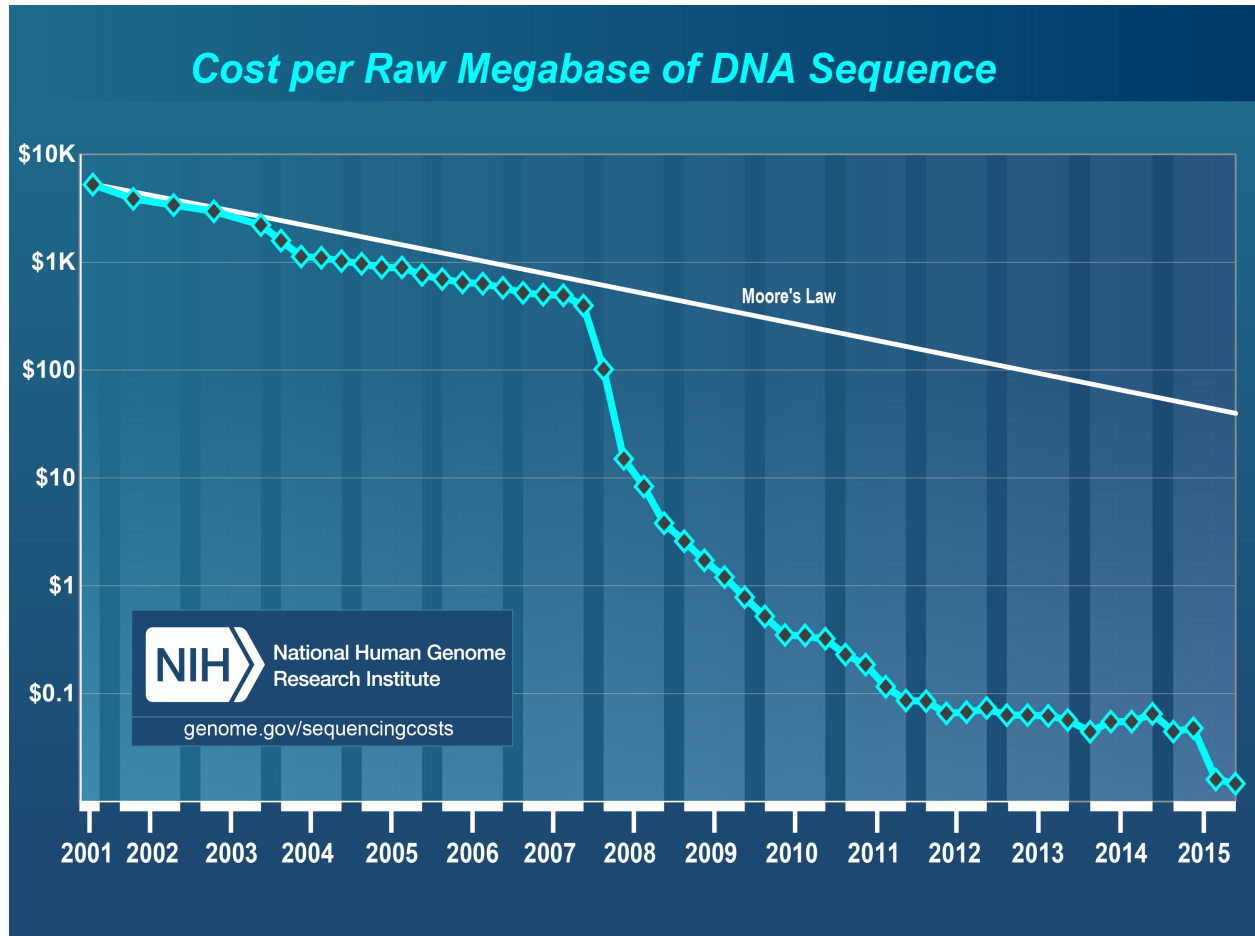
DOST COARE

# REFERENCES

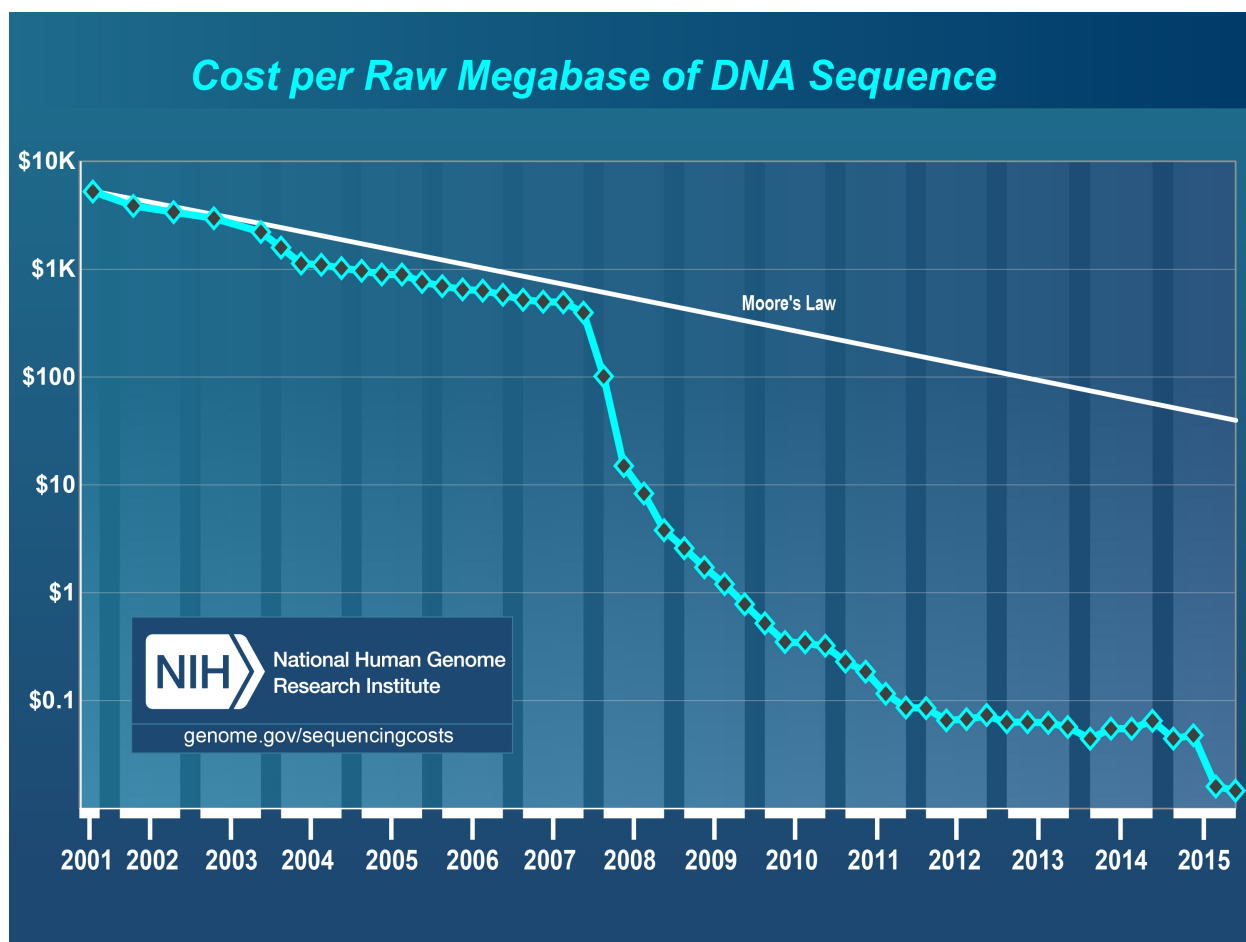
1. Prades, J. D., Cirera, A. & Morante, J. R. Ab initio calculations of NO<sub>2</sub> and SO<sub>2</sub> chemisorption onto non-polar ZnO surfaces. *Sensors and Actuators, B: Chemical* **142**, 179–184 (1 Oct. 2009).
2. Wetterstrand, K. A. *DNA Sequencing Costs: Data from the NHGRI Genome Sequencing Program (GSP)* [www.genome.gov/sequencingcosts](http://www.genome.gov/sequencingcosts).

## APPENDIX

# Appendix A

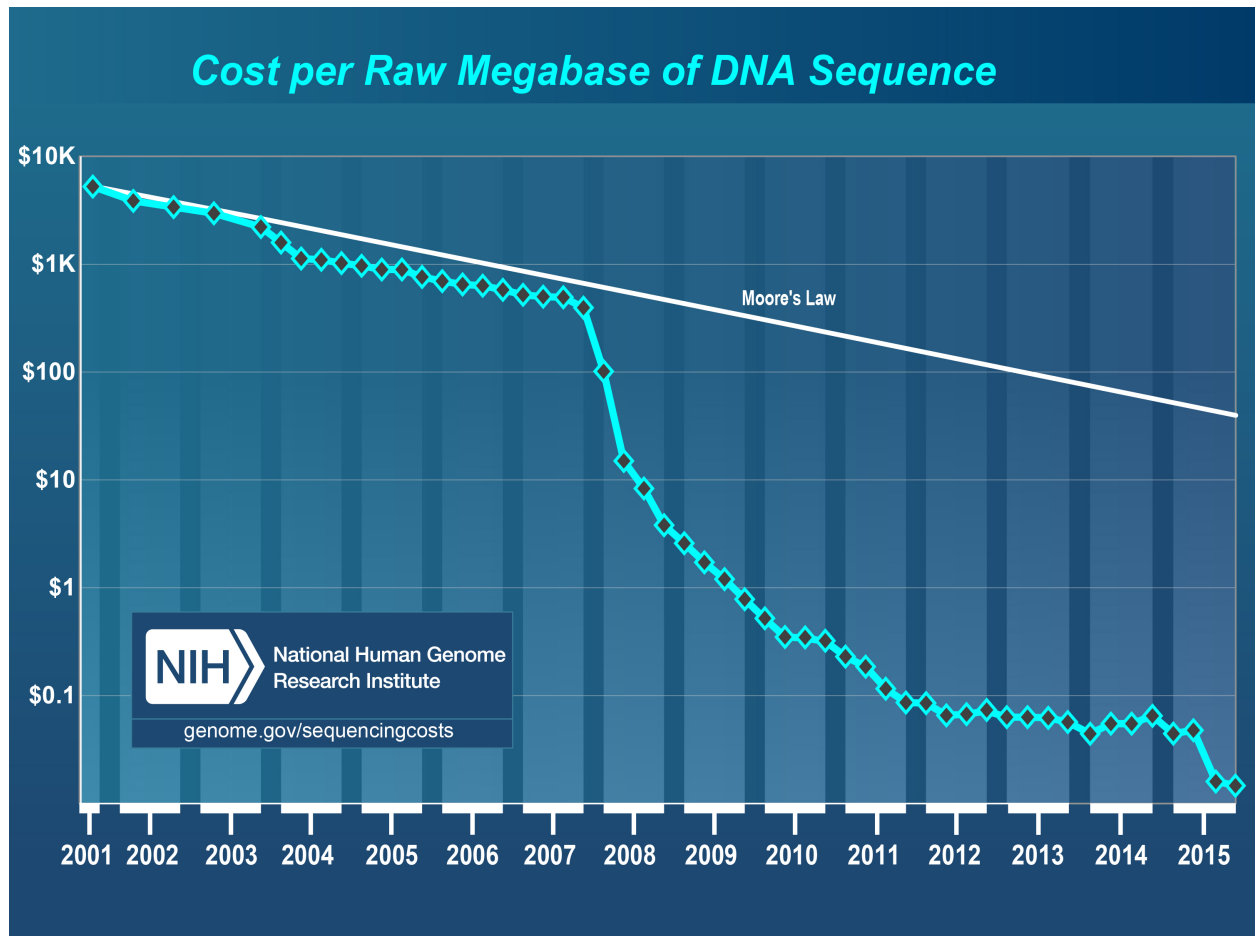


**Figure A.1** Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]



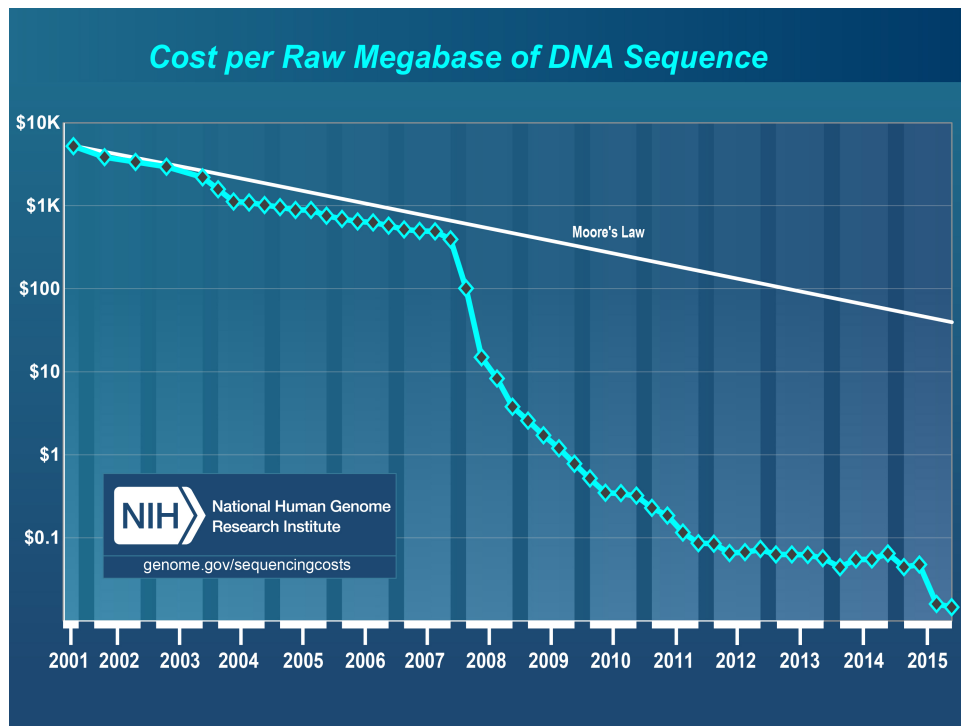
**Figure A.2** Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]

## Appendix B



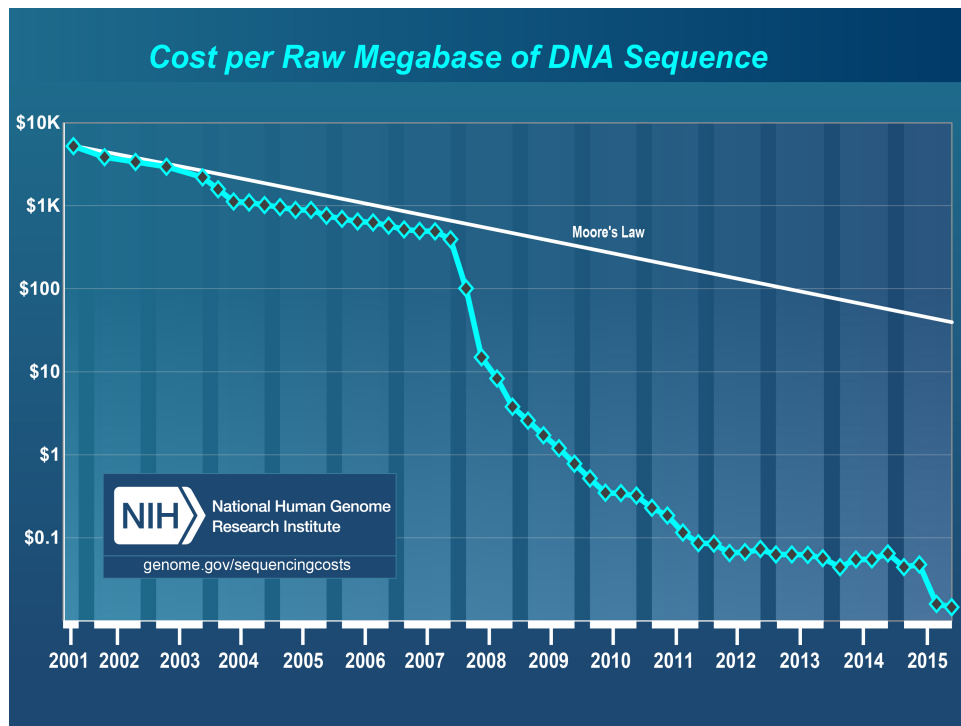
**Figure B.1** Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]

# Appendix C



**Figure C.1** Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]

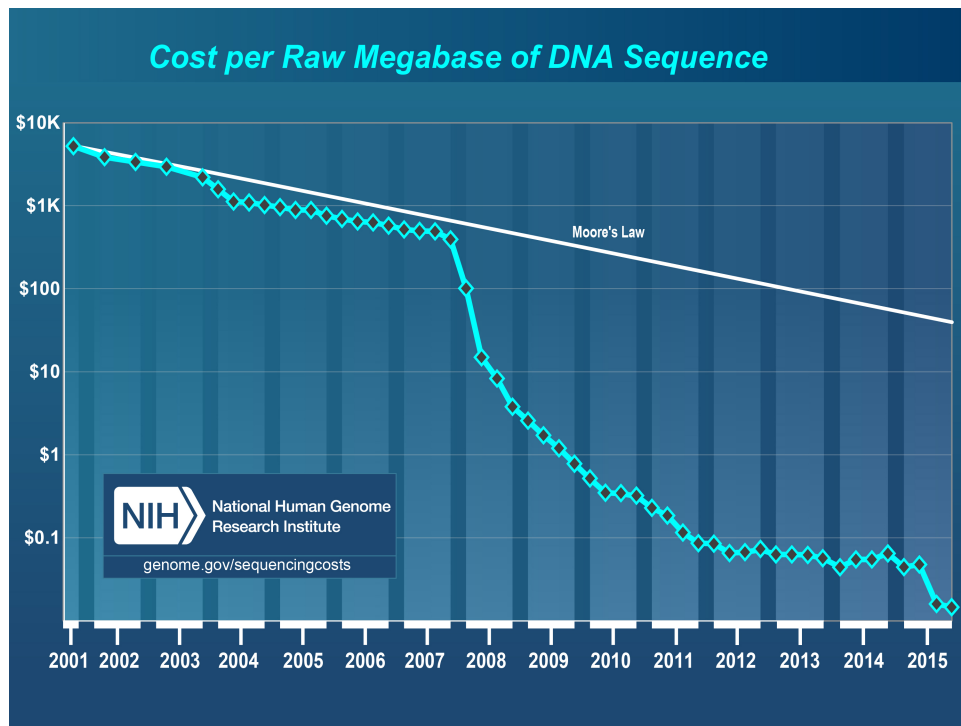
## Appendix D



**Figure D.1** Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]



# Appendix E



**Figure E.1** Cost per raw megabase of DNA sequence from 2001 to 2015. Straight line - Moore's Law, blue curve - cost in US dollars, Y-axis scale is logarithmic. Graph reproduced from [2]