A Concise Course on Advanced Quantum Mechanics

Liu Lianshou Yu Meiling Zhu Yan

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Responsible Editors: Gao Rong, Fang Yang

This book covers the main topics of modern advanced quantum mechanics in a concise way. It meets the requirement of the graduate students who plan to specialize in various fields of physics, e.g. theoretical physics, high energy physics, nuclear physics, condensed matter physics, atomic and molecular physics, optics, astrophysics and etc. It is for use in a one-semester graduate course. The main concepts, theorems and applications of quantum mechanics are written in the text, while most of the derivations are put in the exercises. Hints are given for selected exercises.

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Preface

I have been teaching the course Advanced Quantum Mechanics to graduate students at Huazhong Normal University since 1984. Using various textbooks published inside and/or outside China as references, I was able to assemble together a few topics, such as coherent state, WKB approximation, wave-packet scattering, Lippmann-Schwinger equation, etc for the graduate course that were not already covered by the undergraduate Quantum Mechanics course. The idea of writing a new book first emerged in 2003 under the encouragement of my students, especially Ms. Xiaoyan Lin. A first version of this book appeared in 2004 and was printed for the graduate course to use. From then on the book was revised and printed every year for the course. After several teaching-revision cycles, it is now ready for publication.

Advanced quantum mechanics is a basic course for the graduate students who plan to specialize in various fields of physics, e.g. theoretical physics, high energy physics, nuclear physics, condensed matter physics, atomic and molecular physics, optics, astrophysics, etc. Taking this diversity of specialities into account, in addition to constructing a strict scientific framework for quantum mechanics, the present manuscript covers a comparatively wide range of topics.

Starting from the experimentally observed wave-particle duality of microscopic system, the Hilbert space is introduced naturally. With the exception of the basic principles of quantum mechanics, no other assumption or "principle" is represented directly and simply by writing. In particular, the physical quantities, such as momentum, angular momentum, are not given through writing out manually their operators in some special representation, e.g. coordinate representation, but are defined through their commutators, starting from their fundamental property of being generators of continuous space transformation. The "uncertainty principle", "Pauli incompatibility principle" are no longer principles, but are derivable theorems in quantum mechanics.

There are already quite a number of textbooks for advanced quantum mechanics available. What is the peculiarity of this book that makes it worthy of publication? We have the following considerations.

(1) In studying advanced quantum mechanics, different specialities have somewhat different interest. Take coherent state as an example, students specializing in optics are more interested in the displacement state and squeezed state, while those specializing in high energy physics pay more attention to the coherent states as basis

for expanding quantum state, i.e. the integral-function representation, because it is the base of field quantization. As a basic course, advanced quantum mechanics has to account for the requirements from various specialities.

(2) As the first physics course that the students encounter in their graduate study, advanced quantum mechanics should not only provide the basic knowledge for their forth-coming courses, but also should train the graduate students in self-studying and in mastering English reading and writing, both of which are important for their future physics study and research.

Due to the above considerations we wrote this book in English and covered a comparatively wide range of topics to meet the different demands of various fields. In order to motivate the students to become more independent in learning and also to cover more material in a one-semester course, only the main ideas and methods are written in the text and most of the derivation and proofs are embedded in the exercises. Hints are given for some relatively difficult exercises.

The study of quantum mechanics using this textbook has to be carried out in an interactive way. For the learning to be effective, it is essential that the students take the course actively. In teaching this course, I have always make it a priority to elicit the student's go-aheadism. The questions, comments and recommendations from the students play an important role in finalizing this manuscript. Among the students who have contributed most, Ms. Zhu Yan is one of them. She also compiled the Index. Moreover, Dr. Yu Meiling, a postdoc at Wuhan University, proposed a number of valuable suggestions and comments, and constructed the Hints to Selected Exercises. The manuscript is well finalized under the effective cooperation among the three of us.

I hope that this book may be of some use for the students learning advanced quantum mechanics. Further comments and/or suggestions are heartily welcomed.

Liu Liangshou

April 20, 2009
in Wuhan

Contents

Chapter 1

Quantum states and physical quantities

Experiments show that microscopic particles possess the special property of *particle-wave duality.* They are *particles* in the sense that all their measurable quantities are those of particles, *e.g.* mass, charge, energy, momentum, angular momentum, *etc.* . However, they are not classical particles, because for them the results of measurement are in general probabilistic instead of deterministic. Furthermore, while propagating they can interfere and/or diffract, showing a typical *wave* property. The experimentally observed particle-wave duality is the base of the axioms of quantum mechanics.

1.1 Quantum states as linear vectors in Hilbert space

1.1.1 *Quantum states as linear vectors*

Waves can interfere and/or diffract because they posses the property of *superposition* — two or more waves can exist simultaneously in a same space region. This can be easily checked. For example, in the classroom there are simultaneously electromagnetic waves emitted by various radio-stations. Superposition is the characteristic property of waves.

Microscopic systems, having wave property, obey the *principle of superposition* .

Definition 1.1.1 One or several microscopic particles, together with the interaction between them and the external field in which they are moving, is referred to as a *microscopic system.* A microscopic system may have a certain boundary and the boundary condition is included in its definition.

Definition 1.1.2 The *principle of superposition* can be stated as: if ψ_a and ψ_b are two possible states of a microscopic system, then

$$\psi = c_a\psi_a + c_b\psi_b \tag{1.1.1}$$

is also a possible state of this microscopic system, where c_a and c_b are two constants.

Since ψ_a, ψ_b, $\cdots$ are not directly measurable, c_a, c_b, $\cdots$ are in general complex numbers.

Mathematically, Eq. (1.1.1) means that the set of all possible states of a microscopic system forms a *complex linear space.* The generally accepted symbol, and also

the most convenient one, for the state vector of microscopic system in the corresponding linear vector space is that proposed by Dirac — $|a\rangle$, $|b\rangle$, $\cdots$, which are referred to as *ket vectors.*

These vectors are not directly measurable. What can be measured is the *scalar product* of vectors. In order to account for the fact that measurable quantities could only take real values, we define the *conjugate vectors* of $|a\rangle$, $|b\rangle$, $\cdots$ as

$$|a\rangle^\dagger = \langle a|, \quad |b\rangle^\dagger = \langle b|, \quad \cdots, \tag{1.1.2}$$

which are called *bra vectors.* For a certain microscopic system the set of bra vectors forms a linear vector space conjugate to the space formed by the corresponding ket vectors.

Note that the symbol † (pronounced as "dag") is different from the symbol $*$ (pronounced as "star") of *complex conjugate.* Complex conjugate $*$ concerns complex numbers only, while † concerns state vectors and operators (see below) and is referred to as *Hermitian conjugate.* The Hermitian conjugate of a complex number is just its complex conjugate.

Definition 1.1.3 The *product* of the state vectors of two states a and b, denoted by $\langle a|b\rangle$, is a complex number, linearly dependent on both $\langle a|$ and $|b\rangle$.

A main rule for the *Hermitian conjugate of product* is that: *the Hermitian conjugate of a product of several objects is equal to the product of the Hermitian conjugates of the objects in reverse order.* From this rule we have

$$\langle a|b\rangle^* = [(\langle a|)\,(|b\rangle)]^\dagger = (|b\rangle)^\dagger\,(\langle a|)^\dagger = \langle b|a\rangle, \tag{1.1.3}$$

and, consequently, $\langle a|a\rangle = \langle a|a\rangle^*$ is a positive-definite real number. The physical meaning of this positive-definite real number is that, its square root $\sqrt{\langle a|a\rangle}$, which is referred to as the *norm* of the vector $|a\rangle$, is the probability of finding a particle in the state $|a\rangle$.

If the microscopic system in consideration consists of only one particle, we should have

$$\langle a|a\rangle = 1. \tag{1.1.4}$$

This is called the *normalization condition* of the state vector $|a\rangle$.

1.1.2 *Axiom of quantum mechanics concerning quantum states*

Consider a one-particle system. Its state vector should be normalized to unity. In case $\langle a|a\rangle = N \neq 1$, we can take another vector $|a'\rangle = \sqrt{1/N}\,|a\rangle$ as the state vector, so that $\langle a'|a'\rangle = 1$. This procedure is called the *normalization* of state vector.

A state vector $|a\rangle$ is normalizable if and only if $\langle a|a\rangle$ is finite

$$\langle a|a\rangle < \infty. \tag{1.1.5}$$

Every physically meaningful state vector should be normalizable, therefore, all the vectors in the complex linear space that describe the states of a microscopic system should satisfy the condition (1.1.5). Such a complex linear space is referred to as

the *Hilbert space* corresponding to the microscopic system. The axiom of quantum mechanics concerning quantum states is:

Axiom I *The states of a microscopic system are described by the vectors in the Hilbert space corresponding to the system.*

Since only the scalar product $\langle a|a\rangle$ of a state vector $|a\rangle$ and its Hermitian conjugate $\langle a|$ is measurable, and multiplying $|a\rangle$ by a complex number $e^{i\varphi}$ with unit norm does not affect the scalar product $\langle a|a\rangle$, the vectors $|a\rangle$ and $e^{i\varphi}|a\rangle$, where φ is an arbitrary real number, describe the same quantum state. Therefore, *a quantum state vector is determined within an arbitrary phase.* This statement is valid only for a single state vector. If there are several state vectors then we have only the freedom to multiply them by a global phase factor, while the relative phase between different state vectors are physically relevant and cannot be arbitrarily changed.

The following two definitions are useful:

Definition 1.1.4 Two vectors $|a\rangle$ and $|b\rangle$ are said to be *parallel* to each other if

$$|a\rangle = c\,|b\rangle, \tag{1.1.6}$$

where c is a constant.

Definition 1.1.5 Two vectors $|a\rangle$ and $|b\rangle$ are said to be *perpendicular* or *orthogonal* to each other if

$$\langle a|b\rangle = 0. \tag{1.1.7}$$

1.2 Physical quantities as operators in Hilbert space

1.2.1 *Eigenvalue and eigenvector of Hermitian operator*

An operator F in a Hilbert space is defined by its action on the vectors in the space

$$F\,|a\rangle = |b\rangle. \tag{1.2.1}$$

If this relation is given for every vector $|a\rangle$ in the space, then the operator F is defined.

In general, when an operator F acts on a vector $|a\rangle$ it changes the direction of this vector, *i.e.* $F|a\rangle$ is in general unparallel to $|a\rangle$. But there exist some special directions in the space, when a vector points along these directions, the action of the operator F does not change the direction of this vector. We have the definition.

Definition 1.2.1 If

$$F\,|i\rangle = f_i\,|i\rangle, \tag{1.2.2}$$

where f_i is a number, then $|i\rangle$ is an *eigenvector* of the operator F and f_i is the corresponding *eigenvalue.*

Some other definitions concerning the operators follow.

Definition 1.2.2 An operator F is *linear* if it obeys the following relation:

$$F(c_a|a\rangle + c_b|b\rangle) = c_a F|a\rangle + c_b F|b\rangle, \tag{1.2.3}$$

where c_a and c_b are complex numbers.

Definition 1.2.3 The sum $F+G$ and product FG of two linear operators F and G are defined by their action on vectors:

$$(F+G)\,|a\rangle = F\,|a\rangle + G\,|a\rangle, \tag{1.2.4}$$

$$(FG)\,|a\rangle = F\,(G\,|a\rangle), \tag{1.2.5}$$

where $|a\rangle$ is an *arbitrary* vector.

We see that the *product* of two operators is essentially the successive operation of these two operators. In general, the successive operation of two operators and the same in reverse order are unequal, *i.e.* in general $F\,(G\,|a\rangle) \neq G\,(F\,|a\rangle)$. For this reason, the product of two operators is in general non-commuting, *i.e.* in general $FG \neq GF$.

Let us compare the set of complex numbers and the set of linear operators. Summation and multiplication are both defined in these two sets but the multiplication of two complex numbers is always commuting while that of two operators is in general non-commuting. In this sense the complex numbers are referred to as *c-numbers* while operators as *q-numbers*.

The axiom of quantum mechanics concerning physical quantities is that *the physical quantities of a microscopic system are represented by linear operators in the corresponding Hilbert space.*

The full content and meaning of this statement will be explored in subsection 1.2.3. Here we only point out an important issue: *The result of the measurement of a physical quantity F in the state $|a\rangle$ of a microscopic system is probabilistic. The corresponding average value, or expectation value, is*

$$\bar{F}^{(a)} = \langle a|F|a\rangle. \tag{1.2.6}$$

This value must be a real number, so we must have

$$\langle a|F|a\rangle = \langle a|F|a\rangle^* = \langle a|F|a\rangle^\dagger = |a\rangle^\dagger F^\dagger \langle a|^\dagger = \langle a|F^\dagger|a\rangle.$$

Since $|a\rangle$ is an arbitrary vector, this requirement leads to $F = F^\dagger$, *i.e.* F must be equal to its own Hermitian conjugate.

Let us give the definition concerning different kinds of operator.

Definition 1.2.4 If

$$F^\dagger = F, \quad G^\dagger = -G, \quad U^\dagger = U^{-1}, \tag{1.2.7}$$

where U^{-1} is the inverse operator of U defined by

$$UU^{-1} = U^{-1}U = \mathbf{1}, \tag{1.2.8}$$

then F is referred to as *Hermitian self-conjugate* operator or *Hermitian* operator for short; G is *anti-Hermitian* operator; and U is referred to as *unitary* operator.

Therefore, the axiom of quantum mechanics concerning physical quantities stated above can be expressed more precisely as: *the physical quantities of a microscopic system are represented by Hermitian self-conjugate operators* (or *Hermitian operators* for short) *in the corresponding Hilbert space.*

Before explaining further the contents of this axiom, let us first give a number of important theorems concerning Hermitian operators.

Theorem 1.2.1 *The eigenvalues of a Hermitian operator are real numbers.*

Proof. Multiplying Eq. (1.2.2) from the left by $\langle i|$, we get

$$\langle i|F|i\rangle = \langle i|f_i|i\rangle = f_i\langle i|i\rangle = f_i,$$

which shows that the eigenvalue f_i of an operator F equals the average value of F in the eigen-state $|i\rangle$. Since average values of a Hermitian operator are real, its eigenvalues are real too. □

Theorem 1.2.2 *The eigenvectors of a Hermitian operator corresponding to different eigenvalues are orthogonal.*

Proof. Suppose $F|i\rangle = f_i|i\rangle$, $F|j\rangle = f_j|j\rangle$ and $f_i \neq f_j$. Multiply the two equations from the left by $\langle j|$ and $\langle i|$, respectively,

$$\langle j|F|i\rangle = f_i\langle j|i\rangle, \quad \langle i|F|j\rangle = f_j\langle i|j\rangle.$$

Take the Hermitian conjugate of the first equation and minus the second one. Noticing $F^\dagger = F$, $f_i^* = f_i$, we get $0 = (f_i - f_j)\langle i|j\rangle$. Since $f_i \neq f_j$, the result $\langle i|j\rangle = 0$ follows, *i.e.* $|i\rangle$ and $|j\rangle$ are perpendicular to each other. □

Sometimes, there are several eigenvectors corresponding to one eigenvalue.

Definition 1.2.5 If there are more than one eigenvectors corresponding to one eigenvalue, then this eigenvalue is said to be *degenerate.*

Theorem 1.2.3 *Any linear combination of the different eigenvectors corresponding to a degenerate eigenvalue is still an eigenvector corresponding to the same eigenvalue.*

Proof. Since the eigenvalue equation (1.2.2) is linear, the validity of the theorem is evident. □

In case the eigenvalue f_i is degenerate, there are more than one eigenvectors corresponding to this eigenvalue. Through linear combination we get an infinite number of eigenvectors corresponding to the eigenvalue f_i, *i.e. the number of eigenvectors corresponding to a degenerate eigenvalue is infinite.* These eigenvectors constitute a linear vector space, which is a subspace of the Hilbert space of the system in consideration. We call this subspace the *eigen-subspace* corresponding to the eigenvalue f_i. Let m be the dimension of this space, then there are m and no more than m linearly independent vectors in this space. This m independent vectors can be chosen to be mutually perpendicular and normalized. We denote them as $|i,\nu\rangle$, $\nu = 1, 2, \cdots, m$.

Definition 1.2.6 The dimension of the subspace corresponding to a degenerate eigenvalue is called the *degree of degeneration* of this eigenvalue.

We have the theorem:

Theorem 1.2.4 *Corresponding to a degenerate eigenvalue f_i of degree m there are m mutually perpendicular and normalized eigenvectors $|i,\nu\rangle$, $\nu = 1,2,\cdots,m$, which form an orthogonal base of the subspace corresponding to this eigenvalue.*

A very useful property of *Hermitian operators* is:

Theorem 1.2.5 *Hermitian operators can act on their eigenvectors either from the left or from the right,*

$$\text{if } F^\dagger = F, \text{ then } F|i\rangle = f_i|i\rangle, \quad \langle i|F = \langle i|f_i. \tag{1.2.9}$$

Note that the last equation does not hold for non-Hermitian operators.

Exercise 1.2.1 Prove Eq. (1.2.9).

1.2.2 *Orthogonal-normalization condition of eigenvectors*

From Theorems 1.2.2, 1.2.4, we see that for any Hermitian operator a system of mutually perpendicular and normalized eigenvectors can always be constructed. We can relabel the eigenvectors as $|i\rangle, i = 1,2,\cdots$. This set of eigenvectors satisfy the following orthogonal-normalization condition

$$\langle i|j\rangle = \delta_{ij}, \tag{1.2.10}$$

where

$$\delta_{ij} = \begin{cases} 0, & i \neq j, \\ 1, & i = j \end{cases} \tag{1.2.11}$$

is the Kronecker delta-symbol.

The orthogonal-normalization condition (1.2.10) holds true for the microscopic system moving in a finite volume V. Sometimes the volume V is so large, *e.g.* being a macroscopic volume, then we can take it as infinite. In such case, the spectrum of eigenvalues becomes continuous, and the eigenvalue equation reads

$$F|f\rangle = f|f\rangle. \tag{1.2.12}$$

and, correspondingly, the orthogonal-normalization condition becomes

$$\langle f|f'\rangle = \delta(f - f'), \tag{1.2.13}$$

where

$$\begin{cases} \delta(f - f') = \begin{cases} 0, & f \neq f', \\ \infty, & f = f', \end{cases} \\ \int \delta(f - f')\,\mathrm{d}f' = 1 \end{cases} \tag{1.2.14}$$

is the Dirac δ function.

Some important formulae related to Dirac δ function follow.

$$\int_{-\infty}^{\infty} f(x)\delta(x-x_0)\,\mathrm{d}x = f(x_0). \tag{1.2.15}$$

$$\delta(x-x') = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}k(x-x')}\,\mathrm{d}k. \tag{1.2.16}$$

$$\delta(x) = \lim_{\varepsilon\to 0}\frac{1}{\pi}\frac{\varepsilon}{x^2+\varepsilon^2} = \lim_{\varepsilon\to 0}\frac{1}{2\pi\mathrm{i}}\left(\frac{1}{x-\mathrm{i}\varepsilon}-\frac{1}{x+\mathrm{i}\varepsilon}\right). \tag{1.2.17}$$

$$\lim_{\varepsilon\to 0}\frac{1}{\omega\pm\mathrm{i}\varepsilon} = \mathrm{P}\frac{1}{\omega}\mp\mathrm{i}\pi\delta(\omega), \tag{1.2.18}$$

where P is the symbol of *Cauchy principal value*, which avoids the pole on the integration path along real axis symmetrically,

$$\int_{-\infty}^{\infty} f(\omega)\mathrm{P}\frac{1}{\omega-a}\,\mathrm{d}\omega = \lim_{\varepsilon\to 0}\left(\int_{-\infty}^{a-\varepsilon}+\int_{a+\varepsilon}^{\infty}\right)\frac{f(\omega)}{\omega-a}\,\mathrm{d}\omega. \tag{1.2.19}$$

Basing on Eq. (1.2.18) a technique of *inserting an infinitesimal imaginary part* $(\pm\mathrm{i}\varepsilon)$ *in denominator* to avoid the pole(s) on the integration path along real axis is developed, which is very useful, in particular, in the quantum theory of scattering, *cf.* Chap 7 below. Let us prove this formula.

Proof. We have

$$\frac{1}{\omega\pm\mathrm{i}\varepsilon} = \frac{\omega}{\omega^2+\varepsilon^2}\mp\frac{\mathrm{i}\varepsilon}{\omega^2+\varepsilon^2}.$$

When $\varepsilon\to 0$ the second term is $\mathrm{i}\pi\delta(\omega)$ and the first term, integrating with $f(\omega)$, yields

$$\begin{aligned}\lim_{\varepsilon\to 0}\int_{-\infty}^{\infty} f(\omega)\frac{\omega}{\omega^2+\varepsilon^2}\,\mathrm{d}\omega &= \mathrm{P}\int_{-\infty}^{\infty} f(\omega)\frac{\omega\mathrm{d}\omega}{\omega^2+\varepsilon^2}+\int_{-\varepsilon}^{\varepsilon} f(\omega)\frac{\omega}{\omega^2+\varepsilon^2}\,\mathrm{d}\omega\\ &= \mathrm{P}\int_{-\infty}^{\infty} f(\omega)\frac{\mathrm{d}\omega}{\omega}+f(0)\int_{-\varepsilon}^{\varepsilon}\frac{\omega}{\omega^2+\varepsilon^2}\,\mathrm{d}\omega.\end{aligned}$$

The last integral vanishes because the integrand is an odd function of ω. □

1.2.3 *Axiom of quantum mechanics concerning physical quantities*

Let us come back to the axiom of quantum mechanics concerning physical quantities.

Axiom II *The physical quantities of a microscopic system are represented by Hermitian self-conjugate operators (or Hermitian operators for short) in the corresponding Hilbert space.*

The full content of this axiom is as the following:

- The *possible values* of the results of any measurement on a physical quantity F in a microscopic system are the *eigenvalues* of the operator F in this system.

This is always true regardless the system is in what state. If the system is in a state $|a\rangle$, then we expand $|a\rangle$ using the orthogonal-normalized eigenvectors of the operator F

$$|a\rangle = \sum_i c_i |i\rangle, \tag{1.2.20}$$

if the spectrum is discrete, or

$$|a\rangle = \int c_f |f\rangle \, \mathrm{d}f, \tag{1.2.21}$$

in case the spectrum is continuous. A measurement on F in the state $|a\rangle$ is equivalent to the measurement of F in the eigenstates $|i\rangle$'s or $|f\rangle$'s of F with different probabilities, and the result obtained is the eigenvalues f_i's or f's with different probabilities.

- The probability (or probability density) for a measurement of F in the state a to get the value f_i (or f) is

$$\mathrm{P}_i^{(a)} = |c_i|^2 \quad \text{or} \quad \mathrm{P}_f^{(a)} = |c_f|^2. \tag{1.2.22}$$

Using the orthogonal-normalization condition of eigenvectors (1.2.10), (1.2.13), it is easy to show that

$$c_i = \langle i|a\rangle, \quad c_f = \langle f|a\rangle. \tag{1.2.23}$$

Exercise 1.2.2 Prove Eq. (1.2.23).

Exercise 1.2.3 Show that $\mathrm{P}_i^{(a)}$ and $\mathrm{P}_f^{(a)}$ defined in Eq. (1.2.22) satisfy the requirement for probability, *i.e.* are both positive definite and normalized to unity.

$$\sum_i \mathrm{P}_i^{(a)} = 1 \quad \text{or} \quad \int \mathrm{P}_f^{(a)} \, \mathrm{d}f = 1. \tag{1.2.24}$$

Exercise 1.2.4 Derive Eq.(1.2.6), $\bar{F}^{(a)} = \langle a|F|a\rangle$, from the axiom stated above.

Before measurement the state can be considered as a superposition of different eigenstates $|i\rangle$ $(i = 1, 2, \cdots)$, *cf.* Eq.(1.2.20). After the measurement we get a *definite* eigenvalue f_i of F, which means that the state has been changed to the corresponding eigenstate $|i\rangle$. This is the last part of Axiom II.

- If when measuring a quantity F in state $|a\rangle$ we get a certain eigenvalue f_i of F, then immediately after the measurement the state changes to the corresponding eigenstate $|i\rangle$.

1.2.4 *Completeness condition of eigenvector system*

The possibility for any state vector $|a\rangle$ to be expanded by the eigenvector system $|i\rangle$ or $|f\rangle$ is due to the *completeness* of this system. Substituting the two equations in (1.2.23) into (1.2.20), (1.2.21), respectively, we get

$$|a\rangle = \sum_i |i\rangle\langle i|a\rangle, \tag{1.2.25}$$