Quantum-mechanical systems in traps and density functional theory

by

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Preface

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Quantum Mechanics

Although classical mechanics succeeds at describing the visual objects of the world to great presicion, it does not function as a general framework for the entire universe. The universe consist, physically, of objects of all scales: From galaxies and black holes, stars and planets, to people and everyday objects, all the way down to electrons and light. Whenever we make a change in the scale of our system, there is a chance that our current set of mechanics will not produce a satisfying result.

The complexity of a given mechanics is usually reflected in the complexity of the systems it can describe; a statement which should prove true in the case of quantum mechanics, when it early in the 20th century came to scientists attention that the building blocks of nature was, and still is, incomprehensibly complex.

2.1 Fundamentals

A quantum mechanical system is described by a statistical ensamble of possible states. Unlike other ensambles in statistical mechanics, an object described by quantum mechanics has the possibility to occupy several physical states simultaneously. Each of these states (i.e. the energy levels of hydrogen) is described by a *wave function*.

The nature of quantum mechanics demands a statistical approach in order to retrieve information about the system. To extract this information, we need the full state of the system, and an *operator* corresponding to the quantity of interest. More on this in section 2.1.4.

Performing a measurement on a system will naturally yield only one value corresponding to the value of one of the constituent physical states. The probability of measuring a spesific value equals the absolute square of it's weight in the superposition [1].

This mathematical model is rigid, and works in the sence that it gives accurate results. How to interpret it physically, however, is a completely different question. We will come back to this topic in more detail in section **??**.

2.1.1 Connection to Classical Mechanics

On one part we have the beautiful framework of classical mechanics, deeply rooted in intuition and logic. One the other part we have quantum mechanics, an abstract nest of concepts like uncertainty and mixed states, resembeling chaos theory more than anything.

Simular to chaos theory, quantum mechanics is not a theory about chaos itself. It is a theory about revealing the patterns, the order, in all the chaos.

The vital link which reveals the order in this chaos is *Ehrenfest's theorem*. It ensures that in the *classical limit*, results from Quantum Mechanics will be in agreement with classical mechanics.

Looking mathematically at it, we do not need the classical limit to get an agreement. The expectation value of any observable quantities, *observables*[1], will follow classical paths, or more precisely:

The classical dynamic equations is valid in quantum mechanics if we replace the classical variables with their corresponding quantum expectation values. [2]

This explains perfectly how Quantum Mechanics was able to remain hidden for so long.

2.1.2   Wave Functions

When describing the properties of a one-dimensional free particle, we are used to refering to a point in phase space. However, the statisctical nature of Quantum Mechanics renders this description useless. If we insisted upon representing the particle in phase space, we would have to i.e. color code the points with an intensity proportianal to the probability of the state. If we did this, we would get something resembeling a smoothed out topographical map.

By projecting this surface on the x-axis, we would get a plot resembling that of a wave streching through space. Hence it is called a *Wave Function*. It has to go to zero at the infinite borders[2], and it has to be *square integrable*[3].

In other words, the wave function, $\psi(x,t)$, describes the probability of the particle to be in a position x at a time t, and it is equal $|\psi(x,t)|^2$, or more precisely

$$P_{a,b} = \int_a^b |\psi(x,t)|^2 dx$$

describes the probability of measuring the particle between a and b [1]. This implies that $P_{infty,\infty} = 1$. If this was not the case, the particle can be measured to not exist. This requirement is called a *normalization* of the wave function.

If we have several states from the same physical system, i.e. the hydrogen atom, they should not only be normalized, but also *orthogonal* with respect to the inner product

$$\langle \psi_i(\vec{r},t), \psi_j(\vec{r},t) \rangle = \int \psi_i(\vec{r},t)^* \psi_j(\vec{r},t) d\vec{r} \overset{!}{=} \delta_{i,j},$$

where the last function is the Kroneker Delta, describing both the normalization criteria and the orhogonality, often abbreviated to *orthonormality*. These criteria imply that a

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[1]Observables in quantum mechanics is not necessarily easily observable (because of the scale). A better definition would perhaps be that observables are quantities whose characteristics is able to manifest in nature.

[2]It is highly improbable that a particle will appear on the other side of the universe.

[3]If it is not, the distribution is not normalizable and the system is not physical.

complete set of states from a system form a basis for the space in which they act, which means that we can expand *any* state in these states, or more precisely

$$\Psi(\vec{r}, t) = \sum_{\text{all states}} c_i \psi_i(x, t).$$

2.1.3 Dirac Notation

The nature of an inner product of superposed wave functions, is the fact that alot of the terms will vanish because of orthonormality. This leaves us in a situation where we seldom have to explisitly calculate the integrals. It is therefore common to use a different notation for states, called the *Dirac* or *Bra-Ket* notation.

The notation is designed to be simple. Starting with the inner product in Eq. 2.1.2, we split it into two parts

$$\langle \psi_i(\vec{r}, t), \psi_j(\vec{r}, t) \rangle \equiv \langle \psi_i | \psi_j \rangle = \langle \psi_j | \times | \psi_j \rangle.$$

The object on the right side of the inner product is called a *Ket*, where as the left one is called a *Bra*[4]. In this formalism, we can treat all of the wave function formalism using the ket as a replacement. What we have actually done is to abstract the case from the spesific coordinate representation of $\vec{r}$.

These kets live in an (infinite dimentional) complete *Hilbert Space*[1], which is an inner product space with the different states as unit vectors along the different axes. It is complete in the sence that for every ket, there is a corresponding bra equal to the *Hermitian conjugate* of the ket

$$\langle \psi | = | \psi \rangle^{\dagger} = \left(| \psi \rangle^* \right)^T, \tag{2.1}$$

which is a complex conjucation in addition to a transpose[5].

The states are equal up to a complex phase[6], and the wave function discussed earlier is nothing but the projection of a key on a position basis

$$\psi(\vec{r}) = \langle \vec{r} | \psi \rangle.$$

With this powerful notation at hand, we can easily show properties such as the *completeness relation* of a set. We start by expanding one state $|\phi\rangle$ in a complete set of different states $|\psi_i\rangle$:

---

[4]Together they make a bracket!

[5]We often represent states as vectors, however, you can define properties such as transposed, eigenvalues, determinants, trace, etc. without using this spesific representation.

[6]Any complex phase vanishes when the inner product is calculated.

$$
\begin{aligned}
|\phi\rangle &= \sum_i c_i |\psi_i\rangle && |\langle\psi_k| \\
c_k &= \langle\psi_k|\phi\rangle && \in \mathbb{C}
\end{aligned}
$$

$$
\begin{aligned}
|\phi\rangle &= \sum_i |\psi_i\rangle \langle\psi_i|\phi\rangle \\
&= \left[\sum_i |\psi_i\rangle \langle\psi_i|\right] |\phi\rangle ,
\end{aligned}
$$

which yields that

$$
\sum_i |\psi_i\rangle \langle\psi_i| = \mathbb{1} \tag{2.2}
$$

for any complete set of states $|\psi_i\rangle$.

2.1.4   Operators and Expectation Values

We can generalize the intergral above to any expectation value by using the standard definitions from statistics. However, we cannot give a value to an operator alone. It needs to act on something. Hence we use *local values* of operators. It is defined as

$$
O_{\text{local}} = \frac{1}{\psi(x,t)}\hat{O}\psi(x,t).
$$

If the wavefunction is an eigenstate of the operator, i.e. that $\hat{O}\psi(x,t) = O_\psi\psi(x,t)$, the local value is simply the eigenvalue. If it is not, the local value is proportional to the overlap between the wavefunction and the eigenstates of $\hat{O}$.

Inserting this formalism into the expectation value integral yields

$$
\begin{aligned}
\langle O \rangle &= \int |\psi(x,t)|^2 O_{\text{local}} dx \\
&= \int \psi(x,t)^* \psi(x,t) \frac{1}{\psi(x,t)}\hat{O}\psi(x,t)dx \\
&= \int \psi(x,t)^*\hat{O}\psi(x,t)dx \tag{2.3}
\end{aligned}
$$

2.1.5   The Schrödinger Equation

2.3

Part II

Results

Chapter 3

Results

3.1 Validating the code

3.1.1 Calculation for non-interacting particles

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[2] J. M. Leinaas, "Non-relativistic quantum mechanics," lecture notes FYS4110.