A developmental research on introducing the quantum mechanics formalism at university level

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Citation for published version (APA):
Chapter 8

The Wave Function: Conceptual Understanding and Procedural Fluency

When learning quantum mechanics, first year chemistry students experience difficulties with basic quantum mechanics concepts such as for instance the wave function. A good understanding of such concepts is important to understand chemical bonding. In an experimental introduction, students were guided to formulate a hypothesis for the wave function based on an analogical reasoning [Koopman, Kaper, & Ellermeijer 2009]. After this introduction the Quantum Chemistry course proceeds with the fundamentals of quantum mechanics and its application in understanding chemical bonding. Teaching goals are that students should (a) have a correct conceptual understanding of the wave function, (b) be able to use this conception of the wave function to explain chemical bonding, and (c) be able to work with the basic, mathematical formalism of quantum mechanics. In this article we focus on the development of the students’ conception of the term wave function during the Quantum Chemistry course. We are interested in the interplay between students’ conceptual understanding of the wave function and procedural fluency in performing calculations involving the wave function [Kilpatrick, Swafford, & Findell 2001]. Three student groups were audio recorded throughout the course and transcripts of their discussion analyzed. In addition, these students were interviewed some time after conclusion of the course. This study shows that conceptual understanding supports procedural fluency in this context. However, students were found to have acquired inappropriate rules of thumb to explain chemical bonding, due to the limited examples they were presented with and misconceptions students appeared to hold of the wave function. The effect of the experimental introduction was found to be disappointing due to a lack of integration with the main course.

The wave function is one of the core concepts in quantum mechanics [Griffiths 2005]. It is also a problematic concept in the sense that it is difficult for students to understand and apply [Styer 1996] Johnston, Crawford, & Fletcher.
Even physicists still debate the foundational aspects of quantum mechanics and its interpretation (Van Kampen, 2008; Henry, 2009; Hobson, 2009). For chemists the wave function is an important concept, as with it chemical bonding can be described accurately (Christoffersen, 1989).

To introduce quantum mechanics to first year university chemistry students, four experimental introductory studio course meetings have been designed and tried out (Koopman, Kaper, & Ellermeijer, 2010). A studio course combines several teaching methods: lecture, computer assisted work, paper and pencil assignments, use of demonstrations and tutorial sessions (Wilson & Jennings, 2000). In the experimental introduction, students are presented with (the results of) relevant experiments that require new concepts in order to explain them. For instance, the double-slit experiment is discussed in three domains: water waves, light and electrons. Aiming at an analogical reasoning, students find a mechanism to describe electron interference based on their knowledge of interfering water waves. In order to account for the pattern that appears behind the double-slit, it was expected that students would introduce an electron wave as hypothesis (Koopman et al., 2009). It was our hope that students’ interpretation of the wave function would more closely follow a scientific one. Furthermore, students might benefit from this in the remainder of the quantum chemistry course. After all: the explanatory strength of quantum chemistry relies on a sound conception of this scientific term. After the experimental introduction (referred to as introduction in the remainder of this article), the course continued with lectures and tutorial sessions using a more conventional teaching approach. In this conventional part, the principles of quantum mechanics are discussed and then applied in a chemical context to explain chemical bonding. The teaching objectives for the quantum chemistry course are that students should

- have a correct conceptual understanding of the wave function;
- be able to use this conception of the wave function to explain chemical bonding; and
- be able to work with the basic, mathematical formalism of quantum mechanics.

These objectives revolve around conceptual understanding and applying the wave function in mathematical calculations, which are well described by the first two of five strands of mathematical proficiency:

1. **conceptual understanding** – comprehension of mathematical concepts, operations, and relations,
2. **procedural fluency** – skill in carrying out procedures flexibly, accurately, efficiently, and appropriately (Kilpatrick et al., 2001, p. 106)
In our opinion this description holds equally well for what we may call *physics proficiency*, if we substitute *physics concepts* for *mathematical concepts*. Kilpatrick et al. (2001) emphasize that the five strands they define are interdependent for the development of mathematical proficiency. For instance, a student might be procedurally fluent by having memorized a large set of rules. Conceptual understanding might help reduce this set of rules, enabling the student to achieve at a higher level. For this article we are interested in the interplay between these two strands: conceptual understanding and procedural fluency. Our expectation is that a sound conceptual understanding of the term *wave function* is needed in order for students to successfully work with the wave function within the mathematical formalism (procedural fluency). The goal of the experimental introduction was to improve students’ conceptual understanding of the term *wave function*. The remainder of the course introduced the mathematical formalism of quantum mechanics, thus focusing more on procedural fluency. Our research question is:

How does the conceptual understanding of the wave function and procedural fluency in working with the wave function develop during the quantum chemistry course?

In particular, the following questions are of interest, to answer the above question:

1. What conceptual understanding do students have of the wave function
   (a) after the experimental introduction;
   (b) during the conventional course; and
   (c) some time after the course has ended?

2. Are students procedurally fluent enough to perform tasks involving the wave function during the conventional part of the course?

3. What interplay between the two strands (conceptual understanding and procedural fluency) do we observe when students perform conventional tasks that involve the wave function?

The conceptual understanding we hope students will have of the wave function, can be summarized as:

- Electron interference (as seen in the double-slit experiment) can be explained by hypothesizing that an electron can be described by a wave function.
- Electrons do not interfere with each other; waves interfere with each other.
- The wave function determines the probability of finding an electron in a certain region. Quantitatively, the probability density $\rho$ is given by $|\psi|^2$. 

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• The wave function $\psi(x)$ describes one electron. A superposition of two such wave functions is itself a wave function. In other words: a superposition of two such (interfering) wave functions is not a description of two electrons.

Besides answering the above research questions, we would also like to know whether the teaching objectives of the course have been met.

8.1 Methodology

This research was carried out in a running course on quantum chemistry, given to first year chemistry students. The course was divided in three parts:

• The first part was our experimental introduction consisting of four studio course meetings. These meetings followed a guided discovery approach. After this introduction, the conventional course followed.

• Part two introduced the formalism of quantum mechanics.

• Part three applied the formalism of quantum mechanics in a chemical context (quantum chemistry).

Research question 1a, described in the introduction, is answered in earlier work (Koopman et al., 2009). We will summarize the main findings in this article. To answer research questions 1b, 2 and 3, we selected several assignments from the tutorials in which it was expected that students would need their interpretation of the wave function to complete their task. Close to the introductory meetings, students worked with the quantum wave function without a chemical context. The goal of the course was to use quantum theory to understand chemical bonding. Assignments with this chemical context were scheduled at the end of the course, mainly during the last two tutorial sessions. For each tutorial session a number of assignments were scheduled: some originated from the textbook (Atkins & de Paula, 2006), some were written by the lecturer. Students were free to choose their working pace: some prepared their work at home, others started with the assignments during the tutorial sessions. A teacher and two teaching assistants were available to answer questions. Students were expected to finish problems in their own time if the tutorial session was not enough.

To acquire a coherent image of how students reasoned during the course, three student groups, of two students each, were followed during the whole sequence, as introduced in Koopman et al. (2009). The students were randomly selected from the group of first year students majoring in chemistry. The three groups were audio recorded and transcripts of the audio recordings were analyzed to identify the use of the term wave function when working on the selected problems. In addition, written work of the students was collected. The analysis was done independently by two researchers and afterwards compared.
When the interpretations of the researchers did not agree, a reanalysis would follow to find a coherent interpretation.

The composition of the student groups varied slightly during the course. Table 8.1 shows the composition of the three groups during the sessions of interest: the four introductory meetings, the following three tutorial sessions, and the final two tutorial sessions. The students in group 2′ often worked together with S3 from group 2. They were therefore included in the analysis.

To answer research question 1c, a semi-structured interview with the students that had been followed was held some time after the course. The interview focused on how the students had experienced the course and the experimental introduction, as well as on the conception students had of the wave function. The latter was tested by giving students tasks in which they had to reason about the wave function. Because some time had passed after the course, students were not expected, nor required to perform calculations. Students were asked to express their thoughts. The interviewer would try to avoid interfering students’ reasoning, as much as possible. When students fell silent, neutral questions were asked, such as: “Could you tell something more about that”, “What are you thinking about”, or by simply repeating what a student had said last. Only when these question did not give the desired feedback, more directed questions were asked, such as: “What do you mean by …”. Besides advantages, group interviews are known to have disadvantages (Cohen, Manion, & Morrison, 2007, pp. 373-4). For instance, one interviewee might dominate the interview, or might perhaps be shy in front of peers. However, these students were accustomed to working together, and did so voluntarily. Furthermore, answers given by one interviewee were cross-checked by asking the other interviewee to what extent the response given was also valid for him/her.

Table 8.1: Composition of three observed groups during first four introductory meetings (sessions 1-4), the following three tutorials (sessions 5-7) and the final two tutorials (sessions 15 and 16).

<table>
<thead>
<tr>
<th>Group</th>
<th>1</th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<th>15</th>
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<tbody>
<tr>
<td>1</td>
<td>S1</td>
<td>S1</td>
<td>S1</td>
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<td>S2</td>
<td>S1</td>
<td>S2</td>
<td>S8</td>
<td>n/a</td>
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<td>S2</td>
<td>S2</td>
<td>S13</td>
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<td>2</td>
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</tr>
</tbody>
</table>

a Only a few students attended this last session due to a project festival held later that day, for which many students still needed time to prepare.

b S9 and S13 occasionally join group 1 during meeting 4.
8.2 Results

We present the results of the analyzed problems thematically. Transcripts and quotes of student remarks were translated from Dutch. All students, with the exception of S1 and S7 have passed the final exam (i.e. seven out of nine). Table 8.2 lists their exam grades.

Table 8.2: Final exam grades (points out of 10) for the students discussed in this article, average 8.1 ($SD = 1.4$, $N = 7$).
Average grade of the whole group 6.4 ($SD = 2.1$, $N = 32$).

<table>
<thead>
<tr>
<th>group</th>
<th>student</th>
<th>grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S1</td>
<td>n/a</td>
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<tr>
<td></td>
<td>S2</td>
<td>8.7</td>
</tr>
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<td></td>
<td>S13</td>
<td>9.2</td>
</tr>
<tr>
<td>2</td>
<td>S3</td>
<td>8.2</td>
</tr>
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<td></td>
<td>S7</td>
<td>n/a</td>
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<tr>
<td>2'</td>
<td>S9</td>
<td>9.6</td>
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<td></td>
<td>S15</td>
<td>6.1</td>
</tr>
<tr>
<td>3</td>
<td>S5</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>S6</td>
<td>6.1</td>
</tr>
</tbody>
</table>

8.2.1 Interpretation of the wave function after the introduction

During the introduction students S1 and S2 (group 1) showed that they assumed that electron interference can be explained by describing electrons with a wave function. From the experiment whereby the interference pattern is built up with single electrons, the students conclude that electrons do not interfere with each other. This worries them, because they earlier assumed that the interference pattern is caused by interfering electrons. When seeing the build-up of the interference pattern the students note that the electrons seem to hit the screen at random and that the pattern becomes visible over time. It does not become clear whether a probabilistic interpretation of the wave function follows. Nor do we have any evidence whether students interpret the wave function as describing one electron.

In group 2, S3 and S7 seem to agree that the electron interference pattern is explained by describing electrons by a wave. The students do not arrive at the desired conclusion that electrons do not interfere with each other. It does not become clear what their interpretation is of the wave function they assume for electrons. As a result we also do not know whether they see the wave function as a description of an individual electron.

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1As shown in Table 8.1 only students S3 and S7 were followed during the introduction. The other students, S9 and S15, often joined S3, who is the constant factor in this group.
Students S5 and S6 (group 3) clearly use the term *wave* to describe the electron interference pattern in the double-slit experiment. From the build-up of the electron interference pattern they also conclude that electrons do not interfere with each other. They have difficulty in reconciling these two findings with each other, just as group 1. The students agree that the wave function has something to do with the probability of finding an electron at a certain location. They also articulate a qualitative relation between wave function and probability. However, S6 seems to think that one circular wave (as emitted by a slit) describes one electron. She explicitly says an electron surely cannot be two waves, as is needed to describe the interference pattern. At this point it seems that she has an incorrect conception of the wave function, used in the double-slit experiment.

### 8.2.2 Calculations involving the wave function

In the next two sections we discuss two assignments from the tutorial sessions, both concerning a one-dimensional infinite square potential well. We augment these findings with the results from two multiple choice questions given to the students in the interviews, which presents them with a graph of a one-dimensional wave function. Both interview questions are taken from the Quantum Mechanics Visualization Instrument (Cataloglu & Robinett, 2002).

#### Calculating the probability

In this tutorial problem the probability has to be calculated of finding the electron in the ground state (for which $n = 1$) in a certain region in the potential well. The corresponding interview question asks students to calculate the probability of finding an electron in a given region (Figure 8.1).

![Figure 8.1: Interview question: “What is the probability that upon measurement the particle will be found in the range $2a < x < 3a$?"](image)

S2 and S13 were the only students that succeeded in approaching this tutorial problem. S2 recalls that the square of the wave function gives the probability density and S13 adds that next the probability density needs to be integrated. The students agree upon a method and seem confident. In
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In particular, they are not surprised by the problem: to them it seems evident that with a wave function one can calculate a probability. In what follows, most time is spent on calculus (approx. 30 minutes during this meeting, and 45 minutes during the next). They have difficulty finding the integral. When S2 comes up with an answer that is much larger than one, he notes that this is not possible. After some guidance from one of the teaching assistants, S2 finds a negative value and again concludes that this cannot be right, S13 agrees. This shows that they have a sound conception of a probability (e.g. something with a value between zero and one). On the other hand, the calculus skills of these students are not “up to speed”. Also during the interview, these students had no difficulty to determine the probability of finding the electron in a certain region (Figure 8.1). Although at first they just count the number of squares under the graph of $\psi(x)$, S2 notes that a probability is calculated using the square of the wave function. With this they find the right answer.

The students have an appropriate conceptual understanding of the wave function to solve the problem at hand. In particular, from this assignment it becomes clear that they relate the wave function to a probability density. This had not become clear from the introduction. Their conceptual understanding seems to help them formulate a mathematical expression that has to be worked out. We thus conclude that these students are procedurally fluent in the sense that they are able to formulate the expression that has to be calculated, but they are not fluent enough in the sense that the mathematical operations are performed with unexpectedly large effort.

From group 2 there are only results where S3 and S7 work on the tutorial problem (S9 and S15 do not appear on the audio recording). They have no difficulty with the idea of calculating a probability from a wave function. However, they come up with an incorrect method: they seem to calculate the following difference: $\psi(x = 5.05 \text{ nm}) - \psi(x = 4.95 \text{ nm})$, instead of the difference of the primitive of the square of the wave function. In other words: no integration is performed. S3 notes that their method cannot be right, because they have found a figure too large to be a probability. A teaching assistant asks what the relation is between the wave function and the probability density. S3 promptly notes that this should be the square of the wave function. Apparently, S3 needed this extra step to be reminded of probability density and the relation with the wave function. After this, time is up and the students pack their bags. It seems that S3 knows that the wave function squared gives the probability density, but at first he does not use this in calculating the requested probability. Furthermore, it remains unclear whether S3 now also realizes that an integration has to be performed. His conceptual understanding of the wave function is somewhat weak. As a result, connecting this to a successful procedure or calculation proves to be difficult.

Again, the interview results are in line with the above. Calculating the probability to find the electron in a certain region (Figure 8.1), is considered easy by the students. However, they forget to take the square of the wave function and just calculate the area under $\psi$ itself. S3 does mention something
about the square, but he thinks that in this case it will not make any difference.

The audio recording of group 3 for the relevant tutorial session was incomplete and no dialogue on the problem was found. In the written work it was also absent. Probably the students did not work on this problem during the tutorial session. However, the interview results show that these students clearly have difficulties with the questions where they have to apply the wave function to determine a probability. Most striking is that in no way do they apply their knowledge that the square of the wave function is a probability density.

**Most likely locations**

In the second tutorial problem that was selected, the most probable locations of finding an electron in the state where \( n = 3 \) (second excited state) have to be determined. The corresponding interview question asks students to order the probabilities of finding an electron in one of three given regions (Figure 8.2).

![Figure 8.2: Interview question: “Order the probabilities of finding the particle in one of the regions I, II, or III from largest to smallest.”](image)

The students S2 and S13 (group 1) agree that the particle in a box will most likely be found in the locations where \( \psi \) squared is maximal. They shortly discuss how they will find these places, whether they will “prove” it, or just “say” it. With the latter they mean by arguing where the probability density is maximal. They find these places by using the known values for which the sine is one (i.e. maximal). With this they answer the question. The students show their conceptual understanding of the wave function to be consistent. This time they efficiently use their conception to answer the question. This is a productive interaction between conceptual understanding and procedural fluency. During the interview, these students are also able to arrange the probabilities from high to low, for the three given regions.

From group 2, S3 and S7 do not appear on the audio recording. We only have a discussion between S9 and S15. After reading the question, S15 directly answers that the particle in a box will most likely be found in the middle of the box. Although this is one of the locations for the state with \( n = 3 \), it is not
the only location. Apparently, S15 thinks of the state with \( n = 1 \). S9 looks up the values in the back of the book. He next draws the wave function for the \( n = 3 \) state and points at the places where this function is extreme. From this it does not become clear whether he implicitly reasons that the square of the wave function gives the probability density. During the interview, all students (S3, S7, S9, and S15) find the correct order of probabilities (Figure 8.2). They all answer that the probability has to do with the square of the wave function. S9 and S15 add that the area under the graph of the wave function squared then gives the probability. This shows that they conceptually understand that the probability density needs to be integrated to find a probability.

S5 and S6 (group 3) get really stuck with what was expected to be a straightforward question. After reading the question, S6 notes that \( x \)-values should be given (i.e. locations). Then S5 says she thinks it is not possible to answer this. They do not have a clue how to approach this problem and start browsing in the book for formulas that might help them to answer the question. This only makes things more complicated. For instance, they think they can use the expression for the total energy of the particle in a box: 
\[
E_n = n^2 \frac{\hbar^2}{8mL^2}.
\]
Although this expression does not say anything about a location, they try to apply it. They reason that the exercise after all gives \( n \) and \( L \), and \( \hbar \) is a known constant. It is clear that these students are at a loss. They have a feeling they do not know what they are doing.

When the teacher reminds the students to use \( \psi \) squared to calculate the probability, S6 objects by saying that they do not want to calculate a probability. In a sense this is true: the question is to find locations. But the students do not realize that you first have to know the probability (density) as a function of \( x \), to determine the \( x \) where the density is maximal. In a discussion with the researcher, S6 expresses her indignation: how can they be expected to first calculate the probability, when a location is asked for:

\[
\begin{align*}
S6 & \quad \text{[inaudible] they want to know the position, so they want to know } x. \text{ And in principle they want to know } x, \text{ but they do not want you to get } x \text{ from the wave function, no, they want you to get } x \text{ from the square of the wave function and then differentiate. There they want to get } x \text{ from. Yes, I don’t get that. That is what is difficult...} \\
O & \quad \text{This is where the probability is largest to, eh...}
\end{align*}
\]

\[
\begin{align*}
S6 & \quad \text{The most probable location to find it.}
O & \quad \text{But have you made a graph?}
S6 & \quad \text{Yes, look.}
\end{align*}
\]

\[
\begin{align*}
O & \quad \text{But can you point [in that graph] where the most probable location is?}
S6 & \quad \text{But this is already the square?}
O & \quad \text{This is psi, right?}
S6 & \quad \text{Yes, no, this was psi squared I thought.}
O & \quad \text{No, but that is impossible, is this the } x \text{-axis when } y [\psi] \text{ equals zero?}
S6 & \quad \text{This is zero.}
\end{align*}
\]

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8.2. Results

O Yes, psi squared can never get below zero.
S6 Oh, I thought I had drawn psi squared...
O This is psi. [...] And how do you go from psi to probability?
S6 Yes, psi squared is...
O Yes, actually the square of the norm of psi, but this thing is real, so psi squared, OK. Do you have a probability then?
S6 Probability density?
O OK
S6 And there are three peaks, so when you calculate the derivative, then you know where these peaks are.
O That is a possible method, that is good. [...] Or you can say, well, this is a sine, I know when it equals zero, I know that in between...
S6 Yes, you can divide it in segments, segment two, three, and five.
O That is possible as well.
S6 Then you get a sixth L, and a half L, and, what do you call that...
O Five sixth?
S6 Five sixth L is then a maximum, yes, then you precisely get these L... Oh no, get out of here!
O Was this what you had done?
S6 No, but this is a sixth L and the answer is also just L divided by six. Just precisely, what you get by just, just by looking at it.

S6 thinks she had drawn the graph of \( \psi \) squared, but did not notice that the function was negative for some values of \( x \). She does know that \( \psi \) squared represents the probability density, but only after she has been reminded of this by the teacher earlier on. When she sees the graph S6 appears to understand the approach suggested by the teacher, as is apparent from line 24. When the researcher says there is a second method, S6 feels a bit silly, that it appears to be this simple.

The interview shows the same pattern. These students are unable to apply the wave function in the given tasks. Although on other occasions during the interview they have mentioned that the square of the wave function gives the probability density, they do not apply it here.

These results show that the conception S5 and S6 have of the wave function is very weak. They know the relation between wave function and probability density, but had to be reminded of it. Even then did they have difficulties using it to answer the question. We can think of two possible explanations for the observed difficulties. Firstly, the students have to translate “most likely locations” to an object that gives the probability (density) for a given location, i.e. \( |\psi(x)|^2 \). Thus, conceptually, they need to understand that the wave function contains information about most likely locations. Secondly, when this is clear, remaining difficulties might be caused by a lack of transfer from calculus. During the calculus course they have learned to calculate the extrema of a
function of $x$. Now this function represents some physical quantity (i.e. probability density). There is thus possibly both lack of conceptual understanding and procedural fluency.

Together, these results show two things. Firstly, conceptual understanding of what the wave function is and its relation to probability density plays an important role in applying this to perform calculations. Group 1 is most successful at this. Thus in the cases discussed, conceptual understanding is beneficial for procedural fluency. Secondly, although some conceptual understanding is necessary to answer the selected tutorial problems, these problems are set up such that they are easily answered using the recipe like examples in the text book. They thus only very minimally challenge students to review their conception of the wave function. Furthermore, students are focused mainly on finding and giving a numerical answer. This also does not give them the opportunity to review their conception of the wave function. Further on we shall see that this has an effect on students’ understanding of chemical bonding.

### 8.2.3 Student distilled rules to explain bonding

Near the end of the course, quantum mechanics is used to explain bonding. For example, the next problem from the tutorial sessions is on bonding in the HHe$^+$ molecule.

The relevant molecular orbitals of the molecule HHe$^+$ in its equilibrium geometry, are found to be:

\[
\begin{align*}
1\sigma &= 0.877(\text{He1s}) + 0.202(\text{H1s}), \\
2\sigma &= 0.798(\text{He1s}) - 1.168(\text{H1s}).
\end{align*}
\]

a) Characterize both orbitals in terms of their bonding, or antibonding behaviour.

b) How will the molecular orbital energies of the $1\sigma$ and $2\sigma$ orbitals lie when compared to the energies of the He1s and H1s atomic orbitals? Explain!

It is given that both molecular orbitals are normalised.

c) Calculate the overlap integral between the H1s and He1s orbitals.

Results from group 1 are missing. However, results from all other groups show that students use a rule to answer part a) of this problem: the plus combination molecular orbital (MO) is bonding (i.e. $1\sigma$) and the minus combination MO is anti-bonding (i.e. $2\sigma$). While this results in the correct characterization of the MOs, the rule is incorrect. Students seem to have constructed this inappropriate rule based on an example given during one of the lectures. They do

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2 This problem does not originate from Atkins. It was translated from Dutch.
not give the reasoning behind this rule. The problem asked for an explanation. However, such an explanation is not necessary for answering the question, and thus students do not give it. In fact, they seem to find it only annoying having to give an explanation.

The following transcript is representative for the students’ reasoning that we encountered. S3 is falling behind and has more difficulties answering the questions. The teacher (T) has just told him that his answer to part a) is incorrect. Then the researcher (O) starts a discussion with all three students (S3, S9, and S15), by asking which of the orbitals is bonding and which is anti-bonding:

S9 If you add them it is bonding, if you subtract them…
S15 Plus is always bonding and minus is anti-bonding.
O Always?
S9 Well, it was the case in each lecture.
S3 Well, with [lecturer] it was always the case. Right?
O Mmm…
S15 But not with T…
S3 Now with T…
S15 But we have learned it that way…

O You have got to think… […] Why is that plus sign important? Why is it bonding, according to you? Because you can say, yes, plus is bonding or anti-bonding, but why? Maybe that helps to…
S3 Did he [the lecturer] mention this?
S15 Yes, he used a whole lecture, he explained it. This sign, because this is the bonding, I think…
S3 Yes, that is bonding.
O And what is this little graph?

S3 has drawn two 1s-orbitals, one for each atom in the diatomic molecule. From these orbitals he has constructed a plus combination MO, and a minus combination MO. The students and the researcher discuss what is represented in this graph. After some confusion, the students agree that the square of the drawn graphs gives the probability density. Then the researcher asks what the consequence is of a high probability density between the two nuclei (denoted by A and B):

O OK, what does it mean if between the two nuclei A and B there is a high psi?
S15 Well, that it is probably there.
S3 That it is there, yes, that it is there more.
O So actually here you have, on average, much negative charge, and here is plus and there is plus at A and B. What will this do to the atom?
S15 Because if that one is minus, then it is like this... and then he goes, like, down and then he is, yes, this is wrong, and then he is probably not here. But sometimes he is.

O Well, here precisely in the middle not, never, because then he $|\psi|$ is zero in a point, but anyway, here in this region, the probability to find the electron is very low. While it was very high here.

S15 Yes

O But can you use that to explain whether it causes bonding?

S15 Well, if that... I thought that if here the probability density is large, then the probability is also large that the electron is there. And if it is low, then the probability is low that the electron is there.

O Yes, but why does that explain bonding, or anti-bonding?

S15 If the electron is here, then it won’t bond as well?

S3 Yes, then it cannot bond?

O But why would that bond if the electron is there?

S3 Yes, well you need an electron to, eh... [...]

O I just want to know. Why does an electron bond? [...] Is the electron attractive in some way? Or what?

S3 In terms of what? No, seriously, in terms of what?

O That is the question. Because of its Looks... ?

S3 I would really not know, perhaps something like...

O What makes it bind, if there is an electron there?

S15 If they bind, then the energy will be lower, and if they don’t bind...

O OK, OK, but now we are talking about, it’s correct [what you tell me], but now we are talking about [...] the case when you find an electron in between. You try to explain bonding in terms of the place where you will probably find the electron.

S15 Yes

O What is so special about an electron? What can you tell me about an electron?

S9 That it has a negative charge.

O Yes, a negative charge. And its mass is about 1000 times smaller than that of a proton, for example. And what is so special about the nuclei A and B?

S15 Positive

O Yes, and what happens, according to you, if you think of it very classically? If here is something positive at A and B, and in between something negative?

S15 Well, you would say that negative goes to positive, right?

O So if there is this negative charge in the middle, then the nuclei want to go there.
8.2. Results

To show that the students’ rule is insufficient to describe bonding, O next gives an example where a 1s and a 2p$_z$ orbital are combined to form an MO. First O makes sure that the students know what is represented in the density plots of 1s and 2p$_z$ orbitals. Students associate these plots with the probability of finding the electron in a certain region, but do not exactly know how the graphs are generated from the wave function. More importantly, students appear not to know what the meaning is of the plus and minus sign in the 2p$_z$ orbitals. After this meaning has been made clear, O continues to explain what the effect is on the MO of this plus and minus sign in the 2p$_z$ orbital:

O  [...] Suppose that this is the [...] inter nuclear axis, and that we have some kind of atom A over here and an atom B there. [...] 
S15  [...] And then you can have this one, and you can have that there it is like... but if it is like this, then you do have overlap?
O  What is this addition? So this is the 2p$_z$ on A and this the 2p$_z$ on B, and do you add them or subtract them?
S15  So then you subtract them.
O  Yes, this is 2p$_z$ A minus 2p$_z$ B. [...] Is that bonding, or anti-bonding?
S15  I thought it was anti-bonding, but... 
O  Because?
S15  I haven’t got a clue.
S9  Because these planes, the two plus-planes... 
S15  Yes, they overlap, don’t they? Then it is bonding?
O  Yes, we just discussed this, right? This is supposed to be plus, here?
S15  Yeah, or minus, whatever you want.
O  Might as well be minus, right? So plus, if you subtract them, then it looks like this. This means that here, the wave function will get a high amplitude in the molecular orbital. So then there is a high probability density between the nuclei, just like what we saw with the 2p, eh, the 1s orbital.
S15  Yes
O  So now it [the bonding MO] is the minus combination. That is why T was not satisfied with your answer.
S3  Aha!

The transcript shows that students have memorized a rule, based on the explanation of the lecturer, to tell whether an orbital is bonding, or anti-bonding. They are unaware of the reasoning behind the rule. Only when the researcher presses on, are the students able to reproduce the reasoning. Students also do not realize that the rule is inappropriate to describe bonding.
The following two molecular orbitals (wave functions) are given:

\[ \psi_1 = 0.19(1s_H) + 0.98(2p_{z,F}) , \]
\[ \psi_2 = 0.98(1s_H) - 0.19(2p_{z,F}) , \]

With H, the hydrogen atom and F the fluor atom in the following orientation:

1. Explain which of these wave functions is bonding, and which is anti-bonding.

2. Make a sketch of the wave functions.

3. Using the sketch, how can you tell which function is bonding, and which anti-bonding?

4. How might you calculate the energy corresponding to these wave functions?

Figure 8.3: Problem on chemical bonding used in the interview.

when other AOs than 1s orbitals are involved. Furthermore, the transcript also shows that students do not directly think of the physical properties of the electron when asked why bonding occurs (line 41).

So there are conceptual issues, that become apparent when students have to reason with the wave function. Procedural issues do not surface in the original tutorial problem, because the memorized rules lead to the correct characterization of MOs. In the MO used by O as an example, it becomes clear that the rule is inappropriate.

To further investigate the above observation that students seem to use an inappropriate rule to identify bonding and anti-bonding orbitals, the students were given a problem on bonding in the interviews (Figure 8.3). The problem is an adaptation of an example given in Atkins. The orientation is chosen such that in this case the minus combination MO is bonding, while the plus combination is anti-bonding. Note that, contrary to the problem given earlier, overlap between AOs is set to zero (i.e. the Hückel approximation).
Almost all interviewed students identify the plus combination as bonding and the minus combination as anti-bonding. So the rule students used during the tutorial sessions persists after the course has ended. The exception is S6. She thinks the minus combination is bonding because something is subtracted which she thinks will result in a lower energy. When she sees that the coefficients of the MOs are different, she discards this idea. Thus, none of the students are able to correctly identify the bonding, and anti-bonding orbital.

When asked to sketch the MOs, students draw two different representations of the wave function. The first gives the value of the wave function along the internuclear axis, thus a graph of \( \psi(x = 0, y = 0, z) \). All students here draw what they recall from the text book, i.e. an MO consisting of two 1s AOs. This does not correspond to the MOs given. In addition, some students also draw a cross-section of a probability density plot, where the surface (more or less) represents a constant value of the wave function. Only S2 and S13 from group 1 draw something that corresponds to the given AOs, but they do not draw the resulting MO.

Most students explain that the plus combination adds up between the two nuclei, and that this results in a high probability between the nuclei. On the other hand, the minus combination results in a nodal plane between the two nuclei, and thus in a low probability between the nuclei. They are, however, unable to explain what this probability has to do with bonding, or anti-bonding. The students in group 2 also do not explain what this probability is (i.e. of finding the electron in a certain region). Students S5 and S6 are unable to explain why an MO results in bonding, or anti-bonding. They do not associate the drawn graphs to probability density. In fact they are uncertain what they have drawn and S6 mentions she has drawn a graph representing energy.

8.2.4 Representation of the wave function

During the tutorial sessions it became apparent that students do not exactly know what is represented in density plots of the wave function. In the interviews we investigated this further by presenting students with a density plot of the \( 2p_z \) orbital of hydrogen (Figure 8.4) and asking them to try to explain what is drawn. In addition they were asked to explain in general what a wave function is and why we need a wave function to describe electrons. All students recall that one of the lobes of the \( 2p_z \) orbital had a plus and the other a minus sign. None of the students, however, was able to correctly explain what the meaning of this sign was. Students associate it with spin (S2, S13, S9, S15), angular momentum (S9), or call it the plus and minus trajectory (S3). Although most students relate the graph to the probability of finding an electron in a certain region, their conception of what is exactly drawn, and what the meaning is of the wave function appears to be very diverse. We present each group separately.

The conception S2 and S13 (group 1) have of the wave function most closely
follows a scientific one. According to them, the given 2p$_z$ orbital indicates a region in which the electron can be found with a certain probability. When asked more directly what a wave function is, the students associate this with “the description of an electron”. According to these students, the wave function describes how electrons “oscillate and move around the nucleus of an atom”. Although they have this association, S2 notes that the wave function itself has not been used that much in the course, and adds:

S2 [. . .] The only thing you can do with it, is calculate probabilities, by . . .
S13 Yes, by taking the square. . .
S2 By using some calculus. The calculus, that’s right, multiplied with the inverse, then an integral, that sort of stuff.
S13 Yes, I know the definition. . .

When asked why we describe an electron with a wave function, both students first answer that this enables us to perform calculations. Then they note that the electron also has wave like properties, which can be seen from the fact that “there is interference”.

S3 and S7 (group 2) have more difficulty explaining what is represented with the 2p$_z$ orbital. S3 first notes that the graph represents the region where the electron can be found: either in the top half, or the bottom half of the graph. He also uses the word “trajectory”, however, adds that the electron does not “take this trajectory”, but that it only indicates where the electron can be. During the tutorial sessions there also were several occasions where S3 associated the wave function, or the orbital, with a trajectory of a particle. S7 is confused, but she formulates it as: “Yes, that the probability, that an electron from H, where it can be, that it is inside those two regions. But that’s all I know”. Because S3 uses the word “trajectory”, the researcher asks what he means by this. S3 replies by pointing at a certain location in the graph where the electron can possibly be found. He adds that with another energy the electron can be at another location. (In fact the orbital represents an energy eigenstate, with a definite energy.) He adds that the electron can only be found in the shaded region. (It can in fact be found outside this region,
although with smaller probability.) S3 writes a plus and a minus sign in each of the two lobes of the orbital, but cannot remember what their meaning is. He says that he just knows that “it is a plus trajectory and a minus trajectory”. The researcher asks how many trajectories are drawn. S3 thinks two. In the other interview, S9’s first reaction to the graph is that it indicates the trajectory of the electron in which it moves around the atom. In the graph he indicates the trajectory the electron might take. S15 objects to this idea: she says it has to do with a probability density, that there is a probability of finding the electron in the given region. Her reply is consistent with what we would say is correct. S9 agrees with this, and adds that there also is a certain spin of the electron, plus one half, or minus one half, which has to do with the electron rotating clockwise or counter clockwise (i.e. angular momentum). S9 probably refers to the plus, or minus sign of the two parts of the 2p$_z$ orbital, something S3, and both S2 and S13 (group 1) were also confused about.

When asked to explain what the wave function is, S3 and S7 agree that it indicates where the electron can be, or what the probability is of finding the electron. S7 adds that the square of the wave function gives the probability of finding the electron in a certain region. They are uncertain what the wave function itself is. S3 thinks that only the wave function squared says something about the probability, whereas S7 thinks that the square has to do with the probability density. What is striking is that S9 and S15 both reply that the wave function has to do with the trajectory of the electron. Figure 8.5 shows the drawing S9 makes, as he talks about a trajectory belonging to a $\pi$-orbital (an MO) and an s-orbital (an AO). They add that the square of the wave function is a probability density.

The next question is why we use a wave function to describe electrons. S7 replies along the lines of S2 and S13: it enables one to explain where the electron is. S3 says that we need a wave function because we can only say something about the probability. He is not able to give an example why this is the case, but remarks that quantum mechanics is different from classical mechanics. S9 and S15 emphasize the dual character of electrons: it is not only a particle, “it also makes a wave motion”. S9 explicitly says that an electron is a charged particle which makes a wave motion. When asked to elaborate, he adds that a moving charged particle induces a magnetic field. To explain what he means by wave motion, S9 again draws trajectories belonging to different orbitals. Here S15 again objects, and notes that the electron does not exactly follow such a trajectory. S9 changes his drawing (Figure 8.5) and says that the electron can possibly “shoot out of its orbit”. He insists that the electron orbits the nucleus and that each energy level has its own movement.

These results show that students have a hybrid conception of the wave function. On the one hand they know (or have memorized) the relation between wave function and probability density. In the most straightforward problems they are presented with, they are able to apply this idea and answer consistently. On the other hand, they associate the wave function with a trajectory of a particle, which is a classical notion. They do not seem to have difficulties
with this idea. In the bonding problem, it became apparent that this conception prohibits them from answering correctly. After all, a trajectory does not have a plus or minus sign, which is relevant in explaining bonding. Their explanation is based on what they have memorized from the example of two 1s orbitals. They are unable to apply it in the given situation where a 1s and 2p\(_z\) orbital is involved. This might in part be due to the fact that they do not realize that the 2p\(_z\) orbital has both a negative and a positive part. It is this property of the 2p\(_z\) orbital which breaks the rule the students use.

Both students in group 3 associate the graphic representation of the 2p\(_z\) orbital of hydrogen with probabilities of finding the electron in a certain region. When asked whether an electron might be found outside the drawn region, S5 thinks not. S6 replies that is it possible, although with a small probability. S6 recalls that there was a plus and minus sign also, but she cannot remember what it refers to. According to both students the wave function “describes the particle”. They recall that the square of the wave function is the probability density. S6 tries to draw a graph of a wave function, but she appears to be thinking of an MO. She is also not certain what is set out on the vertical axis.
This should be $\psi$, but she thinks of energy. During the tutorial sessions she also had difficulties with this (transcript on page [168]). When asked why we describe an electron with a wave function, both students answer in line with the other groups: it is used to do calculations. When the researcher asks why a wave function is needed in the first place, they reply that it has to do with binding and energies. The researcher says that in classical mechanics it is also possible to calculate the energy of a particle. Then the students answer that it is not possible to know the position and the momentum of an electron at the same time. While this is correct, they do not know what this has to do with a wave function.

The conception students have of the wave function partly corresponds to what we expected. However, they cannot explain why a wave function is needed in the first place. What stands out in their answers is that they see the wave function as a means to do calculations, not as a necessary description of quantum particles. This is seen in all groups, however it is strongest in group 3. The students are unsuccessful when using the wave function in calculations they are not accustomed to. This might indicate that they mostly have learned a definition relating the wave function to a probability, which they can only apply in situations similar to the ones in which they have practiced this definition. Their conceptual understanding of the wave function is thus limited and the relation between this understanding and applying it in concrete situations is weak.

8.3 Conclusion and discussion

Our main concern in this article was how students’ conceptual understanding of the wave function and procedural fluency in working with the wave function develop during the quantum chemistry course. The questions we asked in the introduction are answered here.

1a. What conceptual understanding do students have of the wave function, after the experimental introduction?

Almost all students acknowledge that a wave function for electrons can explain the double-slit interference pattern. Most ingredients needed to formulate a scientific correct interpretation of the wave function are available. However, it appears to us that not all students have been able to reach a coherent explanation of their findings using the wave function. Especially for group 3, the good initial results from the introduction proved to be not at all enduring. We might say the introduction had three goals regarding the wave function. First, students should understand that the electron interference pattern can be explained by describing the electrons with a wave. Second, the idea that electrons interfere with each other was to be falsified. Here the introduction succeeded. A third goal was to arrive at a clear conclusion about the meaning of the hypothesized wave function. This was done in a plenary discussion. However, no problem followed in which students could test whether they had
understood this conclusion. Furthermore, the integration with the regular lectures was not optimal. The context of the interference experiment and the explanation in terms of interfering waves, was not used in the conventional part of the course to explain bonding. This may have impaired the expected transfer.

1b. **What conceptual understanding do students have of the wave function, during the conventional course?**

During the course, students’ conception of the wave function should become apparent when working on problems that involve the wave function. The selected problems were most promising at revealing this, but only required a very minimal conception of the term wave function. In fact it was enough for students to know that the wave function is a probability amplitude and that the probability of finding an electron in a certain region is given by the integral of $|\psi|^2$ in that region. We still observe that not all students think of this relation when they are asked to calculate a probability.

1c. **What conceptual understanding do students have of the wave function, some time after the course has ended?**

Only one of the observed student groups show a consistent and acceptable conception of the wave function. Other groups have a “hybrid” conception: they know the relation between wave function and probability (density), but view the wave function as describing the “trajectory” of an electron. Also, it is unclear for most students why a wave function is necessary in the first place. The wave function is mainly seen as enabling one to do calculations with. These results might be a consequence of the focus in the course on performing calculations, i.e. a focus on procedural fluency: the tutorial problems have not given students the need, nor the opportunity to revise their conception of the wave function.

2. **Are students procedurally fluent enough to perform tasks during the conventional part of the course?**

Not all students are procedurally fluent enough to perform the tasks during the tutorial sessions. Two kinds of difficulties were observed. First of all, some students are unable to decide upon a solution strategy, or formulating a mathematical expression for the physics problem they are presented with. This already shows an interaction between the conceptual understanding these students have of the wave function, and carrying out the expected procedures. Secondly, students experience difficulties working out mathematical expressions, or performing calculations. This is related to (a lack of) procedural fluency for the calculus involved.

3. **What interplay between the two strands (conceptual understanding and procedural fluency) do we observe when students perform conventional tasks that involve the wave function?**

The minimal conception of the wave function as a probability amplitude, with its relation to a probability, is found to be supportive to performing the needed calculations and is thus beneficiary for students’ procedural fluency. However, even then, it is necessary that students are also procedural fluent regarding
the mathematics involved. A weak conception of the wave function inhibits students in deciding upon a solution strategy, thereby impairing their procedural fluency. Conversely, it may be said that students are pragmatic regarding their conceptual understanding of the wave function in the sense that it should enable them to solve the problems they are presented with. As noted earlier, students will only (potentially) revise their conception of the wave function if the tutorial problems require them to do so.

Stated differently, it seems that students' conceptual understanding consists of a set of rules that enables them to successfully, and perhaps efficiently, perform the procedures that are expected of them. Some of these rules are explicitly taught, some are "distilled" by students themselves. What is striking is that all students rely on such self distilled rules to answer the more complicated problems on chemical bonding. However, these rules are too limited and in fact do not reflect the reason for chemical bonding. This "over generalizing" by students has also been described by Singh (2001) in the context of quantum mechanics and Taber (2009) in the context of chemical bonding.

In this research, the most notable rule is that a plus combination of AOs is always bonding, while the minus combination is anti-bonding. This rule is consistent with our finding that none of the students know what the plus and minus sign in the 2p\(_z\) orbital relates to. Most students are able to explain the effect of a plus or minus combination MO on the probability density, however, only for 1s-orbitals. When a 2p\(_z\)-orbital is involved their explanation is wrong. Furthermore, students are unable to explain why a low (or high) probability density between the two nuclei results in bonding (or anti-bonding). The fact that students do not know the meaning of the plus and minus sign in a 2p\(_z\) orbital, might be a symptom of difficulties students have with visualizing atomic orbitals (Broklová & Koupil, 2006).

All students except S1 and S7 have participated in the final exam and have passed the course. If we assume that the final exam reflects the objective of the course, we would have to conclude that these objectives have been met, at least for the students that were followed. However, the results presented here, in particular the interview results, give a different impression. Not all students have a correct or consistent conceptual understanding of the wave function. To explain chemical bonding, all students rely on a self distilled, inappropriate rule, without being able to explain the quantum mechanical reason why atoms bond. Finally, some students still experience difficulties working with the formalism of quantum mechanics.

Although we have discussed only a small number of the problems students worked on during the tutorial sessions, they are a representative selection. For many of these problems it appears to be sufficient to use a relation from the textbook, such as the relation between wave function and probability density, and use this to answer the questions. As a result, conceptions of the wave function that we consider incorrect, can exist together with the (minimal) conception of the wave function as a probability amplitude. Something similar
happens when applying the wave function in chemical bonding. Rules distilled from a limited set of examples presented to students can survive, because students are not confronted with situations where their rule does not work. In other words: the focus of the tutorial sessions on procedural fluency has not resulted in a firm conceptual understanding. Those students who have a better conceptual understanding do seem to benefit from this when working with the formalism. Conversely, those students who have a weak conceptual understanding also have difficulties with the formalism. Nevertheless, seven out of the nine students observed have passed the exam.

On the other hand, the introduction has not contributed satisfactorily to a firm conceptual understanding of the wave function. The main problem here seems to be that the integration of the introduction in the regular part of the course was not optimal. In the interviews, students noted that they experienced the introduction as a different part of the course. As a result, there was limited transfer from what was learned in the introduction to the conventional part of the course. In particular, much time has been spent on interference. During the interviews students expressed that they could not appreciate this much, because they thought it did not return in the remainder of the course. The fact is that interference (of atomic orbitals) is the main explanation for chemical bonding.

The somewhat disappointing result from the introduction is not surprising when other research in this field is considered. In the case of the model of the atom, Taber (2005) notes: “...research suggests that students are quite resistant to learning about quantum-mechanical models of the atom, with electrons ‘located’ in orbitals defined in terms of probability and not being subject to well-defined boundaries” (p. 95). The fact that students seem resistant to change their views, has also been noted by Duit and Treagust (1995): “...one single piece of empirical evidence usually does not shake students’ conviction that their view is right ...” (p. 51). However, at this point we have made some progress, as the introduction was successful in the sense that it raised fundamental issues, and made students wonder about the theoretical description of electrons. In other words: it did generate a cognitive conflict. Unfortunately, the remainder of the course did not build enough upon this conflict, to let students develop an alternative way of thinking about the wave function, or atomic orbitals.

The focus on procedural fluency in the final exam made students think that all this conceptual understanding was not that important. In a next iteration we shall have to develop some activities shortly after the introduction in which students work with what has been discussed. There are several opportunities throughout the course where the double-slit analogy can be used to explain the characteristics of the wave function. Most explicit is of course the interference between atomic orbitals when forming molecular orbitals. This research shows that a revision of the conventional assignments used can potentially strengthen both conceptual understanding and procedural fluency. In particular, assignments should be set up such that to perform calculations, students have to
reason with the concepts that are taught.

References


**Analogical Reasoning to let Students Hypothesize the Wave Function.**

(Manuscript submitted for publication)


