One electron systems: H and H2+

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In this guide: about study guides; comments on ch120; basic principles of quantum mechanics; applications of chemical bonding to H2+; suggested reading


1 About Study Guides

The purpose of this study guide is to attempt to elucidate and clarify topics that were covered in lecture. Unfortunately, there may be nuances or details in the lecture that cannot be adequately captured by the study guide. This guide should be used as a supplement to your own class notes, not as a substitute for attending lectures.

2 Comments on Ch120

Professor Goddard’s handwriting can be difficult to decipher at times. If you are unsure what he has written and think that it might be important, then by all means ask him or the TAs. If you can’t read it, you can bet that there are others who can’t as well.

Concerns about the mathematical and physics prerequisites for the course are valid. However, while the lecture material will sometimes seem particularly mathy, the math you need to know for the course is mostly algebra. Additionally, as we progress through the course material we will move away from math and more toward chemistry. Familiarity with the notations and mathematical formalisms that Professor Goddard introduces is the most important thing for you to learn, and their importance supersedes any quantum mechanical review you may think you need.

The purpose of this course is to give you the intuition to predict properties and structures of chemicals and materials. If you have any questions or comments please feel free to contact any of the TAs.

3 Basic Principles of Quantum Mechanics

- Why Do We Need Quantum Mechanics?

  We began by discussing the importance of Quantum Mechanics (QM) and how it is necessary due to the failure of Classical Mechanics (CM) to describe the existence of atoms and thus chemical
bonds. The basis for the argument against CM is dependent on using the definition of energy and the hydrogenic atom as a model. The hydrogenic atom has one proton and one electron separated by a distance $R$. We should be able to recall the energy components that comprise the total energy of this system: **Potential Energy (PE)** and **Kinetic Energy**. Solving for the total energy of this system is simply solving for its PE and KE and taking the sum of the two. The classical values for these terms are:

\[
PE = -\frac{e^2}{R} \quad (1)
\]

\[
KE = \frac{1}{2}mv^2 \quad (2)
\]

We often further abbreviate PE and KE to the letters representing their operators in classical and quantum mechanics: $\hat{V}$ and $\hat{T}$, respectively. If we were looking for the lowest energy of a system (i.e. its most probable state), we need to minimize the two components of the total energy $E$. Notice that the classical values of $\hat{V}$ and $\hat{T}$ are independent of each other: $\hat{V}$ is a function of position while $\hat{T}$ is a function of velocity. Thus in a classical system, energy is minimized by having the electron on top of the proton. According to **Coulomb’s Law** as $R \to 0$, $E \to -\infty$, which is not physically possible. Therefore we need a different approach to understanding chemical bonding.

- **Quantum Mechanics in a Very Small Nutshell**

  In order for us to develop a quantum mechanical intuition about chemical and material systems we need to first recognize a few important details of QM. A rigorous QM course will discuss the four postulates of QM. If you are unfamiliar with these postulates, they should be in any standard QM textbook. Instead of going through the postulates individually, we talked about the significance of the postulates as a whole. These are the main points:

  1. The **wavefunction** $\psi(x, y, z, t)$ contains everything we want to know to solve for the energy of a particular state.

  2. The **probability density** of a wavefunction is $\int \rho(x, y, z, t)d\tau$ and must be normalized in order to be relevant. I.e.,

\[
P = \int \rho(x, y, z, t)d\tau = \int \psi^*\psi = \langle \psi \mid \psi \rangle = 1 \quad (3)
\]

  3. **Superposition** allows us to make linear combinations of “good” wavefunctions to make other “good” wavefunctions.

  4. The **Hamiltonian** ($\hat{H}$) determines the time-evolution of $\psi$.

  5. **Phase factors** do not change the state that a wavefunction represents.
6. We can show that if \( \hat{H} \) is independent of time, then \( \psi \) is an eigenfunction for the Time-Independent Schrödinger Equation:

\[
H \psi = E \psi
\]  

(4)

7. By the **variational principle**, the energy of an approximate wavefunction describing a particular state is greater than or equal to the energy of the exact wavefunction describing the state. This means that “better” wavefunctions have lower energy.

8. The **expectation value** for the classical operator \( \hat{V} \) is \(-\frac{e^2}{\bar{R}}\). Since \( \bar{R} \) is the average value of \( R \) over the entire wavefunction, it is dependent on the wavefunction. Similarly, the expectation value for \( \hat{T} \) is dependent on \( \langle \left| \frac{\partial \psi}{\partial x} \right|^2 \rangle \), and it is greater when the gradient (or slope) of the wavefunction is steep.

9. In quantum mechanics \( \hat{T} \) and \( \hat{V} \) are dependent on the same wavefunction \( \psi \); whereas, in classical mechanics \( \hat{T} \) and \( \hat{V} \) can vary independently.

By rigorously following these rules we are now ready to embark on using QM to make predictions.

- **Properties of Characteristic Wavefunctions**

  We then learned how – based on the qualitative shape of a wavefunction – we can determine what its energy components are. PE is most favorable when \( \bar{R} \) is small, i.e. the average distance between the electron and proton is small. Therefore, wavefunctions that are narrow and have a smaller \( \bar{R} \) are favored in terms of PE. Alternatively, KE is more favorable when the wavefunction is more smooth, as is the case with relatively flat wavefunctions (See Figure 1). Deeper discussion of this subject can be found in the suggested reading (Goddard Book 1.2.1).

- **The Atomic Radius of Hydrogen**

  With the previous information we can now determine the qualitative shape of an ideal wavefunction. The ideal wavefunction must minimize the sum of \( \hat{T} \) and \( \hat{V} \). The \( \hat{T} \) term has \( \frac{1}{R^2} \) dependence, and the \( \hat{V} \) term has \( \frac{1}{\bar{R}} \) dependence. Thus, at short \( R \) the \( \hat{T} \) term dominates, but at long \( R \) the \( \hat{V} \) term dominates. The minimum energy of the system is obtained at an intermediate value of \( R \). The optimal distance between an electron and a hydrogen nucleus can be found by taking the derivative of the sum and setting it equal to zero:

\[
E = \hat{T} + \hat{V} = \frac{\hbar^2}{2m} \frac{1}{R^2} - \frac{e^2}{\bar{R}}
\]  

(6)

\[
\frac{\partial E}{\partial R} = -2\frac{\hbar^2}{2m} \frac{1}{R^3} + \frac{e^2}{R^2} = 0
\]  

(7)

\[
R = \frac{\hbar^2}{m e^2} \equiv a_0 = 0.529 \text{\AA}
\]  

(8)
Using this value of R, the energy of the hydrogen atom is:

\[ E = \frac{\hbar^2}{2m a_0^2} - \frac{e^2}{a_0} = -13.6eV \]  

(9)

There are several different units we can use for energy. The energy unit in atomic units is the Hartree, \( E_h \), which is defined as:

\[ 1E_h = 27.2eV = 627.5 \frac{kcal}{mol} \equiv \frac{e^2}{a_0} \]  

(10)

4 Applications of Chemical Bonding to \( \text{H}_2^+ \)

Now that we have solved for the energy of the hydrogen atom (the energy of an electron paired with a proton), we can approach a more applical problem: the energy of an electron paired with two protons. The wavefunction for this system is not unlike that for the hydrogen atom. We considered two protons next to each other at an interatomic distance of \( R \) for \( R \to \infty \). One electron can be centered on either the left proton or the right proton. The wavefunction with the electron centered on the left will henceforth be labeled \( \psi_l \). Similarly, the wavefunction with the electron centered on the right will be labeled \( \psi_r \).

To study the chemical bond of \( \text{H}_2^+ \) we want to consider how the electron behaves at varying \( R \). As we bring the two protons together (i.e. when \( R \) becomes finite), the electron is no longer confined to be on one particular proton, and it can begin to have some probability of being on both protons. Thus our wavefunctions \( \psi_l \) and \( \psi_r \) are no longer realistic wavefunctions to describe the state of \( \text{H}_2^+ \) at finite \( R \). We can generate new (but approximate) wavefunctions from the superposition principle by taking a linear combination of atomic orbitals (LCAO). We will be able to apply the variational principle to evaluate their relative “goodness” by qualitatively determining their relative energies. The LCAO method does not guarantee perfect wavefunctions, but it is a useful first-approximation that can be done without computers with relative ease.

With the LCAO method, besides the two wavefunctions \( \psi_l \) and \( \psi_r \), we can let one wavefunction be \( (\psi_l + \psi_r) \) and the other be \( (\psi_l - \psi_r) \). We then estimate how the energies of these wavefunctions vary with nuclear separation \( R \). Note: While what follows from this appears to be very similar to the hydrogen atom example, this example is being used to determine whether the diatomic \( \text{H}_2^+ \) is bound, or if it will spontaneously fall apart into a H atom and a proton (\( \text{H}^+ \)).

A question appears in that we do not know whether \( (\psi_l + \psi_r) \) or \( (\psi_l - \psi_r) \) is better for describing the bonding of the system. To have good KE, we need a wavefunction that is as smooth as possible. The wavefunction \( (\psi_l + \psi_r) \) fits that criteria, and since there is a relatively high probability of the electron being located between the two protons, its value of \( \bar{R} \) is larger than in the \( \psi_l \) and \( \psi_r \) wavefunctions.

For clarity, we will define \( \psi_g = (\psi_l + \psi_r) \) and \( \psi_u = (\psi_l - \psi_r) \). The subscripts \( g \) and \( u \) will be explained in more detail later. First, we can consider how \( \psi_g \) varies from the single proton-centered wavefunctions
\( \psi_l \) and \( \psi_r \). The KE is small and more favorable for the flatter wavefunction \( \psi_g \). It can be said that \( \psi_g \) is stabilized when the wavefunction is flat over a large region of space (See Figure 2). This leads to the concept of **contragradience** – the KE stabilization that arises when two atomic orbitals (\( \psi_l \) and \( \psi_r \)) have opposing gradients over a large region of space. Consider the following implications at various distances of \( R \):

- \( R \to \infty \): small contragradience over a very large region → no effect
- \( R \to 0 \): large contragradience over a very small region → no effect
- Intermediate \( R \): large contragradience over a large region → favorable KE effect

In the case of \( \psi_u \) the effect is reversed. As \( R \to \infty \) the gradient of \( \psi_u \) at the center of the bond increases greatly causing the overall KE to increase substantially.

The effect of shifting charge density to and from the nuclei also has an effect on the PE of the wavefunctions \( \psi_g \) and \( \psi_u \), however these effects are generally considered secondary to the effect in KE.

Additional discussion of this example can be found in the suggested reading (Chapter 2 of the Goddard Book). This is a very important concept that we will revisit many more times.

### 5 Suggested Reading

- **Quantum Mechanics Review** – (Insert your favorite undergraduate physical chemistry text here, i.e. Atkins, Levine, McQuarrie, etc.)
- **Mathematical Formalisms in Quantum Mechanics** –
  - Liboff, R; *Introduction to Quantum Mechanics*
  - Shankar, R; *Principles of Quantum Mechanics*
  - Szabo, A. and N. Ostlund; *Modern Quantum Chemistry*
- **Class Notes Reading (Goddard Book)** –
  - Basic Principles of QM – Section 1.1.1, 1.1.4-1.1.7
  - The Hydrogen Atom – Section 1.2.0-1.2.3
  - The Nodal Theorem – Section 1.3.0-1.3.1
  - The Chemical Bond of \( \text{H}_2^+ \) – Section 2.0, 2.1.0-2.1.1, 2.1.3

### 6 Figures
Figure 1: Atomic hydrogen orbitals with varying $R$. 

- (a) Delocalized
- 
  - Large $R$
  - $\bar{V}$ slightly negative
  - $\bar{T}$ slightly positive

- (b) Localized
- 
  - Small $R$
  - $\bar{V}$ very negative
  - $\bar{T}$ very positive
Figure 2: An illustration of wavefunctions for the hydrogen atom (top) and the $\psi_g$ (middle) and $\psi_u$ (bottom) states of $\text{H}_2^+$. 