

The Hubbard model for the hydrogen molecule

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Abstract

Using as an example the simplest case of a hydrogen molecule, the basis of the highly oversimplified Hubbard model is presented. This model attempts to understand the physics of both insulating and metallic systems in a unified picture, especially those metallic systems which include transition metals. The results of the analysis are compared with those obtained from independent electrons (delocalized model) which is used in the study of metals and from the Heitler–London (localized model) approach more appropriate for the treatment of molecules or insulating materials.

1. Introduction

The study of spin systems forms a very large part of many-body theory because experimentally many solids display a great variety of types of magnetic arrangement. Many efforts have been made to account for the physical properties of these systems. In this way the quantum theory of magnetism has been developed from two well-defined and opposite starting points [1]:

- (i) The localized model [2] in which each electron remains localized or correlated with a determined atom or ion. The intra-atomic electron–electron interactions are large and determine the magnitude of the localized magnetic moment on each lattice site. In contrast, the interatomic electron–electron interactions are much smaller and compete with the thermal disorder to establish the type of magnetic ordering (ferromagnetism, antiferromagnetism, ...).
- (ii) The band model [3–7], in which each magnetic carrier is itinerant through the solid, moving in the average potential of the other electrons and ions. In this case, the electron levels form energy bands and the weak electron–electron interactions stabilize the ordered magnetic moments which are characterized by different numbers of up and down spins.

From the experimental point of view, however, the ferromagnetism exhibited by metallic systems, especially those including transition metals, has long occupied a controversial place within this framework [8]. This controversy stems from the apparent dual character of the d electrons responsible for the magnetism in transition metals, i.e. they are itinerant electrons described by band theory in their ground state, while at high temperatures they

show several properties that have long been attributed to a system consisting of local magnetic moments. The most well-known example of these properties is the Curie–Weiss law for magnetic susceptibility obeyed by almost all ferromagnetic materials above their ordering temperature.

In attempting to explain these phenomena, many different types of spin model have been introduced, but only a few of the models have solutions which are well understood, in spite of the fact that many of them have been intensively studied. The transfer of model results to real solids, which are strongly interacting systems, has still not been very successful. In the 1960s, Hubbard proposed a highly oversimplified model that attempted to provide a better insight into this problem [7]. The model contains the bare minimum of features necessary to yield both band-like and localized behaviour within suitable limits. In fact the Hubbard Hamiltonian was solved by Lieb and Wu [9], and since then different authors have contributed to this problem obtaining results of different physical magnitude [10–13].

The goal of this paper is to solve the simple Hubbard Hamiltonian for the case of the hydrogen molecule. This problem is proposed in the well-known textbook *Solid State Physics* by Ashcroft and Mermin [14] (ch 32, problem 5). The layout of this paper follows the suggestions given in that book, and includes some complementary plots for the understanding of the physical meaning of the Hubbard analysis.

2. An approximate representation of electron interactions

In this section the approximate model of electron interactions introduced by Hubbard is described. The vast and complex set of discrete (bound) and continuum electron levels of each ion is reduced to a single localized orbital level. So the energy states are given by specifying the four possible electronic configurations of each ion: the level could either be empty, contain one electron with either of two spins, or two electrons of opposite spins according to the Pauli principle. Therefore, the matrix representation of the Hamiltonian for the Hubbard model consists of two types of term: diagonal terms in these states and other off-diagonal terms that have non-vanishing matrix elements between just those pairs of states that differ only by a single electron which has been removed without change in spin from a given ion to one of its neighbours. This last term is related to the electron–electron interactions which are described by the Coulomb potential.

3. Hydrogen molecule

According to the previous section the full two-electron Hamiltonian can be written as

$$H = h_1 + h_2 + V_{12} \quad (1)$$

where h_1 and h_2 are one-electron Hamiltonians and V_{12} is the Coulomb repulsion potential between the two electrons when they are found to be on the same atom. In order to solve the problem we shall use the following procedure. First we consider a hydrogen molecule in which an atom at \vec{R} is described in the spatial representation by a single orbital electronic level $|\vec{R}\rangle$. When there is no electron on the atom $|\vec{R}, 0\rangle_{\text{vacuum}}$, i.e. an empty level, the energy is zero, if there is one electron of either spin in the level $|\vec{R}, \uparrow\rangle_{\text{up}}$ or $|\vec{R}, \downarrow\rangle_{\text{down}}$ its energy is E_0 , and if there are two electrons of opposite spins in the level $|\vec{R}, \uparrow\downarrow\rangle_{\text{singlet}}$ the energy is $2E_0 + U$. The last additional positive energy U represents the intra-atomic Coulomb repulsion between the two localized electrons. Therefore the Hubbard model for a two-atom molecule consists of two such orbital levels $|\vec{R}\rangle$ and $|\vec{R}'\rangle$ (see figure 1) representing electrons localized at \vec{R} and \vec{R}' respectively. For the sake of simplicity, we assume that these two states are orthogonal, $\langle \vec{R} | \vec{R}' \rangle = 0$.

In this way we can now consider the problem of two ‘protons’ and one electron (H_2^+) in the Hamiltonian (1). If the one-electron Hamiltonians, h_1 and h_2 , were diagonal in $|\vec{R}\rangle$ and $|\vec{R}'\rangle$

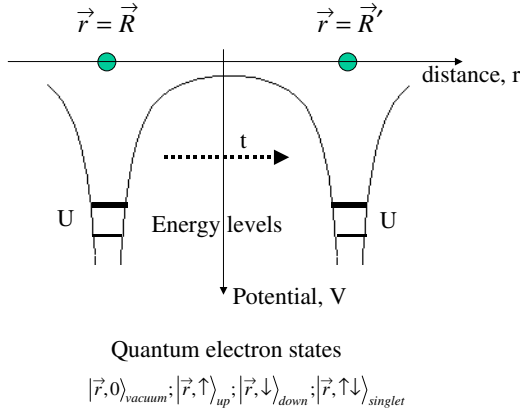


Figure 1. Qualitative illustration for the cross section of the attractive potential due to the two protons at $|\vec{R}\rangle$ and $|\vec{R}'\rangle$ in the hydrogen molecule; the position of the energy levels indicating the possibility of tunnelling from one proton to the other; and the Coulomb repulsion for electrons on the same atom and the quantum electron states (see text).

(This figure is in colour only in the electronic version)

the stationary levels would describe a hydrogen atom and a proton. However, it is well known that if the protons are not far apart, there will be a probability for electron tunnelling from one proton to the other (see figure 1), which leads to an ionized hydrogen molecule. This amplitude for tunnelling is represented by the off-diagonal term in the one-electron Hamiltonian

$$\langle \vec{R} | h | \vec{R}' \rangle = \langle \vec{R}' | h | \vec{R} \rangle = -t \quad (2)$$

where the phases of $|\vec{R}\rangle$ and $|\vec{R}'\rangle$ are chosen to make the number t real and positive. This fact together with the diagonal terms

$$\langle \vec{R} | h | \vec{R} \rangle = \langle \vec{R}' | h | \vec{R}' \rangle = E_0 \quad (3)$$

defines the one-electron Hamiltonian problem. The stationary levels of this Hamiltonian are then obtained from the diagonalization of the Hamiltonian expressed in matrix representation as

$$\begin{bmatrix} E_0 & -t \\ -t & E_0 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = E \begin{bmatrix} a \\ b \end{bmatrix} \quad (4)$$

with the normalization condition $a^2 + b^2 = 1$, a and b being the components of the states $|\vec{R}\rangle$ and $|\vec{R}'\rangle$. These stationary levels are then $\frac{1}{\sqrt{2}}(|\vec{R}\rangle \mp |\vec{R}'\rangle)$ with the corresponding energies $E_0 \pm t$.

An approach to the two-electron problem of the hydrogen molecule is to consider the independent electron approximation (free electrons in the case of metals) for the singlet spatially symmetric ground state, putting both electrons into the one-electron level of lowest energy to get a total energy of $2(E_0 - t)$. This approach ignores entirely the interaction energy U arising when two electrons are found to be on the same proton. As Ashcroft and Mermin proposed [4] the simplest way to improve upon the estimate $2(E_0 - t)$ is to add the intra-atomic Coulomb repulsion U multiplied by the probability of actually finding two electrons on the same proton when the molecule is in the ground state of the independent electron approximation. This probability is $2 \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2}$ considering that both electrons are independent, so the improved independent electron estimate of the ground state is

$$E_{IE} = 2(E_0 - t) + \frac{1}{2}U \quad (5)$$

and the approximate ground state within the independent electron approximation can be written in terms of the states as

$$\Phi_{IE} = \frac{1}{\sqrt{2}}[|\vec{R}\rangle + |\vec{R}'\rangle] \otimes \frac{1}{\sqrt{2}}[|\vec{R}\rangle + |\vec{R}'\rangle] = \frac{1}{\sqrt{2}}\Phi_0 + \frac{1}{2}(\Phi_1 + \Phi_2) \quad (6)$$

where Φ_0 , Φ_1 and Φ_2 are the full set of singlet spatially symmetric states of the two-electron problem given by

$$\begin{aligned}\Phi_0 &= \frac{1}{\sqrt{2}}[|\vec{R}\rangle|\vec{R}'\rangle + |\vec{R}'\rangle|\vec{R}\rangle] \\ \Phi_1 &= |\vec{R}\rangle|\vec{R}\rangle \\ \Phi_2 &= |\vec{R}'\rangle|\vec{R}'\rangle\end{aligned}\quad (7)$$

where $|\vec{R}\rangle|\vec{R}'\rangle$ has electron 1 on the ion at \vec{R} and electron 2 on the ion at \vec{R}' , etc. Therefore, from these states the full two-electron Hamiltonian $H(1)$ has a matrix form $H_{ij} = (\Phi_i, H\Phi_j)$ in the space of the singlet states (7) as

$$\begin{bmatrix} H_{00} & H_{01} & H_{02} \\ H_{10} & H_{11} & H_{12} \\ H_{20} & H_{21} & H_{22} \end{bmatrix} = \begin{bmatrix} 2E_0 & -\sqrt{2}t & -\sqrt{2}t \\ -\sqrt{2}t & 2E_0 + U & 0 \\ -\sqrt{2}t & 0 & 2E_0 + U \end{bmatrix}\quad (8)$$

where the off-diagonal terms are easily obtained as follows

$$\begin{aligned}H_{10} = \langle\Phi_1|H|\Phi_0\rangle &= \frac{1}{\sqrt{2}}[\langle\vec{R}|h_1|\vec{R}\rangle\langle\vec{R}|\vec{R}'\rangle + \langle\vec{R}|h_1|\vec{R}'\rangle\langle\vec{R}|\vec{R}\rangle + \langle\vec{R}|h_2|\vec{R}\rangle\langle\vec{R}|\vec{R}'\rangle \\ &+ \langle\vec{R}|h_2|\vec{R}'\rangle\langle\vec{R}|\vec{R}\rangle] = -\sqrt{2}t.\end{aligned}$$

Some comments deserve to be made about the matrix form of the Hubbard Hamiltonian (8). The diagonal terms in the states Φ_1 and Φ_2 that place two electrons on the same proton contain the extra Coulomb repulsion U (which is a consequence of the electron–electron interaction V_{12}), while this contribution is not present in the diagonal element in the state Φ_0 , since in this case the electrons are on different protons. Furthermore, this diagonal term in the state Φ_0 corresponds to the prediction of the Heitler–London treatment for the hydrogen molecule, and therefore the ground state estimate is just H_{00} , i.e. $E_{\text{HL}} = 2E_0$. Note also that the one-electron tunnelling amplitude t only connects states in which a single electron has been moved from one proton to the other. It would take further two-body interactions to give non-vanishing matrix elements between states in which the positions of two electrons are changed. On the other hand, the first set of diagonal terms, in the absence of the second off-diagonal terms, would favour local magnetic moments, since it would suppress the possibility of a second electron (with oppositely directed spin) at singly occupied sites. On the contrary, the presence of the off-diagonal terms in the absence of the first diagonal ones can be shown to lead to a conventional band spectrum and one-electron Bloch levels in which each electron is distributed throughout the entire crystal. And finally when both sets of terms are present, even this simple model has proved too difficult for exact analysis.

The Hamiltonian (8) then has a solution when

$$\begin{vmatrix} 2E_0 - E & -\sqrt{2}t & -\sqrt{2}t \\ -\sqrt{2}t & 2E_0 + U - E & 0 \\ -\sqrt{2}t & 0 & 2E_0 + U - E \end{vmatrix} = 0$$

where the three eigenvalues are found to be

$$\begin{aligned}E_1 &= 2E_0 + U \\ E_{2,3} &= E_{\pm} = 2E_0 + \frac{1}{2}U \pm \sqrt{4t^2 + \frac{1}{4}U^2}\end{aligned}$$

the lowest eigenvalue being the ground state energy of the Hamiltonian

$$E_{\text{Hubbard}} = 2E_0 + \frac{1}{2}U - \sqrt{4t^2 + \frac{1}{4}U^2}.\quad (9)$$

Energy (eV)

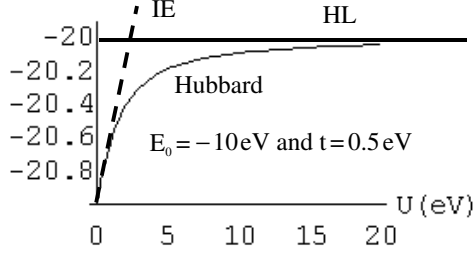


Figure 2. Ground state energy of the hydrogen molecule as a function of the Coulomb repulsion potential U from the case of Hubbard model (continuous line), the independent electron approximation (dashed line) and the Heitler–London method (bold straight line). The calculations are performed using the values of $E_0 = -10$ eV, and $t = 0.5$ eV (see text).

Probability

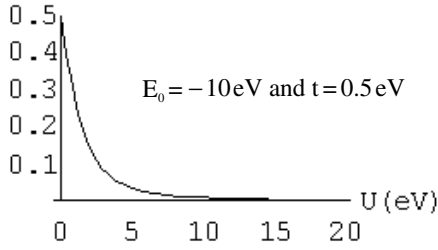


Figure 3. Probability of finding two electrons on the same ion in the hydrogen molecule as a function of the Coulomb repulsion potential U . The calculations are performed using the values of $E_0 = -10$ eV, and $t = 0.5$ eV (see text).

And the ground state eigenstate is (except for a normalization constant)

$$\Phi_{\text{Hubbard}} = \frac{1}{\sqrt{2}}\Phi_0 + \left(\sqrt{1 + \left(\frac{U}{4t}\right)^2} - \frac{U}{4t} \right) \frac{1}{2}(\Phi_1 + \Phi_2). \quad (10)$$

For the representation of the energies and probability depicted in figures 2 and 3, the enhanced version of Mathematica version 4.0 for Windows has been used. In particular the graphic plotting tool `Plot[f, {x, xmin, xmax}` which plots f as a function of x from x_{\min} to x_{\max} has been employed.

In figure 2 the ground state energy of the Hubbard model (E_{Hubbard}), the independent electron approximation (E_{IE}) to the ground state energy, as well as that of the Heitler–London approximation (E_{HL}) as a function of U are represented for the particular case of $E_0 = -10$ eV and $t = 0.5$ eV. The probability of finding two electrons on the same ion in the ground state energy of the Hubbard model obtained from equation (10) is depicted in figure 3.

From the comparison of the different results it is worth noting that the two limits are recovered from the Hubbard model. When $U/t \ll 1$ both electrons are independent and delocalized, this picture corresponding to the case of metals for which the band model is the most relevant treatment. In contrast, when $U/t \gg 1$ the Hubbard model recovers the value of the Heitler–London prediction, in which the two electrons are well localized, each electron on a particular atom. This situation can be applied to the case of insulating or molecular systems. As a consequence the degree of localization is directly related to the competition between hopping energy t and Coulomb energy U : large U values favour the localization of electrons since the charge fluctuations related to hopping have quite a high energy cost.

Finally, from a practical point of view, the determination of the relevant model to describe the physics of these systems is quite difficult and conjecture about the strength and importance of electron–electron interaction and the degree of localization is misleading. For example, the itinerant character of the d electrons in magnetic transition metals has been discussed for a long time and is now well established experimentally; on the contrary, the degree of localization of $4f$ electrons in anomalous Kondo Ce-based materials is still an open question. Moreover,

the inadequacy of these extreme models is clearly shown when they must be both invoked to interpret the physical properties of a given material. As commented in the introduction, the low-temperature properties of ferromagnetic transition metals are well understood using the band model whereas the Curie–Weiss law for magnetic susceptibility is qualitatively explained by the localized model.

In conclusion, in this paper we have attempted to illustrate using the hydrogen molecule the main trends in the study of the Hubbard Hamiltonian which is used for the understanding of correlated electron motion in transition metals. This simple model retains the qualitative properties of an itinerant correlated electron system: the intra-atomic Coulomb repulsion energy U and the hopping energy t . These two magnitudes provide the qualitative trends introduced by the competition between the band-like (delocalized) and the atom-like (localized) models (characters). In order to have a unified theory which can be used between both limits much more work is still necessary.

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