

# ADVANCES IN QUANTUM CHEMISTRY

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PER-OLOV LÖWDIN

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## PREFACE

In investigating the highly different phenomena in nature, scientists have always tried to find some fundamental principles that can explain the variety from a basic unity. Today they have not only shown that all the various kinds of matter are built up from a rather limited number of atoms, but also that these atoms are constituted of a few basic elements or building blocks. It seems possible to understand the innermost structure of matter and its behavior in terms of a few elementary particles: electrons, protons, neutrons, photons, etc., and their interactions. Since these particles obey not the laws of classical physics but the rules of modern quantum theory or wave mechanics established in 1925, there has developed a new field of "quantum science" which deals with the explanation of nature on this ground.

Quantum chemistry deals particularly with the electronic structure of atoms, molecules, and crystalline matter and describes it in terms of electronic wave patterns. It uses physical and chemical insight, sophisticated mathematics, and high-speed computing to solve the wave equations and achieve its results. Its goals are great, but perhaps the new field can better boast of its conceptual framework than of its numerical accomplishments. It provides a unification of the natural sciences which was previously unconceivable, and the modern development of cellular biology shows that the life sciences are now in turn using the same basis. "Quantum biology" is a new field which describes the life processes and the functioning of the cell on a molecular and submolecular level.

Quantum chemistry is hence a rapidly developing field which falls between the historically established areas of mathematics, physics, chemistry, and biology. As a result there is a wide diversity of backgrounds among those interested in quantum chemistry. Since the results of the research are reported in periodicals of many different types, it has become increasingly difficult both for the expert and the nonexpert to follow the rapid development in this new borderline area.

The purpose of this series is to try to present a survey of the current development of quantum chemistry as it is seen by a number of the internationally leading research workers in various countries. The authors have been invited to give their personal points of view of the subject freely and without severe space limitations. No attempts have been made to avoid overlap—on the contrary, it has seemed desirable to have certain important research areas reviewed from different points of view. The

response from the authors has been almost overwhelming, and a second volume is now being prepared.

The editor would like to thank the authors for their contributions which give an interesting picture of the current status of selected parts of quantum chemistry. Special thanks go to two of the great pioneers in the field, Professor Egil A. Hylleraas and Professor John C. Slater, as active as ever, who have taken the trouble to give us their personal views on two fundamental problems.

It is our hope that the collection of surveys of various parts of quantum chemistry and its advances presented here will prove to be valuable and stimulating, not only to the active research workers but also to the scientists in neighboring fields of physics, chemistry, and biology, who are turning to the elementary particles and their behavior to explain the details and innermost structure of their experimental phenomena.

*August, 1964*

PER-OLOV LÖWDIN

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# The Schrödinger Two-Electron Atomic Problem

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## I. Introduction

The present contribution to "Advances in Quantum Chemistry" is not intended to have the character of an encyclopedia article. Those who are interested in a complete treatment of the item should consult the thorough treatment given by Bethe and Salpeter (1957), which is complete up to the year of publication.

In the present article I take this opportunity of freedom to follow up some particularly interesting problems, more or less according to their historical development. This means, for instance, that we shall concentrate mainly upon the ground state problem, because of its ease of comparison with experimental data. From the point of view of quantum chemistry this is also a most important problem, since in the theory of chemical compounds one is mainly looking for ground states.

Because the field of research even within the atomic two-electron problem is so vast, a great number of investigations will be missing in the present article. This does not in any way mean that they are of secondary importance, but only that we are here considering those works which are necessary when talking freely of methods and results. Since a full report of works done in the field together with a documentation of their particular

importance can be found in the above-mentioned encyclopedia article by Bethe and Salpeter, I consider this procedure legitimate.

## II. The Early State of the Helium Problem

### A. The Hydrogen and Helium Atoms in the Bohr Theory

#### 1. The Hydrogen Atom

The natural frequency unit in atomic spectroscopy is the Rydberg constant  $R$ . The practical unit however is a reciprocal length  $R/c$ , which is usually also termed  $R$ . Because of the slight motion of the nucleus with respect to the electron-nucleus center of mass, the  $R$  (or  $R/c$ ) varies a little from atom to atom. For heavy atoms it converges toward a theoretical limit  $R_\infty$ . According to latest expert calculation (Cohen and Du Mond, 1957) the following values can be given:

$$\begin{aligned} R_\infty &= 109,737.309 \text{ cm}^{-1}, \\ R_H &= 109,677.576 \text{ cm}^{-1}, \\ R_{\text{He}^+} &= 109,722.26 \text{ cm}^{-1}. \end{aligned} \quad (1)$$

The natural energy unit in atomic theory therefore becomes

$$Rh = \frac{m_0}{2} \left( \frac{e^2}{\hbar} \right)^2 = \frac{e^2}{2a_H}, \quad a_H = \frac{\hbar^2}{m_0 e^2}, \quad (2)$$

where  $\hbar = h/2\pi$  and  $m_0$  and  $e$  are mass and charge of the electron. This corresponds to the kinetic energy of an electron with velocity  $\alpha c$ , where

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137} \quad (3)$$

is the fine structure constant appearing in the Bohr-Sommerfeld relativistic theory of the hydrogen atom. It is also half the absolute value of the potential energy of an electron at a distance  $a_H$  from the hydrogen nucleus.

At the earliest stage of the Bohr theory, even in its primitive shape of circular electron orbit, a full set of energy levels was found,

$$E_n = -Rh/n^2. \quad (4)$$

When the theory was supplemented with the conception of elliptical orbit, as quantized even with respect to orientation in space, the energy formula remained unchanged. Among the triple of quantum numbers, now denoted by  $n$ ,  $l$ , and  $m$ , i.e., principal, azimuthal, and equatorial quantum numbers, only  $n$  is significant for the energy. The degree of degeneration, i.e., the

numbers of independent states belonging to the same energy level, is  $n^2 = 1, 4, 9, \dots$ , just half the numbers  $2n^2$  characteristic for the various groups of the periodic system of basic elements. The doubling has been explained by the existence of electron spin and the necessity to have it quantized by a double-valued quantum number.

If relativistic theory is applied, a separation of energy states with respect to the azimuthal quantum number  $l$  is produced. The separation is of the order of magnitude  $\alpha^2 Rh$  and is correctly given by the famous Sommerfeld fine structure formula. A slight deviation called the Lamb effect was later found and must be thought of as a reaction from a virtual radiation field.

## 2. The Helium Atom and Ion

With this background of successful treatment of the hydrogen atom one must wonder that no numerical result of any value whatsoever could be obtained for the helium atom with its two electrons. This was caused by the well-known difficulties of many-body problems in classical mechanics. The Bohr rules for quantization of electron orbits

$$\oint p \, dq = nh \quad (5)$$

were inapplicable because the presupposed periodic or quasi-periodic character of the motion did not exist. The division of the procedure of quantization into two steps, solution of classical equations of motion followed by a selection of orbits by quantization rules, became fatal, and this could be mended only by an entirely new form of quantum theory, a true quantum mechanics.

The only state of the He atom which could at all be visualized in some tolerable form was the ground state. The states of the  $\text{He}^+$  ion with only one electron as well as the general one-electron atom (ion) with nuclear charge  $Ze$  are as clear as those of the hydrogen atom, and their energy levels in nonrelativistic treatment are

$$E_n = -Z^2 Rh/n^2. \quad (6)$$

If the two electrons of the He atom are placed on either side of the nucleus, rotating in the same direction on the same circular orbit and with the same appropriate speed, it cannot be denied that they are moving periodically and according to classical mechanical laws. With this specialization, quantum rules can also be applied. The result must be an ionic energy for each electron corresponding to the effective nuclear charge

$Z = 2 - 0.25 = 1.75$ , which gives a total energy  $-6.125Rh$  and an ionization energy for the first electron

$$I_{\text{He}} = 2.125Rh = 28.9 \text{ eV}. \quad (7)$$

This energy is more than 4 eV too large.

From the viewpoint of wave mechanics this is due to a far too strong correlation between the motions of the two electrons which must be very much weakened in order that the configuration can exist.

## B. Simple Wave Mechanics of Two-Electron Atoms

### 1. The Schrödinger Wave Equation in Atomic Units

For a conservative mechanical system, the Schrödinger wave equation reads

$$H\psi = E\psi, \quad (8)$$

where  $\psi$  represents a state and is called the wave function. It is a function of the coordinates of the system, and  $H$  is the energy operator which is found from the classical Hamiltonian of the system in replacing momentum variables  $p$  by differential operators  $-i\hbar\partial/\partial q$ . Hence the wave equation for the H atom is

$$\left(-\frac{\hbar^2}{2m_0}\nabla^2 + \frac{e^2}{r}\right)\psi = E\psi. \quad (9)$$

To simplify the equation it is tempting to apply atomic units, preferably the unit of length  $a_H$  of Eq. (9), which on dividing Eq. (9) by  $e^2/a_H = 2Rh$  yields the equation

$$\left(-\frac{1}{2}\nabla^2 + \frac{1}{r}\right)\psi = E\psi, \quad (10)$$

with coordinates measured in units  $a_H$  and the energy in double Rydberg units. This is seen to be equivalent to choosing  $m_0$ ,  $e$ , and  $\hbar$  for principal units of mass, charge, and action from which other units are obtained as secondary units. The velocity, for instance, is that of the electron velocity  $e^2/\hbar$  on the first Bohr circular electron orbit of the hydrogen atom, which gives to the speed of light the numerical value  $c = 137$ .

Even though this is the most attractive and logical choice, there is another one which sometimes may be preferred on the basis that radial functions are of the confluent hypergeometric type which are most easily expressed by Laguerre functions, using for unit of length  $\frac{1}{2}a_H$ . This system is obtained by changing the unit of mass into  $2m_0$  with the effect that the energy unit

becomes  $4Rh$ . If nevertheless the energy is measured in the conventional unit  $Rh$ , we must replace  $E$  by  $\frac{1}{4}E$  in the wave equation. Hence the hydrogen wave equation becomes

$$\left(-\nabla^2 + \frac{1}{r}\right)\psi = \frac{1}{4}E\psi. \quad (11)$$

Passing to the two-electron atom with nuclear charge  $Ze$ , the wave equation reads

$$\left\{-\nabla_1^2 - \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right\}\psi = \frac{1}{4}E\psi, \quad (12)$$

$r_{12}$  denoting the interelectronic distance. From the point of view of perturbation theory we should rather use the equation

$$\left\{-\nabla_1^2 - \nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Zr_{12}}\right\}\psi = \frac{E}{4Z^2}\psi \quad (13)$$

in changing to the unit of length  $a_H/2Z$ . In this equation  $1/Z$  naturally appears as a perturbation parameter.

## 2. Perturbation Energy

Disregarding the perturbation function

$$V' = \frac{1}{Zr_{12}}, \quad (13a)$$

the unperturbed ground state wave function and energy are

$$\psi_0 = \frac{1}{8\pi} \exp\left[-\frac{1}{2}(r_1 + r_2)\right] \quad \text{and} \quad E_0 = -2Z^2, \quad (13b)$$

the latter being the energy of two one-electron atoms in the ground state. If the volume element is taken to be

$$d\tau = r_1^2 r_2^2 \sin \theta_1 \sin \theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2, \quad (13c)$$

it means that  $\psi_0$  is normalized to unity. Then the first-order perturbation energy is

$$E_1 = 4Z \int \frac{1}{r_{12}} \psi^2 d\tau. \quad (13d)$$

This is the potential energy of two spherically symmetric electric charges for which, in the expansion

$$\frac{1}{r_{12}} = \sum_{i=0}^{\infty} \frac{r_1^i}{r_2^{i+1}} P_i(\cos \theta), \quad (14)$$

$$\cos \theta = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_2 - \phi_1),$$

we need consider only the first term. Hence, performing the integration in the angle variables and taking double the half-space integral, the result is

$$E_1 = 2Z \int_{r_2 > r_1} e^{-r_1 - r_2} \frac{d\tau'}{r_2} = \frac{5}{4} Z, \quad (15)$$

$$d\tau' = r_1^2 r_2^2 dr_1 dr_2.$$

The energy and ionization energy become

$$E = -2Z^2 + \frac{5}{4}Z, \quad I = Z^2 - \frac{5}{4}Z. \quad (16)$$

This means that He has an ionization energy

$$I = 1.5Rh = 20.4 \text{ eV}, \quad (16a)$$

which is about as much too small as the artificial Bohr-Sommerfeld orbital ionization value was too large.

### 3. Improved Perturbation Method

If we take the perturbing function to be

$$V_1 = \frac{1}{Z} \left\{ \frac{1}{r_{12}} - \frac{5}{16} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \right\}, \quad (17)$$

leaving for the unperturbed potential energy only

$$V_0 = -k \left( \frac{1}{r_1} + \frac{1}{r_2} \right), \quad k = 1 - \frac{5}{16} \frac{1}{Z}, \quad (17a)$$

the perturbation energy becomes zero, because of the similarly simple shape  $\exp[-k(r_1 + r_2)/2]$  of the unperturbed energy

$$E = -2Z^2 k^2 = -2Z^2 + \frac{5}{4} Z - \frac{25}{128}. \quad (18)$$

This improves the ionization energy with approximately  $\frac{1}{3}Rh$  or nearly 2.7 eV into  $I = 23.06 \text{ eV}$ .

This, I think, was approximately the reasoning of Kellner (1927) in his first substantial improvement of the ground state energy of He on the basis of an effective nuclear charge, until in a private discussion Max Born pointed out that any effective nuclear charge  $kZ = Z - \delta$  (above  $\delta = 5/16$ ) might be introduced, its actual value having to be fixed by a minimum requirement for the energy.

#### 4. A Simple Form of the Variational Method: the Scale Factor $k$

The wave equation can be derived from, and hence is equivalent to, the variational principle

$$\delta I = 0, \quad I = \int \psi^* H \psi \, d\tau, \quad (19)$$

with the restriction

$$N = \int \psi^* \psi \, d\tau = 1. \quad (19a)$$

Alternatively, the variation  $\delta\psi$  may be unrestricted and the variational principle be replaced by

$$\delta I - E \delta N = 0, \quad (19b)$$

or, finally, the energy may be defined as a stationary value of its mean or expectation value,

$$E = I/N, \quad (19c)$$

with the same free variation  $\delta\psi$  of  $\psi$ .

Again we try a new transformation of the wave equation, choosing for independent variables

$$\mathbf{r}' = k\mathbf{r}, \quad (20)$$

i.e., changing again the unit of length by a scale parameter  $k$ . In such coordinates the two-electron wave equation reads

$$\{k^2 T + kV + kV'/Z\}\psi = (E/4Z^2)\psi, \quad (20a)$$

$$T = -\nabla_{12}^2 = -\nabla_1^2 - \nabla_2^2, \quad V = -\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \quad V' = \frac{1}{r_{12}}, \quad (20b)$$

where, for simplicity, the primed coordinates have again been replaced

by unprimed letters. The expectation energy value for real  $\psi$  is now given by

$$(E/4Z^2)N = -k(L - L'/Z) + k^2M,$$

$$N = \int \psi^2 d\tau, \quad L = \int \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \psi^2 d\tau, \quad L' = \int \frac{1}{r_{12}} \psi^2 d\tau, \quad (21)$$

$$M = -\int \psi (\nabla_1^2 + \nabla_2^2) \psi d\tau = \int \{ (\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 \} d\tau.$$

With the former wave function (13b), now expressed in the new co-ordinates, we have

$$N = 1, \quad L = 1, \quad L' = \frac{5}{16}, \quad M = \frac{1}{2}. \quad (21a)$$

Minimizing the energy with respect to  $k$  we have

$$E = -2Z^2k^2, \quad k = 1 - \frac{5}{16} \frac{1}{Z}, \quad (21b)$$

giving exactly the already discussed energy value from the improved perturbation method of Eq. (18).

### 5. The Virial Theorem

The scaling method is one of highest general interest. Consider any system of charged particles interacting by Coulomb forces. If in a certain system its Hamiltonian is

$$H = T + V \quad (22)$$

and its expectation energy

$$E = M - L, \quad (22a)$$

where  $T$  and  $V$  are kinetic and potential energy operators and

$$M = \int \psi T \psi d\tau, \quad L = -\int \psi V \psi d\tau, \quad \text{with} \quad \int \psi^2 d\tau = 1, \quad (22b)$$

are kinetic and potential expectation values, respectively. The corresponding result in the scaled system is

$$E = k^2M - kL. \quad (22c)$$

If  $\psi$  in the first system is the true wave function, then we have energy minimum at  $k = 1$ . On the other hand, from the minimum condition,  $k = L/2M$ , and the negative potential energy is numerically twice the

kinetic energy. Not only for energy calculations but also for other purposes it is highly important to have the virial theorem fulfilled in this way.

### C. Para and Ortho States of Two-Electron Systems

#### 1. Symmetry Properties of Wave Functions

Consider the many-electron atomic Hamiltonian

$$H = T + V + V', \quad (23)$$

$$T = \sum_{i=1}^N \frac{1}{2m_0} \mathbf{p}_i^2, \quad (23a)$$

$$V = - \sum_i \frac{Ze^2}{r_i}, \quad (23b)$$

$$V' = \sum_{i < k=1}^N \frac{e^2}{r_{ik}}, \quad (23c)$$

and its wave equation

$$H\psi = E\psi. \quad (24)$$

The Hamiltonian is symmetric in the electron coordinates and moments. Hence, introducing the permutation operator  $P_{ik}$ , meaning the interchange of variables  $i$  and  $k$ ,

$$P_{ik}H = H. \quad (24a)$$

Also

$$P_{ik}(H\psi) = (P_{ik}H)(P_{ik}\psi) = H(P_{ik}\psi). \quad (24b)$$

Hence, multiplying Eq. (24) by  $P_{ik}$ , we have

$$H(P_{ik}\psi) = E(P_{ik}\psi), \quad (25)$$

and  $P_{ik}\psi$  is a solution of Eq. (24), belonging to the same energy value  $E$  as  $\psi$  itself.

Since  $P_{ik}^2 = 1$ , the eigenvalues of  $P_{ik}$  are

$$P_{ik} = \pm 1. \quad (25a)$$

From Eq. (24b) it follows that  $P_{ik}$  commutes with  $H$  and hence is a constant of the motion. Its quantized values require either symmetric or antisymmetric wave functions with respect to the variables  $i$  and  $k$ .