Pioneering attempts in Hungary on treating quantum systems

Péter R. Surján

Abstract

A brief cross section of the initial steps taken by Hungarian authors is given, starting from 1929, when von Neumann and Wigner published their paper on level repulsion termed also avoided crossing. The chapter also includes copies of three early seminal research papers with some comments on the context and significance at their time and looking back.

Keywords: Non-crossing rule, Group theory, Wigner's perturbation theory, Pseudopotentials

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1 Introduction

Quantum chemistry is clearly an interdisciplinary field lying on the borderline of physics and chemistry. It can be cultivated by scientists whose backgrounds are either in physics or in chemistry. As known, and as we will illustrate in this Chapter, early results in atomic and molecular quantum theory obtained by Hungarian scientists had strong backgrounds in mathematical physics (e.g., Johnny von Neumann, Eugene Wigner, Pál Gombás, Edward Teller.) While this tradition still continues to some extent in Hungary, other chapters of this book will show that as time has passed, more and more Hungarian chemists have entered the game of quantum chemistry.

2 The Non-crossing Rule and Group Theory

Quantum chemistry was born in 1927, when Heitler and London published their seminal paper on the quantum mechanical description of the H_2 molecule,[1] providing the first evidence that quantum mechanics is working for more than a single electron.

Shortly after this landmark achievement, in 1929, two young Hungarian scientists, Neumann and Wigner published a paper[2] in German language entitled *"Über merkwürdige diskrete Eigenwerte"* (in English: *"On peculiar discrete eigenvalues"*), which discussed the eigenvalue developments of a Hamiltonian depending on a continuously varying parameter. The statements obtained in this early paper became textbook-material, known today as 'level repulsion', 'avoided crossing', or 'non-crossing rule'.

This paper reflects the broad mathematical interest of von Neumann and the affection of Wigner to group theory. The latter developed in the famous book by Wigner on this subject. Its original version[3], written in 1931 in German, entitled: *"Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren",* while Wigner spent his summer holiday in Hungary in the house of his parents. It was translated to English[4] by Griffin in 1959 titled *"Group Theory and its Application to the Quantum Mechanics of Atomic Spectra".* This is the book in which the famous Wigner 3j-symbols (related to the Clebsch-Gordan coefficients) are introduced, followed by the 6j symbols called also Racah coefficients. The Hungarian translation of the book, containing a foreword by Wigner, appeared only in 1979.

3 Brillouin-Wigner Perturbation Theory

In many-particle quantum theory one usually prefers to apply the Rayleigh-Schrödinger perturbation theory (PT) to the Brillouin-Wigner PT due to the extensivity property of the former. Following important early contributions, see e.g. Feenberg[5], Löwdin[6], Hirschfelder[7], interest waned though the topic was never fully abandoned, c.f. Ahlrichs[8], Davidson[9]. A revival, starting in the 90's was driven primarily by Hubac and Wilson[10, 11, 12], Paldus[13], Pittner[14], and Head-Gordon[15].

Wigner's contribution was published in 1935, in the somewhat obscure journal "Mathematical and Natural Science Bulletin" of the Hungarian Academy of Science[16]. The paper, written in English, was based on a lecture Wigner had at a meeting of the Hungarian Academy, on 12 November, 1934. The paper refers to the similar work by Brillouin (hence the name: BWPT), published in the previous year, as well as to a related work by Lennard-Jones in 1930. Since the mentioned Bulletin is not easily available, the present author has received repeated requests in the past years for photocopies. As the Bulletin is not anymore copyright protected, a facsimile copy of Wigner's paper is included below.

ON A MODIFICATION OF THE RAYLEIGH—SCHRÖDINGER PERTURBATION THEORY.

By EUGENE WIGNER.

1. The **Rayleigh—Schrödinger** perturbation theory[1] gives an explicit power series in λ for the characteristic values F_n and the characteristic functions φ_n of a Hermitean operator $H+\lambda V$

$$(H+\lambda V)\varphi_n = F_n \varphi_n \tag{1}$$

if the corresponding quantities E_n and ψ_n for the «unperturbed operator» H are known

$$H\psi_n = E_n\psi_n. \tag{1a}$$

If the so-called matrix elements of V are denoted, as usual, by

$$V_{nm} = (\psi_n, V\psi_m) = V^{*}_{mn} \tag{2}$$

the first terms of the aforementioned series read

$$F_n^{(2)} = E_n + \lambda V_{nn} + \lambda^2 \sum_k{}' \frac{|V_{nk}|^2}{E_n - E_k} \tag{3a}$$

$$\varphi_n^{(1)} = \varphi_n + \lambda \sum_k{}' \frac{V_{kn}}{E_n - E_k}\psi_k. \tag{3b}$$

Generally only these first terms of the series are used in actual calculations, the higher terms become increasingly complicated.

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[1] J. W. S. **Rayleigh**, The theory of Sound. London and New York 1894, vol. 1, p. 113. E. **Schrödinger**, Collected papers on Wave Mechanics. London and Glasgow 1928, p. 64.

We shall fix our attention on the lowest energy value F_1. While it is evident that the first approximation for this $F_1^{(1)} = E_1 + \lambda V_{11}$ is always greater than its real amount — since it is the expectation value of a normalized wave function ψ_1; nothing like this holds for the second and higher approximations. It even happens quite often that the last series in (3*a*) diverges in cases when the lowest energy value is finite itself. In these cases, of course, the RAYLEIGH—SCHRÖDINGER perturbation theory is inapplicable to the problem. The aim of the present paper is to give an approximation formula for F_1 which always yields values that are too high, and which can be proved to converge at least in certain simple cases. Such an expression is naturally provided for by the variational method which had been used frequently indeed in cases for which the general shape of the characteristic functions could be obtained by physical considerations.

The final result, the ∞-th approximation, will appear in the form of an infinite series. This infinite series was first found by L. BRILLOUIN[1] who obtained it by an intuitive consideration of the usual scheme. He has already pointed out in his important paper that his series converges much more rapidly than the power series of SCHRÖDINGER. He has not investigated, however, the successive approximations and their relations to the actual problem.

2. For the sake of convenience we shall denote further on $F_k^{(1)} = E_k + \lambda V_{kk}$ simply by E_k, assuming $V_{kk} = 0$ or that the diagonal part of V is already put into H. In addition to this, we shall put $\lambda = 1$. The expectation value of $H + V - E_1$ for the wave function

$$\varphi_1 = \psi_1 + \sum_{k=2}^{\infty} a_k \psi_k \tag{4a}$$

is (R means that the real part of the ensuing expression must be taken)

$$F_1 - E_1 = \frac{\sum\limits_k (E_k - E_1) \mid a_k \mid^2 + 2R \sum\limits_k V_{1k} a_k + \sum\limits_{kl} V_{kl} a_k^{\star} a_l}{1 + \sum\limits_k \mid a_k \mid^2} \tag{4b}$$

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[1] L. BRILLOUIN, Journal de physique, **4**, 1, 1933. The perturbed energy first appears as resonance denominator in J. E. LENNARD-JONES article, Proc. Roy. Soc. London, A. **129**, 598, 1930.

where all summations must be extended, as always in this paper, from 2 to ∞. Expression (4b) must be made to a minimum by choosing the a 's properly.

To orient ourselves we proceed as follows. We neglect first the double sum in the numerator of (4b), i. e. assume $V_{kl} = 0$ for $k > 1$, $l > 1$. Differentiation of (4b) with respect to a_k gives then

$$a_k^{(1)} = \frac{V_{k1}}{F_1^{(2)} - E_k}. \tag{5a}$$

This, inserted into (4b), gives

$$F_1^{(2)} - E_1 = \sum_k \frac{|V_{1k}|^2}{F_1^{(2)} - E_k}. \tag{5b}$$

This is an implicit equation for $F_1^{(2)}$, which can be solved e. g. by plotting both sides of (5b) against $F_1^{(2)}$. It is an exact solution of the problem if $V_{kl} = 0$ (i. e. it is $F_1^{(2)} = F_1$): the finding of the characteristic values of a Jacobi matrix.[1]

It appears to be natural, now, even if the V_{kl} are different from zero, to try (5a) for $a_k^{(1)}$ but to use instead of (5b) an equation expressing again that $F_1^{(2)} - E_1$ is equal to the total fraction (4b), which, under the present conditions will no longer be equal to the right side of (5b). One obtains, instead of (5b)

$$F_1^{(2)} - E_1 = \sum_k \frac{V_{1k} V_{k1}}{F_1^{(2)} - E_k} + \sum_{kl} \frac{V_{1k} V_{kl} V_{l1}}{(F_1^{(2)} - E_k)(F_1^{(2)} - E_l)}. \tag{6}$$

The value of F_1 obtained from (6), since it is an expectation value of $H + V$, is always too high. For the next approximation one may try

$$a_k^{(2)} = a_k^{(1)} + \beta_k$$

neglect second power terms in the double sum of (4b), then minimize the resulting expression. One obtains, by denoting the total fraction this time with $F_1^{(3)} - E_1$

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[1] (5b) goes over into the usual formula of the Rayleigh—Schrödinger theory if E_1 is doubly degenerate, and E_3, E_4 etc. are far away from $E_1 = E_2$. However, (5b) may be used as it stands, without first solving a «secular equation».

$$a_k^{(2)} = \frac{V_{k1}}{F_1^{(3)} - E_k} + \sum_l \frac{V_{kl} a_l^{(1)}}{F_1^{(3)} - E_k}$$

which is in this approximation equal to

$$a_k^{(2)} = \sum_k \frac{V_{k1}}{F_1^{(3} - E_k} + \sum_{kl} \frac{V_{kl} V_{l1}}{(F_1^{(3)} - E_k)(F_1^{(3)} - E_l)} \,. \tag{7a}$$

Inserting this into (4*b*) again, one obtains

$$\begin{aligned} F_1^{(3)} - E_1 = \sum_l \frac{V_{1l} V_{l1}}{F_1^{(3)} - E_l} + \sum_{lk} \frac{V_{1l} V_{lk} V_{k1}}{(F_1^{(3)} - E_l)(F_1^{(3)} - E_k)} + \\ + \sum_{lkj} \frac{V_{1l} V_{lk} V_{kj} V_{j1}}{(F_1^{(3)} - E_l)(F_1^{(3)} - E_k)(F_1^{(3)} - E_j)} + \\ + \sum_{lkji} \frac{V_{1l} V_{lk} V_{kj} V_{ji} V}{(F_1^{(3)} - E_l)(F_1^{(3)} - E_k)(F_1^{(3)} - E_j)(F_1^{(3)} - E_i)} \,. \end{aligned} \tag{7}$$

This, solved by a graphical or other method, again gives certainly too high values for F_1.

It is evident now, how the higher approximations look. If one inserts

$$a_k^{(n)} = a_k^{(n-1)} + \sum_{\mu_1 \ldots \mu_{n-1}} \frac{V_{k\mu_{n-1}} V_{\mu_{n-1}\mu_{n-2}} \ldots V_{\mu_2\mu_1} V_{\mu_1 1}}{(f - E_k)(f - E_{\mu_{n-1}}) \ldots (f - E_{\mu_1})} \tag{8a}$$

into (4*b*), the right side, which is the expectation value of a normalized wave function minus E_1, becomes

$$\begin{aligned} \frac{1}{N} [T_2 + T_3 + \cdots + T_{2n} + T_{2n+1} + (N-1)(f - E_1)] = \\ = \frac{\left(\varphi_1^{(n+1)}, (H+V)\, \varphi_1^{(n+1)}\right)}{(\varphi_1^{(n+1)}, \varphi_1^{(n+1)})} - E_1 \end{aligned} \tag{9}$$

with

$$N = 1 + \sum_k |a_k^{(n+1)}|^2 \tag{9a}$$

and

$$T_{j+1} = \sum_{\mu_1 \ldots \mu_j} \frac{V_{1\mu_j} V_{\mu_j \mu_{j-1}} \ldots V_{\mu_2\mu_1} V_{\mu_1 1}}{(f - E_{\mu_j})(f - E_{\mu_{j-1}}) \ldots (f - E_{\mu_1})} \,. \tag{9b}$$

Equ. (9) is an identity. If one chooses f such that

$$T_2 + T_3 + \cdots + T_{2n+1} = f - E_1 \tag{8}$$

one sees that the expectation value of the corresponding wave function is just

$$F_1^{(n+1)} = f$$

which can be taken as the $(n+1)$th approximation. One can satisfy oneself easily, that the infinite series, obtained by generalization of (8), together with a similar generalization of (8a) and with (4a), formally satisfie equation (1) with $F_1 = f$. They can diverge, of course, in spite of this. It is true, however, that all equations of the form (8) give too high values for F_1. One easily sees that the odd term of (8) are always negative,[1] (therefore improving on the energy value), while the even ones may be positive or negative.

Of course, (8) converges in many cases in which the usual Rayleigh—Schrödinger method diverges. It can converge even in the case of a continuous spectrum which has been made artificially discrete by setting finite boundaries to an originally infinite problem. There is one, as I think, rather general case, in which it can easily be shown to converge. This is when H is an «even» operator, which remains unaltered under a transformation Q, satisfying the equation $Q^2 = 1$, and V an odd operator which goes over into $-V$ under the same transformation. Then V_{kl} is zero if k and l refer either both to even states, or both to odd states and the even terms of the series (7) drop out. The conditions of the convergence are in this case merely that $H+V$ should be bounded downwards (the lowest energy value finite) and applicable to all characteristic functions of H.

Of course, (8), (8a), (4a) still give a formal solution of the problem, if one inserts other numbers instead of 1. It is not so easy, however, to discuss the resulting equation in these cases.

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[1] The $(2n-1)$st term in (8) is equal

$$T_{2n} = \sum_k (\alpha_k^{(n)} - \alpha_k^{(n-1)})^2 (f - E_k) \qquad (*)$$

which is, of course, negative. Equation (*) is material for the proof of convergence in cases to be mentioned later

3. As an example, I want to discuss the Mathieu-equation

$$\frac{-d^2\varphi}{dx^2} + \sin x\,\varphi = F\varphi(x)$$

in which the total potential $\sin x$ will be regarded as perturbation. The unperturbed characteristic functions are

$$\psi_0 = \frac{1}{\sqrt{2\pi}}\,,\ \psi_1 = \frac{\sin x}{\sqrt{\pi}}\,,\ \psi_2 = \frac{\cos x}{\sqrt{\pi}}\,,\ \psi_4 = \frac{\sin 2x}{\sqrt{\pi}} \cdots$$

and the V_{kl} matrix is

$$\begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \cdots \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{2} & 0 & 0 \cdots \\ 0 & -\frac{1}{2} & 0 & \frac{1}{2} & 0 \cdots \\ 0 & 0 & \frac{1}{2} & 0 & -\frac{1}{2} \cdots \\ 0 & 0 & 0 & -\frac{1}{2} & 0 \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

The equation for the lowest energy is

$$-F_1 = \frac{1}{2(1-F_1)} + \frac{1}{8(1-F_1)^2(4-F_1)} + \\ + \frac{1}{32(1-F_1)^3(4-F_1)^2} + \frac{1}{32(1-F_1)^2(4-F_1)^2(9-F_1)} + \cdots$$

This equation can be solved by successive approximations very easily, one obtains $F_1 = -0{\cdot}37856$.

Another example of a similar simple case will be given by Mr. F. Seitz in the calculation of the Fermi energy of metallic electrons.

(From the meeting of the IIIrd class of the Hungarian Academy of Sciences on the 12th November 1934.)

4 Towards Pseudopotentials

In this section we recover an almost forgotten effort of Hungarian physicists, to deal with the many-electron problem at that time. These considerations have lead to the introduction of a novel method treating inner-shell electrons, called nowadays as the theory of pseudopotentials.

The original idea goes back to Hans Hellmann[17] and Pál Gombás[18, 19, 20], who independently noted that the orthogonality requirement between core and valence electrons can be approximately substituted by a repulsive potential acting on valence electrons, allowing to ignore the explicit treatment of core shells.

4.1 Fényes' contribution

The theory was put in a more detailed form by Imre Fényes in 1945[21], who, right after his doctorate with Gombás, was working as a young professor at the Bolyai University, Kolozsvár (a Hungarian university in Romania at that time[1]). While the names of Hellmann and the Hungarian physicist Gombás are well known among quantum chemists, Fényes is mainly known in the areas of fundamental quantum mechanics, irreversible thermodynamics, and science philosophy[2]. Nevertheless, his early paper on pseudopotentials cited above, published in the Museum Bulletin of Kolozsvár in German language, is historically important and deserves some attention. The paper is in fact an excerpt of Fényes' doctoral thesis, which appeared in print in Hungarian language in *"Csillagászati Lapok"*[22] ("Astronomical Records", a Hungarian journal published by the Society of Natural Sciences) already in 1943. With the permission of the publisher, the English translation of this early and basically forgotten paper[21] is given below. We corrected trivial misprints, but left erroneous formulae as printed originally.

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[1] Today: Babes-Bolyai University, bilingual (Romanian-Hungarian).

[2] Together with Heisenberg, in 1974, he had a series of seminars in Dubrovnik on fundamental problems of quantum mechanics.

Statistical analogy of orthogonality for valance electrons[1]

by Imre Fényes

From: *Múzeumi Füzetek, Kolozsvár*, **3.**, 14, 1945.

(translated from German by András Gombás)

The eigenfunctions of the electrons of an atom are orthogonal, therefore the eigenfunctions of the valence electrons are also orthogonal to that of the electrons of the remaining noble gas-like ions. In this work, we prove that the aforementioned orthogonality relations can be caused by repulsive forces acting between the ion and valence electrons. Since the orthogonality relationships mentioned are equivalent to Pauli principle, the latter is also fulfilled by introducing these forces. The potential of these repulsive forces corresponds in zeroth order approximation to the already known (Gombás) potential derived on the basis of statistical calculations.

1. Hellmann[2] and Gombás[3] replaced the orthogonality relations of the valence electrons' eigenfunctions with repulsive forces for which the potentials were obtained from statistical calculations. Later Gombás[4] corresponded the potential caused by p, d ... valence electrons and the repulsive forces replacing the orthogonality based on a new, but also statistical consideration. According to Gombás, the potential of the force acting on the ith electron reads

$$\begin{aligned} \varphi_i(r) &= -\frac{c}{e}\left(\nu^{2/3} - \nu_i^{2/3}\right) \\ c &= \frac{1}{2}(3\pi^2)e^2 a_H, \end{aligned} \tag{1}$$

where e is the elementary charge, a_H is the Bohr-radius, ν is the electron density of the ion, ν_i is the density caused by those electrons that have less energy than the valence electron would require to enter into the dτ volume element. For example, for the K atom, if the valence electron is in the s state, $\nu_i = 0$; in the p state, since in this case the state of lowest energy is $2p$, ν_i is the electron density of the ion $(1s)^2(2s)^1$; in the d state, $\nu_i = \nu$. Recently, Gombás and Kónya[5] have derived and discussed an expression for the "initial energy" of valence electrons. This expression also led to the cited equation regarding the repulsive potential (1).

The authors mentioned above have all tacitly assumed that the potential mentioned replaces the orthogonality. In the following we prove that the use of $\varphi_i(r)$ actually replaces the orthogonality.

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[1] See also by the author: Csillagászati Lapok 6. 59-69, 1943. In this work I give a more complete and simpler solution.

[2] H. Hellmann, Acta Phisicochimica URSS 1, 913, 1935.

[3] P. Gombás, Ann. d. Phys. (5) 35 65 1939; 36 680 1939; Z. f. Phys. 116, 184, 1940.

[4] Z. f. Phys. 118, 164, 1941.

[5] Mat. és Természettud. értesítő 61, 678, 1942.

2. The Hartree-Fock equations[6] are the Euler-Lagrange differential equations of the following variational problem:

$$\delta\left(\sum_j\int\psi_j^*(r)\left[H_\tau-e\left(V(r)-A(r)\right)\right]\psi_j(r)d\tau_r-\sum_{j\geq l=1}\lambda_{jl}\delta_{jl}\right)=0 \qquad (2)$$

where

$$H_\tau=-\frac{h^2}{8\pi^2m}\Delta_\tau\;-\;\frac{Ze^2}{r},$$

$$V(r)=-e\int\sum_{k=1}^{N}\frac{\psi_k^*(r')\psi_k(r')}{|r-r'|}d\tau_{r'},$$

$$eA(r)\psi_j(r)=e^2\int\frac{\psi_k^*(r')\psi_k(r)}{|r-r'|}\psi_j(r')d\tau_{r'}.$$

$A(r)$ represents[7] the exchange interaction operator, $\psi_j(r)$ is the eigenfunction of the electron in the j-th quantum state, N is the number of electrons, Z is the atomic number, r is the position vector, λ_{ij} are the Lagrange multipliers, Δ_r is the Laplace operator. The constraints of Eq. (2) are:

$$\begin{gathered}\int\;\psi_j^*(r)\;\psi_l(r)d\tau_r\;=\;\delta_{jl}\\ \delta_{jl}=\begin{cases}0, & \text{if}\quad j\neq l\\ 1, & \text{if}\quad j=l\end{cases}\\ j>l;\;l=1,2,\ldots,N\end{gathered} \qquad (3)$$

The Hartree-Fock equations follow from (2) and (3):

$$\left[H_\tau-e\left(V(r)-A(r)\right)\right]\psi_j(r)=\lambda_{jj}\psi_j(r),\quad j=1,2,\ldots,N \qquad (4)$$

where the eigenvalues are denoted by λ_{jj}.

Of the N electrons in the atom, let n denote the number of the core electrons and $q=N-n$ the number of valence electrons.

For distinction, let us denote the eigenfunctions of the valence electrons by ρ, as $\psi_{n+i}=\rho_i$. Furthermore, let $\lambda_{n+i,n+i}\;=\lambda_i$.

The wave equation of the i-th valence electron is

$$\left[H_\tau-e\left(V(r)-A(r)\right)\right]\rho_i(r)=\lambda_i\rho_i(r),\quad i=1,2,\ldots,q \qquad (5)$$

We are now interested in the following question. How does Eq.(5) change if the eigenfunctions of the valence electrons are not orthogonal to the eigenfunctions of the core electrons? In this case we obtain certain deviations from Eq.(5). The eigenfunctions and eigenvalues of the new equations are labeled $\overline{\rho}_i$ and $\overline{\lambda}_i$, respectively. The new equations also result from Eq.(2), but certain constraints of Eq.(3) will be different:

$$\int\psi_j^*(r)\overline{\rho}_i(r)d\tau_r=c_{ij}\neq 0,\quad j=1,2,\ldots n,\quad l=1,2,\ldots,q, \qquad (6)$$

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[6] V. Fock, Zs. f. Phys. 61, 126, 1930; 62, 795, 1930, 81, 195, 1933.

[7] V. Fock, Zs. f. Phys. 81, 195, 1933, Eq. (16).

while the others remain unchanged. Assuming that this change causes the functions $\phi_j(r)$, $V(r)$ and $A(r)$ to change only by negligible amounts, the modified Hartree-Fock equation of the i-th valence electron follows from Eqs.(2) and (6):

$$[H_\tau - e\,(V(r) - A(r))]\,\overline{\rho}_i(r) = \overline{\lambda}_i \overline{\rho}_i(r) + \sum_{l=1}^{n}\ \psi_l(r)\ \lambda_{li} \tag{7}$$

As can be seen, due to the nonorthogonality of the valence eigenfunctions to the eigenfunctions of that of the ion, a new term appears, which can be described as the effect of a force with the potential $\varphi_i(r)$:

$$e\varphi_i(r)\overline{\rho}_i = \sum_{l=1}^{n}\ \lambda_{li}\ \psi_l(r). \tag{8}$$

With this designation, we convert Eq.(7) into the following form:

$$[H_\tau - e\,(V(r) - A(r) + \varphi_i(r))]\,\overline{\rho}_i(r) = \overline{\lambda}_i \overline{\rho}_i(r) \tag{9}$$

Now we have to determine $\phi_i(r)$ from Eq.(8). The factors λ_{li} are unknown here. Since the functions ψ_j are orthogonal to each other, it follows from Eq.(7) that

$$\lambda_{li} = \int \psi_l^*(r)\left[H_\tau - e\,(V(r) - A(r)) - \overline{\lambda}_i\right]\overline{\rho}_i(r) d\tau_r. \tag{10}$$

These values are still unknown because the eigenvalues $\overline{\lambda_i}$ are not known. Our aim is to determine these. We want to tune the $\overline{\lambda_i}$ in such a way that the newly obtained system of eigenvalues matches the old ones, i.e. that $\overline{\lambda_i} = \lambda_i$ holds. However, we still have to introduce an approximation. As known, the statistically determined electron density corresponds to the wave-mechanically calculated value on average. We can therefore assume that those functions $\overline{\rho_i}(r)$, which do not have nodal planes, will on average coincide with $\rho_i(r)$. From this it follows, however, that the wave-mechanical average value of an arbitrary function $F(r)$ is the same for both eigenfunctions:

$$\int \rho^*(r) F(r) \rho(r) d\tau_r \ = \ \int \overline{\rho}^*(r) F(r) \overline{\rho}(r) d\tau_r. \tag{11}$$

Therefore, their distinction is only necessary when differential operators (in this case the Laplacian) are applied to them. In this case, $\Delta_r \rho_i(r)$ does not match $\Delta_r \overline{\rho_i}(r)$ on average due to the oscillations caused by nodal planes.

According to the above, we can therefore substitute the value of $\overline{\lambda_i}\overline{\rho_i}(r)$ in Eq.(10) by $\lambda_i \rho_i(r)$ from Eq.(5), and thus obtain

$$\begin{aligned} \lambda_{li} \ &= \ \int \psi_l^* \frac{h^2}{8\pi^2 m}\ \Delta_r(\rho_i(r) - \overline{\rho}_i(r)) d\tau_r \\ &- \ e \int \psi_l^* \left(\frac{Ze}{r} + V(r) - A(r)\right)(\rho_i(r) - \overline{\rho}_i(r)) d\tau_r. \end{aligned}$$

As said above, the second line is zero, so substituting

$$\lambda_{li} \ = \ \frac{h^2}{8\pi^2 m} \int \psi_l^* \Delta_r(\rho_i(r) - \overline{\rho}_i(r)) d\tau_r$$

into Eq.(8), we get

$$e\varphi_i(r)\overline{\rho}_i = \frac{h^2}{8\pi^2 m} \sum_{l=1}^{n} \psi_l(r) \int \psi_i^* \Delta_r \big(\rho_i(r) - \overline{\rho}_i(r)\big) d\tau_r \tag{12}$$

In a zeroth approximation $\Delta_r \approx -\frac{h^2}{4\pi^2} p^2$ where p is the momentum. So

$$\Delta_r \overline{\rho}_i(r) \approx -\frac{h^2}{4\pi^2} \overline{p}_i^2 \overline{\rho}_i(r) \tag{13}$$
$$\Delta_r \rho_i(r) \approx -\frac{h^2}{4\pi^2} p_i^2 \rho_i(r)$$

In the right-hand side of the last equation we may also write $\overline{\rho_i}(r)$ instead of $\rho_i(r)$, i.e.

$$\Delta_r \rho_i(r) \approx -\frac{h^2}{4\pi^2} p_i^2 \overline{\rho}_i(r). \tag{14}$$

Substituting Eqs.(13) and (14) into Eq.(12) yields

$$e\varphi_i(r)\overline{\rho}_i = -\frac{1}{2m}(p_i^2 - \overline{p}_i^2) \sum_{l=1}^{n} \psi_l(r) \int \psi_l^*(r)\overline{\rho}_i(r) d\tau_r.$$

The sum at the right-hand side represents the first n members of the series development of $\overline{\rho_i}(r)$. If n is sufficiently large,

$$\overline{\rho}_i(r) \approx \sum_{l=1}^{n} \psi_l(r) \int \psi_l^*(r)\overline{\rho}_i(r) d\tau_r,$$

therefore

$$\varphi_i(r) \ = \ -\frac{1}{e}\frac{1}{2m}(p_i^2 - \overline{p}_i^2),$$

where p_i is the orthogonalized, but $\overline{p_i}$ is the non-orthogonalized momenta of the eigenfunctions. The maximal momentum of the electrons of the ion is $p_\mu \leq p_i$, $p_{oi} \leq \overline{p_i}$ means the maximal momentum of those electrons of the ion whose energy is smaller than the energy corresponding to the electron assigned to the eigenfunction $\overline{\rho_i}(r)$. If we replace p_i or $\overline{p_i}$ with smaller p_μ or p_{oi}, the result is

$$\varphi_i(r) \ = \ -\frac{1}{2me}(p_\mu^2 - \overline{p}_{0i}^2). \tag{15}$$

From Fermi statistics:

$$p_\mu = \frac{h}{2}\left(\frac{3}{\pi}\right)^{1/3} \nu^{2/3}$$
$$p_{oi} = \frac{h}{2}\left(\frac{3}{\pi}\right)^{1/3} \nu_i^{2/3}$$

Inserting these results into Eq.(15), we obtain the expression derived by Gombás:

$$\varphi_i(r) \ = \ -\frac{c}{e}\,(\nu^{2/3} - \nu_i^{2/3}), \tag{16}$$

and for all valence electrons:

$$\varphi(r) \;=\; \sum_{i=1}^{q} \varphi_i(r). \tag{17}$$

When applying this potential, the eigenfunctions of the valence electrons must be orthogonalized to each other. The potential (17) therefore only replaces this orthogonalization of the eigenfunctions of the core electrons. When calculating excited states, we have to orthogonalize the eigenfunction of the valence electron with respect to the eigenfunctions of all lower energies, retroactively down to the ground state.

Institute of Theoretical Physics, Hungarian University, Kolozsvár-Cluj.

(From the session of the natural science section of E.M.E., 26 April)[8]

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[8] The abbreviation E.M.E. reads in Hungarian: Erdélyi Múzeumi Egyesület, meaning: Association of Museums of Transilvania.

The essential message from Fényes in the above paper is given in the introductory paragraph: he presents a derivation for the pseudopotential resulting the same expression that was previously written down intuitively by Gombás. Modern readers may certainly notice shortcomings, like erroneous factors in Eqs.(13)-(14) or the use of the same symbol for an integration variable and for an arguments of a function outside the integral. Also, the errors introduced by certain approximations remain undiscussed. These comments should not overshadow the significance of the single-authored paper of a young physicist from 80 years ago, paving the way towards modern pseudopotentials.

4.2 The contribution by Szépfalusy

As a continuation of Fényes' research, Peter Szepfalusy's work is to be mentioned. He corrected and developed the theory in his paper from 1955[23], published in the *Acta Physica Academaiae Scientiarum Hungariae*, the official journal for physics of the Hungarian Academy of Sciences at that time. To our knowledge, this is the only work, in which the theory of Fényes was cited. This paper is also in German.

Similarly to Fényes, the name of Péter Szépfalusy is not generally known among quantum chemists. As a student of Gombás, Szépfalusy started his research with the many-body problem and with the statistical theory of atoms. Later his interest turned to other areas of statistical physics, superfluidity, superconductivity, nonlinear phenomena and chaos theory, and became well known in these fields. To illustrate his sound knowledge of the many-body problem, we give here the translation of the table of contents of a 36-page-long paper by him, appeared in Hungarian in 1963, in the Hungarian Journal of Physics entitled "On the Green Function Method of the Many Body Problem" [24].

1. Introduction
2. The energy of the ground state; Green's functions
3. Equations for the Green's functions
4. Analytic properties of the one-particle Green's function
5. Perturbation theory
6. Wick's theorem and Feynman-diagrams
7. Construction of the one-particle Green's function by connected graphs
8. The self-energy operator and the Dyson equation
9. Quasiparticles
10. Fermionic systems with repulsive short-range interaction

11. Self-consistent field
12. The superfluid state

APPENDIX

a) Goldstone's method
b) Hartree-Fock approximation
c) Brueckner's approximation

Quite a modern and ambitious list, isn't it? In order to fully appreciate this work, we remind that it was published just two years after Thouless' Quantum Mechanics[25] and Pines' Many-body Problem[26], and eight years *before* the book by Fetter and Valecka[27]...

The English translation of paper[23] is given below. To distinguish the literature references used by Szépfalusy from those at other places in this Chapter, the former are identified as [Sz1], [Sz2], etc., and listed at the end of this inset.

On the Orthogonality of Atomic Orbital Wave Functions

by P. Szepfalusy

Institute of Physics, University of Technology, Budapest

(Submitted by P. Gombás. — Received: June 30, 1955)

(translated from German by András Gombás)

Abstract
The wave functions of the valence electrons of an atom are usually calculated as follows: it is assumed that the valence electrons move in a potential field that arises from the combined effect of the atomic nucleus and the electrons of the atomic core. The potential of the atomic core electrons can be determined from statistical atomic theory. If the wave functions of the valence electrons are determined in this way, their radial parts must have a sufficient number of nodes due to the orthogonality that has to be ensured, which leads to enormous difficulties in the calculation. However, Gombás has shown that the orthogonality condition corresponds to a potential energy according to statistical atomic theory, and he derived two forms of the potential that causes this potential energy using statistical atomic theory [Sz1], [Sz2]. The aim of this work is to interpret these potentials from the point of view of quantum mechanics [Sz3].

I

It is well-known that in quantum mechanics, the exact solution of the atomic multi-particle problem is impossible due to mathematical difficulties. The most general solution method is the "self-consistent field" method [Sz4] formulated in its original form by D. R. Hartree. In the following, we will briefly describe those results of this method that form the basis of our considerations. According to the "self-consistent field" method, the wave function of the multi-particle problem is constructed from one-electron wave functions that do not depend on the coordinates of the other electrons. Fock arranged these wave functions in a determinant form [Sz5] that satisfies the antisymmetric property required by the Pauli principle. With the wave function thus obtained, he then formed the quantum-mechanical expectation value of the Hamiltonian operator of the atom and thus arrived at the energy expression named after him. The mathematically simple form of this energy expression is then obtained if one assumes that the elements of the determinant are orthonormalized, an assumption that – as can be easily shown – does not restrict the generality of the discussion. The one-electron wave functions occurring in this energy expression can be calculated with the aid of the "self-consistent field" method from the Fock equations. The Fock equations are Euler-Lagrange differential equations of the variational problem $\delta W = 0$, where W denotes the total energy of the atom. The orthogonality of one-electron wave functions must be ensured via an auxiliary condition.

In the Fock equations that apply to the atom, none of the wave functions belonging to the variables of the individual electrons plays a distinguished role. The Fock one-electron equation, which can be conveniently used to determine the optical terms, can be obtained as follows. First, one forms the energy expression of the highlighted electron, which is equal to the difference between the energy expression of the complete atom and that of the atomic residue remaining after the removal of one electron. (Here we restrict ourselves to the case of a single electron, but this procedure can be easily generalized to the case of several electrons.) It is assumed that the variation of the wave function of the highlighted electron does not entail a change in the remaining one-electron wave functions. This assumption is particularly well fulfilled in the case of a valence electron lying outside a closed electron shell, and it is precisely this case that will form the subject of our investigations below. Based on the above considerations, the following Fock equation [Sz6] results for the wave function of the valence electron – taking into account the corresponding side conditions:

$$\mathbf{H}\varphi_0(q) + V(r)\varphi_0(q) - \mathbf{A}\varphi_0(q) = E\varphi_0(q), \tag{1}$$

where q represents the three spatial variables and the spin variable, $\varphi_0(q)$ is the wave function of the valence electron, $\mathbf{H} = -\frac{\hbar^2}{2m}\Delta - \frac{Ze^2}{r}$ denotes the operator of the kinetic energy of the valence electron and its interaction with the nucleus, and finally E represents the energy eigenvalue of the valence electron. The operator $\mathbf{A}$ is the exchange energy operator, which, when applied to a function $g(q)$, corresponds to the following operation:

$$\mathbf{A}\ g(q) = e^2 \int \frac{\varrho_0(q, q')}{|r - r'|}\ g(q')\ \mathrm{d}q', \tag{2}$$

where $\varrho_0 = \sum_{i=1}^{n} \varphi_i^*(q)\varphi_i(q')$ represents the charge density of the n core electrons, and $\varphi_i(q)$ denotes the wave function of the ith core electron.

Finally,

$$V(r) = e^2 \int \frac{\varrho_0(q, q')}{|r - r'|}\ \mathrm{d}q' \tag{3}$$

is the Coulomb interaction energy of the valence electron with the other electrons. The wave functions of the electrons in the atomic core must be determined in such a way that the energy of the atomic core is minimized. This condition is met when the wave functions of the core electrons satisfy the following system of Fock equations:

$$\mathbf{H}\varphi_i(q) + V(r)\varphi_i(q) - \mathbf{A}\varphi_i(q) = \sum_{l=1}^{n} E_{il}\ \varphi_l(q). \tag{4}$$

$$(i = 1, 2, ..., n)$$

Here, E_{il} is the Lagrange multiplier, while the other symbols have the same meaning as in Eqs. (1), (2), and (3).

II

It should be recalled that Eqs. (1) and (4) are valid only if the wave functions of the electrons in the atom are orthogonal to each other. We will now examine how Eq. (1) changes if the wave function of the valence electron is not orthogonalized to the wave functions of the core electrons, but the orthogonality of the core electron wave functions to each other is maintained. As a consequence of the latter condition, the energy expression of the core electrons and, together with it, Eq. (4) will remain unchanged. The energy expression of the valence electron was obtained as the difference between the energy expression of the entire atom and the core atom. Therefore, it is the change in the energy expression of the entire atom that needs to be examined. The wave function of the entire atom is given by the following expression:

$$\Phi = \mathrm{A} \begin{vmatrix} \varphi_1(q_1) & . & . & . & . & . & . & \varphi_1(q_n) & \varphi_1(q) \\ \varphi_2(q_1) & . & . & . & . & . & . & \varphi_2(q_n) & \varphi_2(q) \\ . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . \\ \varphi_n(q_1) & . & . & . & . & . & . & \varphi_n(q_n) & \varphi_n(q) \\ \varphi(q_1) & . & . & . & . & . & . & \varphi(q_n) & \varphi(q) \end{vmatrix}, \tag{5}$$

where A is the normalization factor and $\varphi(q)$ is the wave function of the valence electron that is not orthogonalized to the wave functions of the core electrons.

To derive the Fock equation for $\varphi(q)$, one could consider the following line of thought: one could use the wave function (5) to form the energy expression of the atom (the wave-mechanical mean value of the atom's Hamiltonian operator). This energy expression would already be much more complicated than the previously mentioned Fock energy expression [Sz5], since not all one-electron wave functions are orthogonal to each other anymore. By now subtracting the unchanged energy expression of the core electrons from the energy expression obtained in this way, one would arrive at the energy expression of the valence electron. From the vanishing of the variation after $\varphi(q)$ of this energy, one could derive the Fock equation valid for $\varphi(q)$. As a side condition, it would only have to be noted that the wave function $\varphi(q)$ of the valence electron is normalized to 1.

The lengthy calculation described here can now be avoided on the basis of the following consideration.

It is immediately obvious that the determinant (5) does not change if, instead of $\varphi(q)$, the function

$$\varphi(q) + \sum_{i=1}^{n} \mathbf{c}_i \varphi_i(q)$$

is used, where the $\mathbf{c}_i$ are arbitrary constants for the time being. This function can in turn be equated to $\mathbf{c}\varphi_0(q)$, where $\varphi(q)$ is the valence electron wave function orthogonal to the wave functions of the core electrons. The factor $\mathbf{c}$ is therefore necessary because each one-electron wave function is assumed to be normalized to 1. So we have

$$\varphi(q) + \sum_{i=1}^{n} \mathbf{c}_i \varphi_i(q) = \mathbf{c}\ \varphi_0(q), \tag{6}$$

where

$$\mathbf{c}_i = -\int \varphi(q')\varphi_i^*(q')\ \mathrm{d}q',$$

and

$$|\mathbf{c}|^2 = 1 - \sum_{i=1}^{n} |\mathbf{c}_i|^2.$$

Thus, the Fock equation for $\varphi(q)$ can be obtained directly by substituting $\varphi_0(q)$ from Eq. (6) into Eq. (1). When making the substitution, it must be ensured that the wave functions of the core electrons satisfy Eq. (4). This results in the following integro-differential equation for $\varphi(q)$

$$\begin{aligned}\mathbf{H}\varphi_i(q) + V(r)\varphi_i(q) - \mathbf{A}\varphi_i(q) + \sum_{i=1}^{n} \int \varphi(q')\varphi_i^*(q')\ \mathrm{d}q' \Big[E\ \varphi_i(q) - \sum_{l=1}^{n} E_{il}\ \varphi_l(q)\Big] \\ = E\ \varphi(q).\end{aligned} \tag{7}$$

It is evident that this equation - similar to Eq. (1) - is linear in the wave function of the valence electron. This is because a linear operator can be assigned to the sum appearing on the left side of Eq. (7). If this operator is denoted by $\mathbf{O}$, then its matrix element is defined by the following equation:

$$\big(q|\mathbf{O}|q'\big) = \sum_{i=1}^{n} \varphi_i^*(q') \Big[E\ \varphi_i(q) - \sum_{l=1}^{n} E_{il}\ \varphi_l(q)\Big] \tag{8}$$

and it follows that

$$\mathbf{O}\ \varphi(q) = \int \varphi(q') \sum_{i=1}^{n} \varphi_i^*(q') \left[E\ \varphi_i(q) - \sum_{l=1}^{n} E_{il}\ \varphi_l(q) \right] \mathrm{d}q'. \tag{9}$$

If this notation is introduced in Eq. (7), then the equation can be written as follows:

$$\mathbf{H}\varphi_i(q) + V(r)\varphi_i(q) - \mathbf{A}\varphi_i(q) + \mathbf{O}\varphi(q) = E\ \varphi(q). \tag{10}$$

The result obtained in this way can be formulated as follows: if the wave function of the valence electron is not orthogonalized to the wave functions of the core electrons, then in addition to the operator **A**, the operator **O** must also be considered in the Fock equation of the valence electron.

III

The spin variable can be explicitly introduced into Eq. (10). In zeroth-order approximation, the spin state can be considered independent of the state of orbital motion. In this case, the description of the spin state is possible by a spin function $\eta_{m_{si}}(\sigma)$ that depends only on the spin variable [Sz7]. Here, m_{si} is the spin quantum number, σ is the spin variable, and by definition $\eta_{m_{si}}(\sigma) = \delta_{\sigma m_{si}}$ where δ denotes the Kronecker delta symbol. In this approximation, the wave function $\varphi_i(q)$ can be written as the product of a wave function $\psi_i(r)$ that depends only on the spatial coordinates and the spin function as follows:

$$\varphi_i(q) = \psi_i(r)\ \eta_{m_{si}}(\sigma). \tag{11}$$

Correspondingly,

$$\varphi_0(q) = \psi_0(r)\ \eta_{m_s}(\sigma), \tag{12}$$

and

$$\varphi(q) = \psi(r)\ \eta_{m_s}(\sigma). \tag{13}$$

This separation of the variables in the one-electron wave functions leads, in the case of Eq. (1), according to the aforementioned Ref. [Sz6], since the orbitals around the atomic nucleus are occupied by pairs of electrons with opposite spin, to the following result:

$$-\frac{\hbar^2}{2m}\Delta\psi_0(r) + \left[V(r) - \frac{Ze^2}{r} \right]\psi_0(r) - \mathbf{A}\psi_0(r) = E\ \psi_0(r). \tag{14}$$

If the operator **A** is applied to a function $g(r)$ after integration over the spin variable according to Eq. (2), then one has

$$\mathbf{A}\ g(r) = \frac{e^2}{2} \int \frac{\varrho_0(r, r')}{|r - r'|}\ g(r')\ \mathrm{d}r', \tag{15}$$

where

$$\varrho_0(r, r') = \sum_{i=1}^{n} \psi_i^*(r)\psi(r').$$

The potential $V(r)$ in Eq. (3) will take the following form after integration over the spin variable:

$$V(r) = e^2 \int \frac{\varrho_0(r, r')}{|r - r'|}\, g(r')\, \mathrm{d}r'. \tag{16}$$

Eq. (10) differs from Eq. (1) only in the operator $\mathbf{O}$, so now we need to examine how the expression in Eq. (9) of the operator $\mathbf{O}$ changes when we integrate over the spin variable. Due to the orthogonality of the spin functions, only those wave functions $\psi(r)$ associated with the wave functions $\varphi_i(q)$ remain in the matrix element of the operator, in which the spin state of the corresponding core electrons coincides with the spin state of the valence electron. Since the orbitals around the atomic nucleus are occupied by pairs of electrons with opposite spin, this means that in Eq. (9) after summing over the index i the result must be divided by two. After that, it is still to be determined how the quantity $\sum_{i=1}^{n} E_{il}\phi_l(q)$ contained in the expression for the operator behaves when explicit spin dependence is introduced. This quantity is the right-hand side of Eq. (4). If one takes into account that the orbitals around the atomic nucleus are occupied by pairs of electrons with opposite spin, then due to Eq. (4), the parts of the wave functions $\phi_i(q)$ depending on the spatial coordinates, given by Eq. (11), satisfy the following equations:

$$\mathbf{H}\psi_i(r) + V(r)\psi_i(r) - \mathbf{A}\psi_i(r) = \frac{1}{2}\sum_{l=1}^{n} E_{il}\ \psi_l(r) \tag{17}$$

$$(i = 1, 2, ..., n).$$

On the right-hand side, the result was divided by two instead of summing over states with the same spin, i.e., over half of all core states $n/2$, while the limit of the summation was not changed.

Considering the above explanations, we have from Eq. (9):

$$\mathbf{O}\ \psi(r) = \int \psi(r')\ \frac{1}{2}\sum_{i=1}^{n} \psi_i^*(r')\Big[E\ \psi_i(r) - \frac{1}{2}\sum_{l=1}^{n} E_{il}\ \psi_l(r)\Big]\mathrm{d}r', \tag{18}$$

where $\psi(r)$ represents the part of the valence electron wave function $\varphi(q)$ that depends on the spatial coordinates according to Eq. (13). According to Eqs. (10), (14), and (18), the wave function $\psi(r)$ therefore satisfies the following integro-differential equation:

$$-\frac{\hbar^2}{2m}\Delta\psi(r) + \Big[V(r) - \frac{Ze^2}{r}\Big]\psi(r) - \mathbf{A}\psi(r) + \mathbf{O}\psi(r) = E\ \psi(r). \tag{19}$$

In his work [Sz6], which has already been cited frequently here, Fock showed that the valence electron wave function $\psi_0(r)$ appearing in Eq. (14) can be represented in the following form:

$$\psi_0(r) = \frac{1}{\sqrt{4\pi}}\frac{f_0(r)}{r}\ Y_l(\vartheta, \varphi), \tag{20}$$

where $Y_l(\vartheta, \varphi)$ represents the spherical harmonics. According to the relation

$$\int Y_l^* Y_l\ \mathrm{d}\omega = 4\pi, \qquad (\mathrm{d}\omega = \sin\vartheta\ \mathrm{d}\vartheta\ \mathrm{d}\varphi), \tag{20$'$}$$

it is a normalized spherical surface function. The normalization condition for $f_0(r)$ is as follows:

$$\int_0^\infty f_0^*(r) f_0(r)\ \mathrm{d}r = 1. \tag{20$''$}$$

Fock obtained the following equation for $f_0(r)$ after transformations that will not be reproduced here in detail [Sz6]:

$$-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2 f_0(r)}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} f_0(r)\right] + \left[V(r) - \frac{Ze^2}{r}\right] f_0(r) - \mathbf{A}_r f_0(r) = E\ f_0(r). \tag{21}$$

Here is the exchange operator $\mathbf{A}_r$, defined as follows:

$$\mathbf{A}_r\ g(r) = \int_0^\infty G_l(r, r')\ g(r')\ \mathrm{d}r', \tag{22}$$

where $g(r)$ represents an arbitrary function and the detailed form of $G_l(r, r')$ can be found in the frequently cited work of Fock [Sz6].

The Coulomb potential V appearing in Eq. (21), which originates from the electrons of the atomic core, is spherically symmetric if there is an atomic core with a closed electron shell below the valence electron, which was already assumed here from the beginning. This can be easily seen on the basis of the form of $V(r)$ given in Eq. (16), if one takes into account that in the case of an atomic core with closed shells $\varrho_0(r, r')$ is spherically symmetric.

Let us now investigate whether, similarly to Eq. (20), the wave function $\psi(r)$ can also be represented in the following form:

$$\psi(r) = \frac{1}{\sqrt{4\pi}} \frac{f(r)}{r}\ Y_l(\vartheta, \varphi), \tag{23}$$

where the normalization conditions of the individual point functions correspond to those in Eqs. (20$'$) and (20$''$).

Eq. (19) differs from Eq. (14) only in the term $\mathbf{O}\psi(r)$. It is therefore sufficient to prove that the form of the operator $\mathbf{O}$ given in Eq. (18) acts only on the radial part of the given wave function according to Eq. (23). For this purpose, one can represent the variables in the core electron wave functions $\psi_i(r)$ similarly to Eq. (23) as follows:

$$\psi_i(r) = \frac{1}{\sqrt{4\pi}} \frac{f_i(r)}{r}\ Y_{li}(\vartheta, \varphi). \tag{24}$$

The normalization conditions are also similar to Eqs. (20') and (20").

It can be easily shown that if the form of the wave functions given in Eq. (24) is inserted into Eq. (17), only those factors E_{il} will be different from zero for which the spherical functions that describe the angular coordinate-dependent parts of the core electron wave function $\psi_l(r)$ are the same as those of the ith core electron. Thus, only these factors will also appear in the form of the operator $\mathbf{O}$ given in Eq. (18). On the other hand, in Eq. (18), only the radial parts of those wave functions $\psi_i(r)$ will remain in the matrix element of the operator, for which the angular coordinate-dependent spherical functions – due to the orthogonality of the spherical functions with different indices – are the same as the angular coordinate-dependent part of the valence electron wave function. It already follows from these considerations that the operator $\psi(r)$ of Eq. (18) does not act on the angular coordinate-dependent part of the wave function.

Thus, taking into account Eq. (21), the following equation can be set up for the part $f(r)$ of the wave function $\psi(r)$:

$$-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2 f(r)}{\mathrm{d}r^2}-\frac{l(l+1)}{r^2}f(r)\right]+\left[V(r)-\frac{Ze^2}{r}\right]f(r)-\mathbf{A}_r f(r)+\mathbf{O}f(r)=E\ f(r), \tag{25}$$

where

$$\mathbf{O}\ f(r)=\int_0^\infty f(r')\ \frac{1}{2}\sum_i f_i^*(r')\left[Ef_i(r)-\frac{1}{2}\sum_l E_{il}f_l(r)\right]\mathrm{d}r'. \tag{26}$$

Here, according to the above explanations, the summation over the indices i and l is to be extended to those core electron wave functions whose spherical functions describing the angular coordinate-dependent part coincide with that of the valence electron.

IV

In the following, we will turn to the determination of the semiclassical analog of the operator $\mathbf{O}$ occurring in Eq. (25). For this purpose, an approximation will be used that greatly simplifies our result. The behavior of the wave function $f(r)$ is such that it forms the average of the wave function $f_0(r)$ – which performs the oscillations necessary for orthogonalization. For this reason, it can be assumed that the quantum-mechanical expectation value of any sufficiently smooth function (e.g. the electrostatic and exchange potentials in our case) is the same for both wave functions. This means, for example:

$$\int_0^\infty f^*(r)V(r)f(r)\ \mathrm{d}r=\int_0^\infty f_0^*(r)V(r)f_0(r)\ \mathrm{d}r. \tag{27}$$

This is naturally not fulfilled for the differential operator of kinetic energy.

Let Eqs. (21) and Eq. (25) be multiplied with $f_0^*(r)$ and with $f^*(r)$, respectively, and integrated over the entire range of r. If the first equation is subtracted from the second and the approximation in Eq. (27) is used, the following result is obtained:

$$\int_0^\infty f^*(r)\mathbf{O}f(r)\ \mathrm{d}r=-\frac{\hbar^2}{2m}\int_0^\infty\left[f_0^*(r)\frac{\mathrm{d}^2}{\mathrm{d}r^2}f_0(r)-f^*(r)\frac{\mathrm{d}^2}{\mathrm{d}r^2}f(r)\right]\mathrm{d}r. \tag{28}$$

If one now treats the atom semiclassically, i.e., neglects the commutation relation between the coordinate and the canonically conjugate momentum component, then one can write:

$$-\hbar^2\frac{\mathrm{d}^2 f_0(r)}{\mathrm{d}r^2}=p_{r0}^2(r)f_0(r) \tag{29}$$

and

$$-\hbar^2\frac{\mathrm{d}^2 f(r)}{\mathrm{d}r^2}=p_r^2(r)f(r),$$

where p_{r0} and p_r denote the radial momentum of the valence electron in the orthogonalized and non-orthogonalized cases, respectively.

Substituting Eq. (29) into Eq. (28) and using again the approximation introduced in Eq. (27), we obtain:

$$\int_0^\infty f^*(r)\mathbf{O}f(r)\ \mathrm{d}r = \frac{1}{2m}\int_0^\infty f^*(r)\Big[p_{r0}^2(r) - p_r^2(r)\Big]f(r)\ \mathrm{d}r. \tag{30}$$

This means that the energy represented by the operator $\mathbf{O}$ can be interpreted as the effect of a potential Φ, if this potential is defined as follows:

$$\Phi = -\frac{1}{e}\frac{1}{2m}\Big[p_{r0}^2(r) - p_r^2(r)\Big]. \tag{31}$$

Eq. (25) can now be written as follows using this expression:

$$-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2 f(r)}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2}f(r)\right] + \left[V(r) - \frac{Ze^2}{r}\right]f(r) - \mathbf{A}_r f(r) - e\Phi f(r) = E\ f(r). \tag{32}$$

Let us now examine Eq. (31) for the potential Φ in detail and transform it using the statistical atomic model. According to statistical atomic theory, the kinetic energy resulting from the orthogonalization of the valence electron wave function to the core electron wave functions is a consequence of the so-called "exclusion principle." This principle states that in a phase space cell of size $h^3/2$, due to the Fermi-Dirac statistics of electrons, at most one electron can be present. If, therefore, in the atom, in the vicinity of an arbitrary location r, we assume such a volume element Δv in which many electrons are already present, but in which the potential can still be considered constant, then at this location the individual electrons occupy cells in momentum space of size $h^3/2\Delta v$. The cells with lower energy are gradually filled by the core electrons. In this way, the radial momentum of the valence electron must be greater than the maximum radial momentum $p_{r\mu}(r)$ of the core electrons, which have an azimuthal kinetic energy that coincides with the azimuthal kinetic energy of the valence electron. If we assume that the valence electron cannot be located in the cells occupied by the core electrons in momentum space – in other words, if we do not orthogonalize the valence electron wave function to the wave functions of the core electrons – then the radial momentum of the valence electron decreases from $p_{r0}(r)$ to $p_{r0}(r)$, where $p_{r0}(r)$ is the so-called radial eigenmomentum of the valence electron [Sz8]. Therefore, we can write:

$$p_{r0}(r) = p_{r\mu}(r) + p_r(r) \tag{33}$$

and from Eq. (4) it follows thus

$$\Phi = -\frac{1}{e}\frac{1}{2m}\Big[p_{r\mu}^2(r) + 2p_{r\mu}(r)p_r^2(r)\Big]. \tag{34}$$

Since $p_r, << p_{r\mu}$ in the case of the valence electron, Eq. (34) can be simplified in a first approximation as follows:

$$\Phi = -\frac{1}{e}\frac{1}{2m}p_{r\mu}^2(r). \tag{35}$$

If one disregards the grouping of core electrons according to the azimuthal quantum number and denotes the maximum momentum of the core electrons at a given location in momentum space as p_μ, then

$$p_{r\mu}^2 = p_\mu^2 - p_\varphi^2, \tag{36}$$

where p_ϕ represents the azimuthal momentum of the valence electron.

According to statistical atomic theory

$$p_\mu = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2} h\varrho^{1/2} \tag{37}$$

and

$$p_\varphi = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2} h\varrho_i^{1/2},$$

where ϱ represents the total electron density of the atomic core and ϱ_i represents the density of those core electrons whose kinetic energy is less than the azimuthal kinetic energy of the valence electron, which is completely determined by the azimuthal quantum number of the valence electron [Sz1].

Substituting the values from Eq. (37) into Eq. (36), one obtains, due to the form of the potential Φ given in Eq. (35), the Gombás potential F derived from statistical atomic theory [Sz1]:

$$F = -\gamma_0\big(\varrho^{2/3} - \varrho_i^{2/3}\big), \tag{38}$$

where $\gamma_0 = \frac{1}{2}(3\pi^2)^{3/2} e a_0$ in atomic units.

On the other hand, if a more detailed grouping of electrons according to the azimuthal quantum number is carried out [Sz2], then the maximum radial momentum of a core electron with azimuthal quantum number l is given by

$$p_{r\mu} = \frac{h}{4(2l+1)} D_l, \tag{39}$$

where D_l is the radial density of core electrons with azimuthal quantum number l.

In this case, the potential Φ, which is analogous to the Gombás potential G, can be set as follows:

$$\Phi = -\frac{\pi^2}{8(2l+1)^2} e a_0 D_l^2, \tag{40}$$

while the form of the Gombás potential G is [Sz2]:

$$G = -\frac{\pi^2}{8(2l+1)^2} e a_0 D_l^2 - \frac{1}{4} e a_0 \frac{1}{r^2}. \tag{41}$$

The second term on the right-hand side is a consequence of the statistically averaged azimuthal kinetic energy, which always occurs when one transitions from quantum mechanics to the approximation of statistical atomic theory [Sz2]. This means that instead of the azimuthal kinetic energy $\frac{1}{2} e^2 a_0 \frac{l(l+1)}{r^2}$ given by quantum mechanics, the quantity $\frac{1}{2} e^2 a_0 [l(l+1) + \frac{1}{2}]/r^2$ is to be taken. If this transformation is carried out in Eq. (32) and the quantity appearing as a new term is added to the potential Φ, then one arrives at the complete potential G.

In Eq. (34), the second term on the right-hand side has been neglected here. This term can also be derived from statistical atomic theory as a secondary effect, but this will not be discussed here.

The above discussions thus prove that the orthogonalization of the ”wave function of the valence electron” to the wave functions of the core electrons can be replaced by a linear operator whose semiclassical analogies are the potentials F and G derivable from statistical atomic theory.

At this point, I would like to express my sincere thanks to Professor Dr. P. Gombás for his valuable advice.

LITERATURE

[Sz1] See e.g. P. Gombás, Die statistische Theorie des Atoms und ihre Anwendungen, S. 150, Springer, Wien, 1949.

[Sz2] P. Gombás, Acta Phys. Hung., **1**, 285, 1952.

[Sz3] For the potential F, which is applicable to a narrower field, partially similar calculations were carried out by I. Fenyes, Muzeumi Füzetek, **3**, 14, 1945.

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[Sz7] See e.g. P. Gombás, Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellen-mechanik, S. 54, Birkhäuser, Basel, 1950.

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4.3 Coda

Szépfalusy's paper was not the only publication from the Gombás school that dealt with pseudopotentials. Another member emitted from this group, Levente Szász, settled in the USA and published several papers on the subject in journals including Physical Review,[28, 29, 30] and Journal of Chemical Physics,[31, 32, 33]. He also wrote a review[34] on pseudopotentials in 1977 with full credits to the early works of Gombás and Szépfalusy.

Rezső Gáspár, who is mostly known in the international community for his contribution to Slater's X_α theory, was also a member of the Gombás group. He became full professor in Debrecen, member of the Hungarian Academy of Sciences, as well as a member of the International Academy of Quantum Molecular Sciences. He continued research in pseudopotential theory, publishing a few dozens of paper on this subject. His contributions are summarized in a Festschrift of THEOCHEM Vols.**151-152.**, edited by Imre Csizmadia and Ágnes Nagy on the occasion of his 80th birthday. Legacy of Gáspár and his school are summarized in part III., Chapter 7. of this book.

An important development in pseudopotential theory was done by Phillips from 1958. In his first paper[35] he wrote: *Gombás[36] and his associates have independently given a semiclassical treatment that is in many respect parallel to that of Hellman. In particular, Szepfalusy[23] has shown that the orthogonality terms can be replaced by a linear operator...* Albeit the name of Fényes is not mentioned here, it is apparent that a sufficient credit was given to the Hungarian school, even if in subsequent papers by Phillips[37] only his original work Ref.[35] was referenced, and due to its importance, modern authors tend to cite only Ref.[37].

However, the results of Gombás and Szépfalusy were not forgotten. In a more recent review by Schwerdtfegel[38], both of these early authors are properly referenced.

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