

On the long way from the Coulombic Hamiltonian to the electronic structure of molecules

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Abstract.- The mathematical foundation for the present quantum theory of atoms and molecules is discussed. After a brief review of the mathematical properties desired of operators corresponding to physical observables and the tool of operator inequalities, the basic properties of the Coulombic Hamiltonian for a system of electrons and atomic nuclei are studied. It is shown that this operator is not only self-adjoint - as proven by Kato - but also bounded from below, and that its lowest eigenvalue is negative and is situated at the bottom of a continuum due to the motion of the center of mass. After removing the motion of the center of mass, the remainder Hamiltonian is investigated in view of the WHVZ-theorem to show a sufficient condition for the mathematical existence of a molecule in its ground state. Some general aspects on the connection between the Coulombic Hamiltonian and present molecular theory are also discussed.

INTRODUCTION

In 1929 Dirac made a famous prediction about the future of physics and chemistry: "*The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact applications of these laws leads to equations much too complicated to be soluble*". In studying this statement, one has to remember that Newton's laws of gravitation and classical mechanics regulate the planetary motions in our solar system, but they don't describe the system itself: the various planets and their masses, and the initial conditions for studying their motions. In the same way, quantum theory does not describe the system under consideration, but it may tell us the laws which are valid for it. One should further observe that the *mathematical theory* of the quantum-mechanical equations involved is a research field itself dealing with the existence, nature and character of the solutions, whereas the numerical evaluation of the solutions belongs to the fields of *applied mathematics* and *computational science*. There is hence a long way to go - perhaps even longer than Dirac anticipated - from the Schrödinger equation for a system with a Coulombic Hamiltonian to an understanding of the electronic structure of atoms and molecules, and, in this paper, we will try to discuss and highlight certain aspects of this problem. It should further be emphasized from the very beginning that, even if the atomic nuclei may be considered as point charges described by their atomic numbers and masses, our current *ab-initio* quantum chemistry is to a large extent still based on a great deal of chemical and physical insight of mostly experimental nature.

SCHRÖDINGER EQUATION AND ITS BOUNDARY CONDITIONS

Modern quantum mechanics [ref.1] is built on the idea that a physical situation is described by a state vector or wave function Ψ , which obeys the Schrödinger equation

$$-\frac{\hbar}{2\pi i} \frac{\partial \Psi}{\partial t} = H \Psi, \quad (1)$$

with the initial condition $\Psi = \Psi(0)$ for $t = t_0$. Here H is the classical Hamiltonian in which each momentum \mathbf{p}_k is replaced by the operator $\mathbf{p}_k = -(\hbar/2i)(\partial/\partial x_k, \partial/\partial y_k, \partial/\partial z_k)$. In principle, this equation is easily solved by means of the evolution operator $S(t, t_0) = \exp\{-(\hbar/2i) H (t - t_0)\}$ leading to the solution $\Psi(t) = S(t, t_0) \Psi(0)$. If $H = H_0 + \lambda V$, and the operators H_0 and V do not commute, one has also the famous solution in terms of the *interaction picture*, which forms the basis for the *time-dependent perturbation theory*. The so-called stationary states are given by solutions, where the space part satisfies the time-independent Schrödinger equation:

$$H \Psi = E \Psi. \quad (2)$$

As a partial differential equation of the second order, this equation has solutions for every real or complex value of the parameter E . However, only a few of these solutions satisfy the physical boundary conditions, and the corresponding parameter values are said to form the energy spectrum (E) of the system. The quantity $|\Psi|^2$ is usually interpreted as being proportional to the *probability density*, and solutions which correspond to the condition $\int |\Psi|^2 dX < \infty$ are said to correspond to *closed states* associated with a *discrete* eigenvalue E . Usually the wave functions are normalized so that $\int |\Psi|^2 dX = 1$. In physics, there are also *scattering states*, for which the integral $\int |\Psi|^2 dX$ is divergent but which instead have the property that the absolute value $|\Psi|$ is finite "almost everywhere". These states are associated with *continuous* eigenvalues E which form intervals on the real axis.

The Hilbert space. One of the foremost mathematical tools used in modern quantum theory is the concept of the *abstract Hilbert space* [ref.2], which is a linear space $\mathbb{H} = \{\Psi\}$ having a binary product $\langle \Psi_1 | \Psi_2 \rangle$ which is linear in the second position, hermitean symmetric, and positive definite, so that:

$$\begin{aligned} \langle \Psi_1 | \Psi_2 + \Psi_3 \rangle &= \langle \Psi_1 | \Psi_2 \rangle + \langle \Psi_1 | \Psi_3 \rangle, \quad \langle \Psi_1 | \Psi_2 \alpha \rangle = \alpha \langle \Psi_1 | \Psi_2 \rangle, \\ \langle \Psi_2 | \Psi_1 \rangle &= \langle \Psi_1 | \Psi_2 \rangle^*, \\ \| \Psi \|^2 &= \langle \Psi | \Psi \rangle \geq 0, \quad \text{and} = 0, \text{ if and only if } \Psi = 0. \end{aligned} \quad (3)$$

The abstract Hilbert space consists of all elements Ψ having a finite norm $\| \Psi \| < \infty$. It is further assumed to be *complete*, in the sense that it contains all its limit points in the norm, i.e. to every fundamental sequence $\Psi_1, \Psi_2, \Psi_3, \Psi_4, \dots$ with the property $\| \Psi_m - \Psi_n \| < \epsilon$ for $m > n > N(\epsilon)$, there is a limiting element Ψ having the property $\| \Psi - \Psi_n \| < \epsilon$ whenever $n > N(\epsilon)$. It is also assumed to be *separable*, in the sense that there exists an enumerable set $\Phi = \{\Phi_k\}$ which is everywhere dense in \mathbb{H} , so that to any element Ψ there exists at least one element Φ_k for which $\| \Psi - \Phi_k \| < \epsilon$. The separability axiom makes sure that there exists at least one complete orthonormal set, which spans the abstract Hilbert space, and we note that it is also the basis for all approximate calculations of arbitrary accuracy in this space.

In ordinary quantum mechanics, one deals with at least two realizations of the abstract Hilbert space. The first one is the *sequential Hilbert space* consisting of all infinite column vectors $\mathbf{c} = \{c_k\}$ having a finite norm $\| \mathbf{c} \|$ in terms of the binary product $\langle \mathbf{a} | \mathbf{b} \rangle = \mathbf{a}^\dagger \mathbf{b} = \sum_k a_k^* b_k$. The second one is the *L^2 Hilbert space* consisting of all wave functions $\Psi = \Psi(X)$, where X is a many-particle coordinate $X = (x_1, x_2, x_3, \dots, x_N)$ consisting of combined space-spin coordinates $x_k = (r_k, \zeta_k)$, having a finite norm $\| \Psi \| = \langle \Psi | \Psi \rangle^{1/2}$ in terms of the binary product:

$$\langle \Psi_1 | \Psi_2 \rangle = \int \Psi_1^*(X) \Psi_2(X) dX, \quad (4)$$

where the symbol \int indicates that a Lebesgue integration is to be carried out over all the space coordinates r_k and a summation over all spin coordinates ζ_k .

It is now convenient to reformulate the boundary conditions to the eigenvalue problem (2) in terms of the L^2 Hilbert space. It is evident that an eigen-function Ψ corresponds to a closed state and a discrete eigenvalue E , if Ψ is an element of the L^2 space: i.e. $\Psi \in L^2$. For the scattering states, on the other hand, it is clear that the eigenfunction $\Psi(E)$ does not belong to L^2 , since it has an infinite norm. A closer study of the continuum wave functions shows, however, that they are also related to the L^2 space, in the sense that they are derivatives of principal functions $\Phi(E)$ which are in fact elements of the L^2 space, so that $\Psi(E) = d\Phi(E) / dE$. A good elementary example is provided by the wave function for a free particle. Using the definition of the derivative, one finds the relation

$$\Psi(X,E) = \lim_{n \rightarrow \infty} \frac{\Phi(X,E + 1/n) - \Phi(X,E)}{1/n} = \lim_{n \rightarrow \infty} f_n(X,E) \quad (5)$$

which shows that $\Psi(X,E)$ is a limit point of the L^2 Hilbert space - not in the norm - but in *absolute value*, so that there exists a series of elements $f_n(X,E)$ in L^2 such that $|\Psi(X,E) - f_n(X,E)| < \epsilon$, whenever $n > N(X, \epsilon)$, which implies point-by-point convergence of the sequence $f_n(X,E)$ towards the continuum wave function $\Psi(X,E)$. This result is of essential importance in the quantum theory of scattering phenomena, since it means that one can apply L^2 -methods also in this case.

Expectation values. If F is an operator corresponding to a physical observable F , its *expectation value* $\langle F \rangle$ in a physical situation represented by the wave function Φ is given by the well-known expression:

$$\langle F \rangle = \frac{\langle \Phi | F | \Phi \rangle}{\langle \Phi | \Phi \rangle} \quad (6)$$

It is evident that, if F is a physical observable, the expectation value $\langle F \rangle$ ought to be a *real* quantity, i.e. $\langle F \rangle = \langle F \rangle^*$. Since the denominator $\langle \Phi | \Phi \rangle$ is always real, the same must apply to the numerator $\langle \Phi | F | \Phi \rangle$. Hence, one has $\langle \Phi | F | \Phi \rangle = \langle \Phi | F | \Phi \rangle^* = \langle F \Phi | \Phi \rangle$. At this stage, one may apply the so-called *polarization identity*, which gives:

$$\begin{aligned} \langle \Phi_1 | F | \Phi_2 \rangle &\equiv (1/4) \{ \langle \Phi_1 + \Phi_2 | F | \Phi_1 + \Phi_2 \rangle - \langle \Phi_1 - \Phi_2 | F | \Phi_1 - \Phi_2 \rangle \} + \\ &\quad + (1/4i) \{ \langle \Phi_1 + i\Phi_2 | F | \Phi_1 + i\Phi_2 \rangle - \langle \Phi_1 - i\Phi_2 | F | \Phi_1 - i\Phi_2 \rangle \} = \\ &= (1/4) \{ \langle F(\Phi_1 + \Phi_2) | \Phi_1 + \Phi_2 \rangle - \langle F(\Phi_1 - \Phi_2) | \Phi_1 - \Phi_2 \rangle \} + \\ &\quad + (1/4i) \{ \langle F(\Phi_1 + i\Phi_2) | \Phi_1 + i\Phi_2 \rangle - \langle F(\Phi_1 - i\Phi_2) | \Phi_1 - i\Phi_2 \rangle \} = \\ &= \langle F \Phi_1 | \Phi_2 \rangle. \end{aligned} \quad (7)$$

An operator having this property is said to be *hermitean symmetric*. It is easily shown by partial integration that Schrödinger's momentum operator $p = (\hbar/2\pi i) \partial / \partial x$ has this property. In the mathematical theory of the Hilbert space, a linear operator T is said to have the *adjoint* operator T^\dagger defined through the relation:

$$\langle \Phi_1 | T \Phi_2 \rangle = \langle T^\dagger \Phi_1 | \Phi_2 \rangle \quad (8)$$

An operator T is further said to have the domain $D(T) = \{ \Phi \}$ if - for each of its elements - both Φ and $T\Phi$ belong to L^2 . In the same way, the adjoint operator T^\dagger has its own domain $D(T^\dagger)$. A linear operator F is further said to be *self-adjoint*: $F = F^\dagger$, if it satisfies the relation $\langle \Phi_1 | F \Phi_2 \rangle = \langle F \Phi_1 | \Phi_2 \rangle$ and if F and F^\dagger have the same domain: $D(F) = D(F^\dagger)$. Even if it may be comparatively easy to show that the operators in quantum mechanics corresponding to physical observables are hermitean symmetric, it is much more difficult to show that they are also self-adjoint, and we will return to this question at a later stage.

Operator inequalities. An important mathematical tool in quantum theory is the use of operator inequalities. If a self-adjoint operator Ω has the property $\langle \Phi | \Omega | \Phi \rangle > 0$ for all Φ in the domain of Ω , one says that the operator Ω is *positive definite* and writes $\Omega > 0$. Similarly, if A and B are two self-adjoint operators and if $\langle \Phi | A | \Phi \rangle > \langle \Phi | B | \Phi \rangle$ for all Φ in the common domain of A and B , one writes $A > B$. Putting $\Phi = T\Theta$ and using (8), one gets further the relation $T^\dagger A T > T^\dagger B T$, so that

$$A > B, \quad \Rightarrow \quad T^\dagger A T > T^\dagger B T. \quad (9)$$

Let us now consider a self-adjoint projector O having the properties $O^2 = O$, $O^\dagger = O$, or in one relation $O = O^\dagger O$. Such a projector fulfills the inequality

$$0 \leq O \leq 1, \quad (10)$$

i.e. the projector O is situated between the zero operator and the identity operator. The proof is simple and follows from the fact that $\langle \Phi | O | \Phi \rangle = \langle \Phi | O^\dagger O | \Phi \rangle = \langle O \Phi | O \Phi \rangle = \| O \Phi \|^2 \geq 0$, which gives $O \geq 0$. Since the same reasoning applies to the projector $P = 1 - O$, one has also $P = 1 - O \geq 0$, which proves the remaining part of the theorem. Combining (9) and (10), one gets further

$$0 \leq T^\dagger O T \leq T^\dagger T. \quad (11)$$

If A is a positive definite operator, and $T = T^\dagger = A^{1/2}$ is chosen as the positive square root of A , one has the operator inequality

$$0 \leq A^{1/2} O A^{1/2} \leq A, \quad (12)$$

and the operator $A' = A^{1/2} O A^{1/2}$ is often referred to as the *inner projection* of A with respect to the projector O [ref.3]. It provides apparently a *lower bound* to the operator A . The concept may be further generalized to other types of operators.

Let us next consider a self-adjoint operator F having only discrete eigenvalues f_k associated with the eigenfunctions φ_k , which form a complete orthonormal set $\varphi = \{ \varphi_k \}$. The orthonormality may be expressed in the relation $\langle \varphi_k | \varphi_l \rangle = \delta_{kl}$ or in matrix form $\langle \varphi | \varphi \rangle = 1$, and the completeness in the relation $1 = \sum_k |\varphi_k\rangle \langle \varphi_k| = |\varphi\rangle \langle \varphi|$, which is a *resolution of the identity*. Letting F work on the last relation, one gets also $F = \sum_k f_k |\varphi_k\rangle \langle \varphi_k| = |\varphi\rangle f \langle \varphi|$, which is the *spectral resolution* of the operator F . Here f is the diagonal matrix formed by the eigenvalues f_k . In "fat symbols", one has hence the relations

$$\langle \varphi | \varphi \rangle = 1, \quad 1 = |\varphi\rangle \langle \varphi|, \quad F = |\varphi\rangle f \langle \varphi|. \quad (13)$$

We note that the operators $O_k = |\varphi_k\rangle \langle \varphi_k|$ are self-adjoint projectors, which satisfy the inequality (10). Let us now assume that the operator F has a lowest eigenvalue f_0 , so that $f_k \geq f_0$ for all k . Using the spectral resolution and the fact that $(f_k - f_0) O_k \geq 0$, one gets immediately

$$F - f_0 \cdot 1 = \sum_k (f_k - f_0) |\varphi_k\rangle \langle \varphi_k| = \sum_k (f_k - f_0) O_k \geq 0, \quad (14)$$

i.e.

$$F \geq f_0 \cdot 1 \quad (15)$$

which means that the operator F is *bounded from below*. The proof is easily extended also to the case when F has partly a continuous spectrum.

On the other hand, if a self-adjoint operator F is bounded from below, so that $F > \alpha \cdot 1$, it has always a lowest eigenvalue, which is either *discrete or continuous*. In order to prove this statement, we will assume that the number f_0 is the best lower bound, so that $F \geq f_0 \cdot 1$. It is evident that the operator $\Omega = F - f_0 \cdot 1$ is positive semi-definite, so that $\Omega \geq 0$. Let us further assume that the equality sign in the relation $\langle \Phi | \Omega | \Phi \rangle \geq 0$ is attained for a normalizable wave function φ_0 in the domain of Ω , and let us then consider the normalizable trial function $\Phi = \varphi_0 + \lambda \psi$ - where λ is a real parameter - and the associated inequality

$$\langle \Phi | \Omega | \Phi \rangle = \langle \varphi_0 + \lambda \psi | \Omega | \varphi_0 + \lambda \psi \rangle = \lambda \langle \psi | \Omega | \varphi_0 \rangle + \lambda \langle \varphi_0 | \Omega | \psi \rangle + \lambda^2 \langle \psi | \Omega | \psi \rangle \geq 0, \quad (16)$$

which becomes a contradiction unless $\langle \psi | \Omega | \varphi_0 \rangle = 0$. Putting $\psi = \Omega \varphi_0$, one gets $\langle \psi | \Omega | \varphi_0 \rangle = \langle \Omega \varphi_0 | \Omega \varphi_0 \rangle = \| \Omega \varphi_0 \|^2 = 0$, i.e. one has $\Omega \varphi_0 = 0$. Hence f_0 is a discrete eigenvalue to F corresponding to a closed state with the normalizable eigenfunction φ_0 .

It should be observed, however, that the best bound may not be attained for any normalizable wave function. A simple example is provided by the operator $T = p^2/2m$ for the kinetic energy. One gets directly $\langle \Phi | T | \Phi \rangle = \langle \Phi | p^2 | \Phi \rangle / 2m = \langle p\Phi | p\Phi \rangle / 2m = \| p\Phi \|^2 / 2m \geq 0$, and the best lower bound is hence 0. We note, however, that there is no normalizable wave function for which this value is attained, and the reason is, of course, that the value 0 is the lower limit of the continuous spectrum for the operator $T = p^2/2m$. These preliminary considerations are enough to permit us to go to the main problem of this paper.

THE COULOMBIC HAMILTONIAN AND ITS PROPERTIES

Let us consider a system of particles k with mass m_k and charge e_k having the Coulombic Hamiltonian:

$$H = \sum_k \frac{p_k^2}{2m_k} + \sum_{k < l} \frac{e_k e_l}{r_{kl}} = T + C, \quad (17)$$

where T is the kinetic energy and C the Coulomb energy. It was early proven by Schrödinger that this Hamiltonian was hermitean symmetric, but it would take until 1951 until Kato [ref.4] proved that it was *essentially self-adjoint*. Kato's proof takes about 18 pages, and it gives a great deal of insight into the mathematical properties of the Coulombic Hamiltonian.

Let us assume that the system under consideration consists of N electrons having mass m and charge e and being labeled with the index $i = 1, 2, 3, \dots, N$ and the additional index j whenever electron pairs are studied, and of A atomic nuclei considered as point charges being labeled with the index $g = 1, 2, 3, \dots, A$ and the additional index h whenever pairs are involved. In such a case, the Hamiltonian (17) may be separated into four terms:

$$H = \sum_g p_g^2 / m_g + e^2 \sum_{g < h} Z_g Z_h / r_{gh} + \sum_i (p_i^2 / m - e^2 \sum_g Z_g / r_{ig}) + \sum_{i < j} e^2 / r_{ij}, \quad (18)$$

with obvious physical interpretations. The first, second, and fourth terms are all positive definite and have no upper bounds. The main problem is the nature of the third term, and the mathematicians have intricate methods to show that it is bounded from below. Here we will try to give a simple proof using only the principles outlined in the first section.

A hydrogen-like ion consisting of a single electron and a nucleus with atomic number Z and infinite mass has a Hamiltonian of the form:

$$H_1 = p_1^2 / m - e^2 Z / r_{1g}, \quad (19)$$

the eigenvalue problem of which may be solved exactly analytically. The energy spectrum consists of a series of discrete levels

$$E_n = -2\pi^2 m e^4 Z^2 / n^2 h^2, \quad \text{for } n = 1, 2, 3, \dots \quad (20)$$

and a continuum covering the interval $[0, +\infty]$. Using the theorem that a self-adjoint operator is bounded from below by its lowest eigenvalue - if it has one - one obtains the operator inequality

$$H_1 = p_1^2 / m - e^2 Z / r_{1g} \geq -2\pi^2 m e^4 Z^2 / h^2, \quad (21)$$

and in general for electron i and nuclei g :

$$H_i = p_i^2 / m - e^2 Z_g / r_{ig} \geq -2\pi^2 m e^4 Z_g^2 / h^2, \quad (22)$$

which is still a "sharp" inequality. For the third term of the Hamiltonian (18), one obtains then the following rough estimate

$$\begin{aligned} \sum_i (p_i^2 / m - e^2 \sum_g Z_g / r_{ig}) &= \sum_i \sum_g A^{-1} (p_i^2 / m - e^2 A Z_g / r_{ig}) \geq \\ &\geq \sum_i \sum_g A^{-1} (-2\pi^2 m e^4 A^2 Z_g^2 / h^2) = (-2\pi^2 m e^4 A N / h^2) \sum_g Z_g^2. \end{aligned} \quad (23)$$

Hence also the total Coulombic Hamiltonian is *bounded from below*, and the spectrum has a lowest eigenvalue E_0 , so that

$$H \geq E_0.1. \quad (24)$$

This in turn gives rise to the relation $\langle \Phi | H | \Phi \rangle \geq E_0 \langle \Phi | \Phi \rangle$ and to the well-known *variation principle*:

$$\langle H \rangle = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E_0, \quad (25)$$

which forms the basis for most of computational quantum chemistry. It is interesting to observe that the lowest eigenvalue E_0 is always *negative*, and for the proof we will use the scaling procedure introduced by Hylleraas in 1929 [ref.5]. Using a positive scale factor η , he scaled all the coordinates according to the formula $r_k' = \eta r_k$ and the wave function Φ by the relation

$$\Phi' = \eta^{3(N+A)/2} \Phi(\eta r_k). \quad (26)$$

Observing that the normalization integral stays invariant, so that $\langle \Phi' | \Phi' \rangle = \langle \Phi | \Phi \rangle = 1$, he obtained for the expectation values of the kinetic energy and the Coulomb energy, respectively:

$$\langle T \rangle' = \langle \Phi' | T | \Phi' \rangle = \eta^2 \langle \Phi | T | \Phi \rangle = \eta^2 \langle T \rangle, \quad (27)$$

$$\langle C \rangle' = \langle \Phi' | C | \Phi' \rangle = \eta \langle \Phi | C | \Phi \rangle = \eta \langle C \rangle, \quad (28)$$

and

$$\langle H \rangle' = \eta^2 \langle T \rangle + \langle C \rangle = \langle T \rangle \{ \eta + \langle C \rangle / 2 \langle T \rangle \}^2 - \langle C \rangle^2 / 4 \langle T \rangle, \quad (29)$$

which assumes the minimum value $-\langle C \rangle^2 / 4 \langle T \rangle$, which is negative. For the value $\eta = -\langle C \rangle / 2 \langle T \rangle$, the virial theorem is automatically satisfied [ref.6]. Hence one has the inequality

$$E_0 \leq \langle H \rangle' \leq 0, \quad (30)$$

which proves our statement. As we will see in the next section, the lowest eigenvalue E_0 of the Coulombic Hamiltonian lies at the *bottom of a continuum*, and this means that the associated eigenfunction Ψ_k corresponds to a scattering state. At first sight, this may seem confusing, but we will see below that there are good physical reasons for this type of behaviour.

Constants of motion and the separation of the motion of the center of mass. The Coulombic Hamiltonian is translationally and rotationally invariant, and it is further invariant under permutations of the electronic coordinates r_i and of such nuclear coordinates r_g as are associated with nuclei having the same mass m_g . These invariance properties indicate that the Coulombic Hamiltonian has the following *constants of motion*:

- 1) The total momentum: $\mathbf{P} = \sum_k \mathbf{p}_k$,
- 2) The total angular momentum: $\mathbf{L} = \sum_k \mathbf{r}_k \times \mathbf{p}_k$,
- 3) The permutations P of the electronic coordinates x_i leading to the Pauli principle and the antisymmetry property of the wave function: $P \Psi = (-1)^P \Psi$.
- 4) The permutations of such nuclear coordinates as are associated with nuclei of the same mass and the symmetric group in general.

Needless to say, there may also be more complicated constants of motion - like the Runge-Lenz vector for the hydrogen atom - but those have to be worked out in every special case.

According to the laws of quantum mechanics, the center of mass of our system

$$\xi = \frac{1}{M} \sum_k r_k, \quad M = \sum_k m_k, \quad (31)$$

is moving like a *free particle* having an energy spectrum covering the interval $[0, +\infty]$,

and this means that the lowest eigenvalue E_0 is at the bottom of a continuum. From many points of view, it is hence desirable to separate the motion of the center of mass and to write the total Hamiltonian in the form:

$$H = (\mathbf{p}_\xi^2 / 2M) + H' = T_\xi + H', \quad (32)$$

where the remainder term H' may have discrete or continuous eigenvalues. This may be achieved by introducing a specific reference point \mathbf{r}_0 and the position vectors with respect to this point $\mathbf{r}_{k0} = \mathbf{r}_k - \mathbf{r}_0$. As to choice of reference point, one has several possibilities

- 1) the center of mass of the entire system,
- 2) the center of mass of the atomic nuclei involved,
- 3) one of the moving particles (electron or nucleus) of the system.

The explicit forms of the remainder Hamiltonian H' may look completely different, but one should observe that they are always identical $H' = H - T_\xi$. In the special case 3), the kinetic energy takes the form

$$\begin{aligned} T &= \mathbf{p}_0^2 / m_0 + \sum_{k=1} \mathbf{p}_k^2 / m_k = \\ &= \mathbf{p}_\xi^2 / 2M + \sum_{k=1} \mathbf{p}_{0k}^2 / m_k + (1/2 m_0) (\sum_{k=1} \mathbf{p}_{0k})^2. \end{aligned} \quad (33)$$

The derivation is elementary, but for details the reader is referred elsewhere [ref.7]. Since the Coulomb energy depends only on the relative coordinates, i.e. $r_{kl} = |\mathbf{r}_k - \mathbf{r}_l| = |\mathbf{r}_{k0} - \mathbf{r}_{l0}|$, it is evident that the total Hamiltonian is separable and that one should look for wave functions of the product type:

$$\Psi(\mathbf{r}_k) = \varphi(\xi) \Psi'(\mathbf{r}_{k0}), \quad (34)$$

where the second factor $\Psi'(\mathbf{r}_{k0})$ is an eigenfunction of the remainder Hamiltonian H' . We note that discrete eigenvalues of H' are associated with *closed states* - atoms and molecules - whereas continuous eigenvalues are associated with *scattering states* involving separated clusters of particles. It should be observed that both types of states may be calculated by essentially the same L^2 -methods, as long as one observes that the type of convergence obtained by using larger and larger orthonormal basis sets are very different. Of course, any mathematical theorems about the nature of the energy spectrum of H' are highly useful in this connection.

Once one has removed the motion of the center of mass, it is practical to remove the *rotation* of the system as a whole by studying the total angular momentum in terms of specific Eulerian angles. Even if this problem is elementary, some of the transformations involved are lengthy and far from trivial, and for details the reader is referred elsewhere. Fortunately, the eigenvalues of the total angular momentum are all discrete, so they will not influence the general character of the spectrum of H' . There are other difficulties which - at least for the moment - have higher priority.

Difficulties associated with the Coulombic Hamiltonian H' . From the point of view of physics and chemistry, a molecule consists of atoms, which can be arranged in different ways - leading to the phenomenon of *isomerism*. For a specific isomer, there may be many different arrangements of the atoms around the various bonds corresponding to different *conformations*. From this point of view, the Coulombic Hamiltonian H' does not provide much obvious information or guidance, since there is no specific assignments of the electrons occurring in the systems to the atomic nuclei involved - hence there are no atoms, isomers, conformations, etc. In particular, one sees no *molecular symmetry*, and one may even wonder where it comes from. Still it is evident that all this information must be contained somehow in the Coulombic Hamiltonian H' . In this situation, it is possible to proceed in two completely different ways:

- 1) One may use physical and chemical insight of essentially experimental nature as to the existence of molecules, their shape, symmetry, etc. to get started. In the Born-Oppenheimer approximation [ref.8], one assumes that the nuclei of a molecule are in fixed positions with infinite masses $m_g = \infty$, and studies the electronic structure of the system by solving the corresponding Schrödinger equation. Once this structure has been determined, one may evaluate the force fields working on the nuclei, now with finite

masses, and study the vibrations, rotations, and vibrational-rotational couplings. This is certainly a natural approach, since the nuclei are so much heavier than the electrons. An important problem in this connection has been the derivation of the *Eckart-Hamiltonian* from the true Coulombic Hamiltonian, and one should perhaps note that this problem is still not completely solved [ref. 9]. It should be observed that most current *ab-initio* quantum chemistry is of this type, and that it is hence still highly dependent on empirical experience.

2) One may use mathematical analysis and solve the Coulombic Schrödinger equation $H' \Psi = E \Psi$ at least in principle. In order to show the *existence* of a molecule in its ground state, one has to show that the lowest eigenvalue E_0 of the associated Hamiltonian H' is discrete and corresponds to a *closed state*. Since one usually cannot solve the many-body problem involved exactly, one has to proceed by using some fundamental mathematical theorems. During the sixty years of the development of quantum chemistry, one has often used the *conjecture* that, if one can find a trial wave function Φ for which the expectation value $\langle H' \rangle$ is not only negative but below the estimated energy of all separated fragments, then the Hamiltonian H' has at least one discrete energy level below $\langle H' \rangle$, and the system has a closed ground state.

If we consider a system of two electrons and two protons, we have the possibility that they may form a hydrogen molecule H_2 or occur in the form of the following fragments or *separated clusters*: $H + H$, $H^+ + H^-$, $H_2^+ + e$, $H^+ + H^+ + e + e$, etc. In the scattering theory describing chemical reactions, these separations represent different possible *channels*. The existence of a ground state of the H_2 -molecule in quantum chemistry was hence based on the fact that the pioneers [ref.10] had found electronic trial wave functions $\Phi = \Phi(1,2)$ with lower expectation values $\langle H' \rangle$ than the estimated energy of the separated clusters. Even the nuclear motions have now been included in the non-adiabatic framework described by Kolos [ref.11]

The main problem is now whether one can rely on this conjecture, and - in this situation - it is worthwhile to turn to the mathematicians for help. Already in 1909 Weyl [ref.12] proved a theorem for self-adjoint operators which in current terminology states that, if one can find a trial function Φ , for which the expectation value $\langle H' \rangle$ is lower than the bottom of the *essential spectrum* of the operator, then the operator has at least one discrete eigenvalue situated below $\langle H' \rangle$. In this context, one should observe that the essential spectrum consists essentially of the entire spectrum $\{E\}$ excluding all the discrete eigenvalues of finite multiplicity. It took quite some time before the nature of the bottom of the essential spectrum could be precisely clarified for a Coulombic Hamiltonian. In the years 1960-80, the so-called HVZ-theorem named by Barry Simon [ref.13] after Hunziker, Van Winter, and Zhislin [ref.14] was proven: it states that, for an N-body system, the bottom of the essential spectrum of H' is precisely obtained by looking at the lowest energy of all separated clusters. Hence it confirms the previous conjecture. An important mathematical problem is further whether one can predict the number of discrete states below the continuum in an atom or atomic ion [ref.15]- and later in a given molecule. For more references to the mathematical literature, the reader is referred elsewhere [7].

In quantum chemistry, we are not only interested in the ground state of a molecule but also in its isomers and their conformations, and the question is how one may tackle this problem. For this purpose we will consider a general energy surface, which is constructed in the following way: Let X be all the electronic coordinates and Q all the nuclear coordinates with respect to a specific reference point, and let us consider the Hamiltonian $H' = H'(X, Q)$ and all the possible trial wave functions $\Phi = \Phi(X, Q)$. The binary product is defined by the standard formula

$$\langle \Phi_1 | \Phi_2 \rangle = \int \Phi_1^*(X, Q) \Phi_2(X, Q) dX dQ, \quad (35)$$

where one integrates over both the electronic and nuclear coordinates. The energy surface is then constructed by considering the expectation value

$$\langle H' \rangle = \frac{\langle \Phi | H' | \Phi \rangle}{\langle \Phi | \Phi \rangle}, \quad (36)$$

as a function of $\Phi = \Phi(X, Q, \alpha)$, where $\alpha = (\alpha_1, \alpha_2, \alpha_3, \dots, \alpha_p)$ is a set of parameters.

The energy surface $E = \langle H' \rangle = E(\alpha)$ shows minima, maxima, terrace points, etc. , and the minima are supposed to correspond to stationary states of the system under consideration. At this point, it should be mentioned that there are currently many scientists [ref. 16] who claim that there are no isolated molecules and that molecules exist only in a specific environment. In order to consider this problem, we have to leave pure quantum mechanics.

General quantum theory. Pure quantum mechanics does not contain such concepts as temperature, entropy, free energy, etc. In order to incorporate such concepts into quantum theory, one has to go over to the more general formulation developed by v. Neumann [ref.2], which is an ensemble theory built on the use of density matrices ρ or system operators Γ having the properties [ref.17] :

$$\Gamma^\dagger = \Gamma, \quad \Gamma \geq 0, \quad \text{Tr } \Gamma = 1. \quad (37)$$

The set $\{\Gamma\}$ of all system operators is a *complex set*, which is determined by its limits points having the additional property $\Gamma^2 = \Gamma$. The expectation value of the operator F is defined by the relation

$$\langle F \rangle = \text{Tr } F \Gamma. \quad (38)$$

In the case of a limit point, the system operator Γ is a projector with the range $\{\Phi, \alpha\}$, and it has then the explicit form $\Gamma = |\Phi\rangle\langle\Phi| \Phi^{-1} \langle\Phi|$; in such a case, formula (38) reduces to the form (6), and it is then clear that the limit points correspond to pure quantum mechanics, whereas the interior points describe the more general ensembles.

In the operator space $\{\Gamma\}$, it is feasible to define the binary product of the two operators A and B by means of the expression:

$$(A|B) = \text{Tr } A^\dagger B = \sum_{k,l} A^\dagger_{kl} B_{lk} = \sum_{k,l} A_{lk}^* B_{lk}. \quad (39)$$

For the norm square, one has in particular $\|A\|^2 = (A|A) = \sum_{k,l} A_{lk}^* A_{lk} = \sum_{k,l} |A_{lk}|^2 \geq 0$. All the linear operators T having a finite norm $\|T\|$ form another realization of the abstract Hilbert space called the Hilbert-Schmidt space [ref.18]. Let us now consider the positive semi-definite operator $\Omega = H' - E_0.1$, and in particular the product of the positive square roots $T = (H' - E_0.1)^{1/2} \Gamma^{1/2}$. One gets immediately

$$\begin{aligned} \|T\|^2 &= \text{Tr } T^\dagger T = \text{Tr } \Gamma^{1/2} (H' - E_0.1)^{1/2} (H' - E_0.1)^{1/2} \Gamma^{1/2} = \\ &= \text{Tr } (H' - E_0.1) \Gamma = \langle H' - E_0.1 \rangle \geq 0, \end{aligned} \quad (40)$$

i.e.

$$\langle H' \rangle = \text{Tr } H' \Gamma \geq E_0. \quad (41)$$

Even in general quantum theory, one has hence a variation principle for the energy. If a system operator Γ is a function of some parameters α , one can now construct the energy surface $E = \langle H' \rangle = E(\alpha)$ and study its minima, maxima, and terrace points, etc. One may find that some molecules have rather deep minima, others have symmetric or asymmetric double-well minima, whereas certain molecules - like the giant biomolecules with all their conformations - have energy surfaces which are rough "landscapes" with numerous minima. For each minimum, one may study the molecular structure by calculating the expectation values of e.g. the internuclear distances r_{gh} to get the "shape" of the molecule. In this connection, one is particularly interested in the question of the existence of symmetry properties [ref.19], and the origin of such symmetries. It is evident, however, that the calculation of energy surfaces $E = \langle H' \rangle = E(\alpha)$ as functions of the parameters α is a computational effort which is much larger than anything undertaken so far in the so-called *ab-initio* quantum chemistry, and that one may have to wait for a new form of computer architecture before it can be done. In the meantime, it may be feasible to carry out the mathematical analysis and to develop theoretical methods for handling these types of problems. Even if it is a long way from the Coulombic Hamiltonian H' to the electronic structure of molecules, we may one day find new and forceful short-cuts. In this connection, we should also acknowledge the tremendous help our field has had from the pure mathematicians.

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