

## Some comments on the present situation of quantum chemistry in view of the discussions at the Dubrovnik workshop on the electronic structure of molecules

By Per-Olov Löwdin\*

Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, FL 32611, USA.

\*Professor Emeritus at Uppsala University, Uppsala, Sweden.

**Abstract.**- A review is given of certain parts of current quantum chemistry, with emphasis on the structure of the theory. It is stressed that a great deal of experimental insight is needed not only in finding the initial conditions  $\Psi = \Psi(0)$  for solving the time-dependent Schrödinger equation but also for solving the eigenvalue problem  $H\Psi = E\Psi$ . The standard methods based on the quantum-mechanical variation principle  $\delta\langle H \rangle = 0$  are discussed. It is pointed out that the transition-value formula  $\langle H \rangle_{tr} = \langle \varphi | H | \Phi \rangle / \langle \varphi | \Phi \rangle$ , where  $\varphi$  is a reference function and  $\Phi$  is a trial wave function, is an excellent mathematical tool for solving the Schrödinger equation, but also that it sometimes gives energy results which are fortuitously good. The resolvent methods, the partitioning technique, the concepts of wave and reaction-operators as well as perturbation theory are discussed from this point of view. Finally a comparison between the variational expression and the transition-value formula is made.

### INTRODUCTION

The Dubrovnik Workshop on the Electronic Structure of Molecules is now coming to an end, and the Organizers have kindly asked me to make some concluding remarks. This is a great honour and privilege for me, and at the same time I realize that it is impossible to give a proper summary of all the nice presentations - in lectures as well as in posters - and discussions which have occurred during this week. Instead I will only make a few short comments which are inspired by what has been going on during the week, dealing particularly with the *structure* of the theory.

Quantum chemistry is certainly a very rapidly developing field, which has greatly benefited from an intense international collaboration in which the Ruder Boskovic Institute in Zagreb has played a very important role. Our problems come from many different areas: from industry and technology, from experiments in chemistry and physics, and from theory itself, so the background is certainly very rich and varying. A leading theoretician working as a consultant for industrial applications said some time ago that once a problem in technology or experiments had been properly defined and formulated, it was already halfway solved, and the same statement is certainly true even today. The question of the *formulation of the problem* is particularly pronounced in the time-dependent quantum mechanics, which is based on the solution of the time-dependent Schrödinger equation:

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

with the initial condition  $\Psi = \Psi(0)$  for  $t = t_0$ , where  $H$  is the Hamiltonian for the system under consideration. The initial condition is not given by theory itself but by the experimental set-up, and the proper definition of the complex wave function  $\Psi(0)$  - as to absolute value as well as phase - may require a great deal of collaboration between an experimentalist and a theoretician. The latter may try to circumvent this problem by

writing the solution in the form  $\Psi(t) = S(t, t_0) \Psi(0)$ , where the so-called evolution operator  $S = S(t, t_0)$  satisfies the Schrödinger equation

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

with the simple initial condition  $S(t_0, t_0) = 1$ , where 1 is the identity operator. If the Hamiltonian does not contain the time  $t$  explicitly, it has the well-known exponential solution  $S(t, t_0) = \exp\{H(t - t_0)\}$ . This solves the mathematical part of the problem, at least in principle, but - in order to study the physics or chemistry of the system under consideration - one still has to determine  $\Psi(0)$ . It should be observed that this problem is still far from being solved.

In time-independent quantum mechanics built on the Schrödinger equation  $H\Psi = E\Psi$  as an eigenvalue problem, the question of the solution is essentially a mathematical problem, and one is hence inclined to consider this equation as the basis of *ab-initio* quantum chemistry. As I have pointed out in another lecture at this symposium, the study of a molecular problem based on the Coulombic Hamiltonian may - in the current situation - still require a great deal of physical and chemical insight of an experimental nature. This means that in the future perhaps somewhat more attention should be given to the formulation of the problem itself.

#### VARIATION PRINCIPLE AND ASSOCIATED METHODS

The theoretical methods for treating the eigenvalue problem  $H\Psi = E\Psi$  come essentially from *mathematics*, and there is no question that, during the first six decades of quantum chemistry, the Rayleigh-Ritz *variation principle* [ref.1] has played a dominating role. It is based on the expectation value

$$\langle H \rangle_{Av} = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle}. \quad (3)$$

where  $\Phi$  is a trial wave function, and the statement that the best approximation is obtained whenever  $\delta \langle H \rangle = 0$ . Quite a few of the standard computational methods are based on this approach, and at this workshop we have had reports about recent progress in the Hartree-Fock (HF) scheme [ref.2], in the Multi-Configurational-Self-Consistent-Field (MC-SCF) method [ref.3], and in the Configurational Interaction (CI) approximation [ref.4]. Of particular importance is the Graphical Unitary Group Approach (GUGA) [ref.5], which has made large-scale CI-calculations possible. Of a somewhat different variational nature is the Electron-Density-Functional-Method (EDFM) [ref.6], where one starts only from the knowledge of the one-electron density, and some of the old favorites - as the  $X_\alpha$ -method [ref.7]- may be considered as special cases of this approach.

A characteristic feature of all the methods based on the variation principle is that they give *upper bounds* to the energy values, which give a clue also to the accuracy of the wave functions. The rapid developments in these areas as reported at this workshop depend not only on progress in methodology but also on the developments of the modern electronic computers.

#### TRANSITION FORMULAS, WAVE AND REACTION OPERATORS, PERTURBATION THEORY

In addition to the variation principle, one has during the last decade studied the *bi-variational principle*. If  $T$  is an arbitrary linear operator with the adjoint  $T^\dagger$ , it is easily shown [ref.8] that the eigenvalue problems  $TC = \lambda C$  and  $T^\dagger D = \mu D$  are equivalent with the relation  $\delta \langle T \rangle_{12} = 0$  for the bi-variational expression

$$\langle T \rangle_{12} = \frac{\langle \Phi_1 | T | \Phi_2 \rangle}{\langle \Phi_1 | \Phi_2 \rangle}. \quad (4)$$

where  $\Phi_1$  and  $\Phi_2$  are two arbitrary trial wave functions. This approach is of particular

value in the current *method of complex scaling*, which deals with the study of physical resonances and their life-times by means of non-self-adjoint Hamiltonians [ref.9].

In many cases, one prefers to work with one of the variational functions fixed, say with  $\Phi_1 = \varphi$ , and one is then often speaking of  $\varphi$  as the *reference function*, which is usually chosen normalized so that  $\langle \varphi | \varphi \rangle = 1$ . Instead of the variational expression (3), one is then using the *transition formula*:

$$\langle H \rangle_{tr} = \frac{\langle \varphi | H | \Phi \rangle}{\langle \varphi | \Phi \rangle} \quad (5)$$

where  $\Phi$  is a trial wave function; for  $\Phi = \Psi$ , one has  $\langle H \rangle_{tr} = E$ , and the formula becomes exact. We note further that, since one may choose  $\Phi$  so that  $\langle \varphi | \Phi \rangle \approx \pm 0$ , one has  $\langle H \rangle_{tr} \approx \pm \infty$ , which means that the quantity  $\langle H \rangle_{tr}$  is *unbounded*. The transition formula has been used for a long time in quantum mechanics, and it has been given different names in various connections. It has turned out to be one of the strongest *mathematical tools* used in quantum theory, and - at the same time - it should be remembered that the transition formula has no direct physical interpretation, even if many of the "interpretations" given in this context may have value as mnemonic rules.

Let us for a moment consider the ground state energy  $E_{gr}$ , so that the operator  $\Xi = H - E_{gr}$  is a positive definite operator. Let us further consider two normalized functions  $\varphi$  and  $\Phi$ , so that  $\|\varphi\| = \|\Phi\| = 1$ . Using Schwartz's inequality in the special form  $\|\langle \varphi | \Xi | \Phi \rangle\|^2 \leq \langle \varphi | \Xi | \varphi \rangle \langle \Phi | \Xi | \Phi \rangle$ , one obtains

$$E_{gr} - \Delta \leq \frac{\langle \varphi | H | \Phi \rangle}{\langle \varphi | \Phi \rangle} \leq E_{gr} + \Delta, \quad (6)$$

where

$$\Delta = \{ \langle \varphi | H | \varphi \rangle - E_{gr} \}^{1/2} \{ \langle \Phi | H | \Phi \rangle - E_{gr} \}^{1/2} / |\langle \varphi | \Phi \rangle|. \quad (7)$$

This *transition formula inequality* tells us that, if one of the two expectation values  $\langle \varphi | H | \varphi \rangle$  and/or  $\langle \Phi | H | \Phi \rangle$  becomes close to  $E_{gr}$ , then  $\langle H \rangle_{tr}$  also becomes close to  $E_{gr}$ , as long as  $|\langle \varphi | \Phi \rangle|$  is bounded.

The transition formula is dangerous from the point of view that, for certain trial wave functions  $\Phi$ , one may have  $\langle H \rangle_{tr} = E$ , and still  $\Phi$  may be far from the correct wave function  $\Psi$ . Good agreement with experiments or bench-mark values may hence be completely fortuitous! At the same time, it should be observed that, if the transition formula is properly handled, it may give strict *upper and lower bounds* to the energy  $E$ .

In the early 1950's, Schwinger [ref.10] introduced the idea that perhaps one could obtain the exact eigenfunction  $\Psi$  as a mapping of the reference function  $\varphi$  through a particular wave operator  $W$ , so that  $\Psi = W \varphi$ . This operator is by no means unique, and Brueckner and his collaborators [ref.11] concentrated on finding the form which corresponds to quantum-mechanical perturbation theory in the case when  $H = H_0 + V$ . We note that, in order to treat the discrete and continuous part of the energy spectrum  $\{E\}$  on an equal footing, one does not require the function  $\Psi$  or its approximate form  $\Phi$  to be normalized. Instead it is convenient to introduce the *intermediate normalization* through the relation:

$$\langle \varphi | \Phi \rangle = \langle \varphi | W | \varphi \rangle = 1, \quad (8)$$

and the transition formula now takes the simple form

$$\langle H \rangle_{tr} = \langle \varphi | H | \Phi \rangle = \langle \varphi | HW | \varphi \rangle. \quad (9)$$

Mathematically this looks like an expectation value, but physically it is not. The operator  $\Omega = HW$  is sometimes referred to as the *bracketing operator* for reasons we will see later.

If one chooses the reference function  $\phi$  so that it becomes an eigenfunction to  $H_0$ , i.e.  $\phi = \phi_0$  and  $H_0 \phi_0 = E_0 \phi_0$ , and uses (9), one obtains

$$\langle H \rangle_{tr} = \langle \phi_0 | (H_0 + V) W | \phi_0 \rangle = E_0 + \langle \phi_0 | V W | \phi_0 \rangle = E_0 + \langle \phi_0 | t | \phi_0 \rangle, \quad (10)$$

where  $t = VW$  is Schwinger's *scattering operator* for the continuous case, and Brueckner's *reaction operator* for the discrete case. Replacing the Hartree-Fock energy  $E_{HF} = \langle \phi_0 | H_0 + V | \phi_0 \rangle$  with the exact energy  $E = \langle \phi_0 | H_0 + t | \phi_0 \rangle$ , Brueckner could, with the recipe  $V \rightarrow t$ , formulate an *exact self-consistent field theory* for many-particle systems [ref.12], and one obtained for the first time a simple formula for the inter-particle *correlation energy*:

$$E_{corr} = E - E_{HF} = \langle \phi_0 | t - V | \phi_0 \rangle. \quad (11)$$

Brueckner's research was in the field of nuclear physics. However, also in quantum chemistry, one had similar developments, and Nesbet [ref.13] had discovered that, if  $H$  is a Hamiltonian which contains one- and two- particle operators like the Coulombic Hamiltonian, if  $\phi_0 = D$  is a single Slater determinant and if the exact wave function  $\Psi$  is expanded in terms of excitations of this determinant:

$$\Psi = D + D_{s.e.} + D_{d.e.} + D_{t.e.} + \dots + D_{(N)}, \quad (12)$$

where the symbols s.e., d.e., t.e., etc. indicate sums of singly excited, doubly excited, triply excited terms, etc. to orthogonal orbitals with respect to  $D$ , then Brillouin's theorem gives  $\langle D | H | D_{s.e.} \rangle = 0$ , and one obtains simply

$$E = \langle D | H | \Psi \rangle = \langle D | H | D \rangle + \langle D | H | D_{d.e.} \rangle = E_{HF} + \langle D | H | D_{d.e.} \rangle, \quad (13)$$

since all other terms disappear identically depending on the orthogonality requirements and the nature of the operator  $H$ . Relation (13) gives another simple formula for the correlation energy. Since the term  $D_{d.e.}$  relative to  $D$  could be expressed in terms of a finite number of *pair functions*, Nesbet [ref.14] and Sinanoglu [ref.15] devoted a great deal of time and effort to the study of these functions. In view of some presentations at this workshop, we can see that the philosophy of this approach is still alive - even if it has taken a somewhat modified form.

In the treatment of many-particle systems, it is evident that it may be practically very difficult to find a reference function  $\phi_0$  which is an exact eigenfunction to the unperturbed Hamiltonian  $H_0$ . For this reason we will now return to the choice of an arbitrary normalized reference function  $\phi$ , and we will particularly consider the inhomogeneous Schrödinger equation

$$(H - z.1) \Psi_z = a \phi, \quad (14)$$

where  $z$  is a complex variable, and the coefficient  $a$  is chosen so that the solution  $\Psi_z$  satisfies the intermediate normalization  $\langle \phi | \Psi_z \rangle = 1$ . If one introduces the *resolvent* operator  $R(z) = (z.1 - H)^{-1}$ , one finds immediately the explicit solution  $\Psi_z = -a R(z) \phi = R(z) \phi / \langle \phi | R(z) | \phi \rangle$ , and one has  $a = -\langle \phi | R(z) | \phi \rangle^{-1}$ . The function  $W(z) = \langle \phi | R(z) | \phi \rangle^{-1}$  is sometimes referred to as the *Weinstein function*. The resolvent is complex symmetric, i.e.  $R^\dagger(z) = R(z^*)$ , and hence the function  $a(z)$  has the property  $a(z^*) = \{a(z)\}^*$ ; it is obvious that it is real on the real axis. Since  $dR(z)/dz = -R^2(z)$ , one immediately gets the relation

$$da(z)/dz = -\langle \Psi_z | \Psi_z \rangle, \quad (15)$$

which quantity is negative on the real axis, and - as a rule - non-vanishing.

We note that the inhomogeneous equation (14) goes over into the ordinary Schrödinger equation whenever  $a(z) = 0$ , i.e. whenever the Weinstein function has a pole  $z = E$ . One would hence anticipate that the equation  $a(z) = 0$  would be equivalent to the characteristic equation for the eigenvalues  $z = E$ , but the existence of relation (15) indicates that all the multiple roots have been reduced to single roots, and that  $a(z) = 0$  hence corresponds to the *reduced characteristic equation* for the eigenvalues. The

relations given here form the background for the *resolvent operator methods*, or - if one is using the associated kernels - the *Green's functions method*. Through the relation  $R(z) = z^{-1} + z^{-1} H R(z)$ , they are also associated with the propagator technique [ref.16]. These methods are very forceful, and it is hence remarkable that we have not seen more of them at this workshop.

The resolvent  $R(z)$  is a *bounded* operator for  $|z - E| > \rho$ , and one has  $\|R(z)\Phi\| < (1/\rho) \|\Phi\|$ , which explains the usefulness of this approach. It should be observed, however, that the resolvent is *singular* for  $z = E$ , and that the expression for  $\Psi_z$  then takes the form  $\infty/\infty$ . In this situation, one may start from the identity  $(z.1 - H) R(z) \varphi = \varphi <\varphi| (z.1 - H) R(z) |\varphi>$  and derive the *resolvent identity* [ref.17]:

$$\Psi_z = \frac{R(z)\varphi}{<\varphi|R(z)|\varphi>} \equiv (1 - PH/z)^{-1}\varphi, \quad (16)$$

where  $P = 1 - |\varphi><\varphi|$  is the projector for the orthogonal complement to the projector  $O = |\varphi><\varphi|$  associated with the reference function  $\varphi$ . This gives a very simple expression for the wave operator:

$$W = (1 - PH/z)^{-1}, \quad (17)$$

which may be used as a convenient starting point for further studies. We note that the same expression may be obtained also in the *partitioning technique*, in which the Hilbert space is partitioned into two parts by means of the projectors  $O$  and  $P$  forming a resolution of the identity  $O + P = 1$ , [ref.19]. In this connection, one should observe the existence of the useful operator identities

$$(A - B)^{-1} \equiv A^{-1} + A^{-1}B(A - B)^{-1} \equiv A^{-1} + (A - B)^{-1}BA^{-1}, \quad (18)$$

$$(1 - RS)^{-1}R \equiv R(1 - SR)^{-1} \quad (19)$$

For the wave operator, this gives the alternative expression

$$W = 1 + TH, \quad T = (z.1 - PH)^{-1}P = P(z.1 - PH)^{-1} = P(z.1 - PHP)^{-1}P, \quad (20)$$

where the operator  $T(z) = (z.1 - PH)^{-1}P$  is the so-called *reduced resolvent*. The last form in (20) is of particular importance, since  $\bar{H} = PHP$  is the *outer projection* of  $H$  with respect to the projector  $P$  with eigenvalues  $\bar{E}_k$  satisfying the inequality  $\bar{E}_k > E_k$  in order from below [ref.19] and having a resolvent  $\bar{R} = (z.1 - PHP)^{-1}$  which exists whenever  $z \neq \bar{E}_k$ . Since  $T = P\bar{R}P$ , the reduced resolvent  $T(z)$  exists for  $z \neq \bar{E}_k$ , [ref.20].

Let us now return to the solution of the eigenvalue problem in the form  $a(z) = 0$ . Multiplying the relation (14) to the left by  $<\varphi|$  and  $<\Psi_z|$ , respectively, and using the normalization relations  $<\varphi|\varphi> = 1$  and  $<\Psi_z|\varphi> = 1$ , one obtains

$$a(z) = <\varphi|H - z.1|\Psi_z> = <\varphi|H|\Psi_z> - z = <\varphi|HW|\varphi> - z = f(z) - z, \quad (21)$$

$$a(z) = <\Psi_z|H - z.1|\Psi_z>. \quad (22)$$

The function  $z_1 = f(z)$  has the derivative  $df(z)/dz = 1 - <\Psi_z|\Psi_z>$ , which is always negative on the real axis, and Lagrange's mean-value formula shows then that, between  $z$  and  $z_1$ , there is always at least one true eigenvalue  $E$ . For this reason, the  $z_1 = f(z)$  is often referred to as the *bracketing function*. If one solves the "algebraic" equation  $a(z) = 0$ , by means of the Newton-Raphson formula, one gets further

$$z_{NR} = z - \frac{a(z)}{a'(z)} = z - \frac{z_1 - z}{<\Psi_z|\Psi_z>} = z - \frac{<\Psi_z|H - z.1|\Psi_z>}{<\Psi_z|\Psi_z>} = \frac{<\Psi_z|H|\Psi_z>}{<\Psi_z|\Psi_z>}, \quad (23)$$

where the right-hand member - for complex  $z$  - is identical to the bi-variational expression, which - for real  $z$  - reduces to the variational expression.

Let us now consider the case when  $H = H_0 + V$  for an arbitrary reference function  $\phi$ . It is now convenient to introduce the operators  $W_0$  and  $T_0$  associated with the unperturbed Hamiltonian  $H_0$ :

$$W_0 = (1 - PH_0/z)^{-1}, \quad T_0 = (z.1 - PH_0)^{-1}, \quad (24)$$

and observe the existence of the alternative forms for  $T_0$ . Putting  $H = H_0 + V$  into the original expressions for  $W$  and  $T$ , and using (18), one obtains

$$W = (1 - PH_0/z - PV/z)^{-1} = (1 - T_0V)^{-1} W_0, \quad (25)$$

$$T = (z.1 - PH_0 - PV)^{-1} P = (1 - T_0V)^{-1} T_0, \quad (26)$$

and it is evident that the operator  $(1 - T_0V)^{-1}$  is going to play an important role in the theory. Using (18), one obtains directly  $(1 - T_0V)^{-1} = 1 + T_0V(1 - T_0V)^{-1}$ , and it is then easily seen that the operator

$$t = V(1 - T_0V)^{-1}, \quad (27)$$

is a generalization of Brueckner's *reaction operator* satisfying the relation  $VW = t W_0$ . One gets further the *reciprocity relations*:

$$T = T_0 + T_0 t T_0, \quad t = V + V T V, \quad (28)$$

by means of which one can expand  $T$  in an infinite series in terms of powers of  $T_0$  and  $V$ . If the perturbation  $V$  has an inverse, one has also the simple two-term formula

$$t^{-1} = V^{-1} - T_0, \quad (29)$$

which plays an important role in the treatment of the theory by means of *inner projections* and in the development of *rational approximations* [ref.21]. The bracketing function may now be expressed in the form  $z_1 = f(z) = \langle \phi | HW | \phi \rangle = \langle \phi | \Omega | \phi \rangle$ , and for the bracketing operator  $\Omega = HW$ , one obtains

$$\begin{aligned} \Omega = HW &= (H_0 + V) (1 - T_0V)^{-1} W_0 = H_0 \{1 + T_0V(1 - T_0V)^{-1}\} W_0 + t W_0 = \\ &= H_0 \{1 + T_0 t\} W_0 + t W_0 = H_0 W_0 + H_0 T_0 t W_0 + t W_0 = \Omega_0 + W_0 t(z^*) t W_0(z), \end{aligned} \quad (30)$$

which means that even the bracketing operator may be expressed in terms of the reaction operator  $t$ .

If one puts  $H = H_0 + \lambda V$ , it is possible to expand the fundamental operators  $W$ ,  $T$ ,  $\Omega$ , and  $t$ , in power series of the perturbation parameter  $\lambda$ . In the conventional perturbation theory developed in quantum mechanics, one simply assumed that the wave function  $\Psi$  and the energy  $E$  were analytic around the point  $\lambda = 0$ , and the strict mathematical background for this approach was finally given by Rellich and by Kato [ref.22]. A closer study of the mathematical foundation for the partitioning technique briefly described above has also been started, but it may take some time before it is completed.

In connection with the developments in perturbation theory, one should perhaps also mention the current studies of the *free energy* expressed in the form  $F = -kT \log \text{Tr} \exp \{ - (H_0 + \lambda V) / kT \}$ . Large-scale calculations of free energy differences for various types of biomolecules have recently been carried out under the assumption that the Hamiltonians involved are classical [ref.23], but also perturbation expansions of the free energy for quantum systems have been studied [ref.24]. One can anticipate that, in the future, it will be of great importance to incorporate such concepts as temperature, entropy, free energy, etc. into quantum chemistry.

### COMPARISON BETWEEN TRANSITION VALUES AND EXPECTATION VALUES

In the previous section, we have emphasized that the variational expression (3) and the computational methods based on the variation principle  $\delta\langle H \rangle = 0$  give *upper bounds* to the energy values  $E$ . On the other hand, the transition formula (5) is a very strong mathematical tool, but - since it is unbounded - it may sometimes give fortuitously good results. In terms of the wave operator  $W$ , we are dealing with the two expressions

$$\langle H \rangle_{tr} = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\langle \Phi | HW | \Phi \rangle}{\langle \Phi | W | \Phi \rangle}, \quad (31)$$

$$\langle H \rangle_{Av} = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\langle \Phi | W^\dagger H W | \Phi \rangle}{\langle \Phi | W^\dagger W | \Phi \rangle}, \quad (32)$$

and we will now try to compare them in somewhat greater detail. For the exact wave operator  $W$  and  $z = E$ , the two expressions are identical, of course, so we will concentrate our interest on the approximate case.

For the wave operator we have according to (20) the expression  $W = 1 + TH$  with  $T = P(z.I - PHP)^{-1}P$ . The problem is apparently to evaluate the resolvent  $\bar{R} = (z.I - PHP)^{-1}$  for the outer projection  $\bar{H} = PHP$  of the Hamiltonian. For a moment, we will let  $\bar{R}_a$  be an arbitrary approximation to this inverse operator. We note that, if  $A$  is an arbitrary linear operator having an inverse  $A^{-1}$ , and if  $I$  is a first-order approximation to this inverse, then the operator  $I^\# = 2I - |A|$  is a second-order approximation. The proof follows from the

fact that, if  $I = A^{-1} + \delta$ , then  $I^\# = A^{-1} - \delta A \delta$ . Hence if  $\bar{R}_a$  is an approximation to the resolvent correct to order  $n$ , then  $\bar{R}_a^\# = 2\bar{R}_a - \bar{R}_a A \bar{R}_a$  is an approximation correct to order  $(2n+1)$ . Multiplying this relation to the left and right by  $P$  and observing that  $P T_a = T_a P = T_a$ , one obtains for the associated approximations of the reduced resolvent:

$$T_a^\# = 2T_a - T_a(z.I - PHP)T_a = 2T_a - T_a(z.I - H)T_a. \quad (33)$$

Introducing the approximate wave operator  $W_a = 1 + T_a H$ , one obtains directly

$$\begin{aligned} W_a^\dagger (H - z.I) W_a &= (1 + H T_a) (H - z.I) (1 + T_a H) \\ &= (H - z.I) + H T_a (H - z.I) + (H - z.I) T_a H + H T_a (H - z.I) T_a H = \\ &= (H - z.I) - z H T_a - z T_a H + H \{2T_a - T_a(z.I - H)T_a\} H = \\ &= (H - z.I) - z H T_a - z T_a H + H T_a^\# H = H W_a^\# - z.I - z(H T_a + T_a H), \end{aligned} \quad (34)$$

and further, since  $P \Phi = 0$  and  $T_a \Phi = 0$ :

$$\langle \Phi | W_a^\dagger (H - z.I) W_a | \Phi \rangle = \langle \Phi | H W_a^\# | \Phi \rangle - z. \quad (35)$$

This means that, one has the following connection formula:

$$\begin{aligned} \langle H \rangle_{Av} &= \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} = z + \frac{\langle \Phi | H - z.I | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \\ &= z + \frac{\langle \Phi | W_a^\dagger (H - z.I) W_a | \Phi \rangle}{\langle \Phi | W_a^\dagger W_a | \Phi \rangle} = z + \frac{\langle \Phi | H W_a^\# | \Phi \rangle - z.}{\langle \Phi | W_a^\dagger W_a | \Phi \rangle}, \end{aligned} \quad (36)$$

which is a generalization of the Brillouin-Wigner theorem [ref.25]. It is hence always possible, at least in principle, to go from transition values to expectation values, but one should observe that the good agreement provided by the transition formula may not necessarily hold for the expectation value.

At the Vålådalen symposium in 1958, the author pointed out [ref.26] that a characteristic feature of quantum chemistry was that even a fairly simple theory could sometimes give excellent agreement with experimental experience, but that this agreement may

disappear whenever one tries to improve the theory. The point of excellent agreement was coined the "*Pauling point*" in honour of one of the great pioneers in our field who is also present here in Dubrovnik, not only because he could construct simple theories built on physical and chemical insight, but also because of his mastership in predicting figures which had not yet been measured. In the beginning of the 1930's, one had constructed theories of chemical reactivity based on the properties of the valence electrons only to find that the good agreement disappeared when one included the inner shells leading to the concept of the "nightmare of the inner shells". In the MO-LCAO treatment of large molecules, one could get very good results without including the atomic overlap integrals, whereas in solid-state theory the inclusion may lead to the famous "non-orthogonality catastrophe". In the treatment of metal complexes, the original crystal-field theory for some reason seemed to give better agreement than the improved ligand-field theories. In the treatment of magnetic phenomena, the Hartree method seemed to give better results than the Hartree-Fock method, simply because the errors in treating parallel and antiparallel spins were better balanced in the former. Let me quickly add that my own doctoral thesis in 1948 treating the properties of ionic crystals by means of the independent-particle model is a typical example of a "Pauling point", where the good agreement with the experiments would disappear when one tries to include e.g. correlation in an unbalanced way. It goes without saying that, if one improves the theory more and more, the good agreement is expected to come back, but the simplicity of the theory is usually lost in this connection.

One should hence be somewhat suspicious, if a low-order perturbation theory seems to give excellent results - one may be at a "Pauling point". In current quantum chemistry, the exact wave function may be expressed in the form (12), i.e. as a finite sum of singly, doubly, triply, ... excited states, and - in many different approaches - various authors are surprised at what good results one can be obtained by including only the first few terms. Some estimates have indicated, that unfortunately there might be a "night-mare of higher excitations".

Here at the Dubrovnik workshop and other conferences, we are accustomed to see how well low-order Møller-Plesset or many-body perturbation theory may work for particular systems. In the higher-order perturbation theories based on the use of Feynman diagrams, the linked-cluster theorem [ref.27] plays an important role in connection with the property of separability or "size extensiveness". We note that, for this purpose, one is using an exponential form of the wave operator  $W = \exp(T)$  in the coupled-cluster method [ref.28] and in the finite-order many-body perturbation theory approximations [ref.29]. A crucial test of a good transition formula result may be obtained by comparing it with the corresponding expectation value, and Bartlett has recently devoted some efforts to this problem [ref.30].

If a quantity cannot be evaluated exactly, a mathematician would try to calculate upper and lower bounds to it until the difference between the two bounds is smaller than the accuracy desired. If the problem is difficult, he may have to be satisfied by calculating "upper bounds to upper bounds" and "lower bounds to lower bounds". In the applications to molecular physics, many of us are delighted to calculate "lower bounds to upper bounds" or "upper bounds to lower bounds", since the results are often in good agreement with experimental experience or bench-mark calculations. Sometimes the goodness of the results may be systematic, sometimes it may be fortuitous, and it is of importance for us to know when and why. One should always remember that good agreement with experiments is a *necessary* but by no means *sufficient* criterion for the goodness of a theory, and that the reliability of the results is ultimately going to determine the lifetime of a particular approach.

## CONCLUSIONS

On behalf of all the participants in the Dubrovnik Workshop, the author would finally like to thank Professor Z.B. Maksic and his Organizing Committee for the excellent work they have done in organizing this conference and for all the warm hospitality extended to us.

## REFERENCES

- [1] W. Ritz, *J. Reine Angew. Math.* **135**, 1 (1909).
- [2] See e.g. N. Bohr, *Proc. Phys. Soc. (London)* **35**, 296 (1923); D. R. Hartree, *Proc. Cambridge Phil. Soc.* **24**, 89 (1928); J. C. Slater, *Phys. Rev.* **35**, 210 (1930); V.



- Fock, *Z. Physik* **61**, 126 (1930); P.A.M. Dirac, *Proc. Cambridge Phil.Soc.* **26**, 376 (1930); **27**, 240 (1931); D.R. Hartree, *Mem.Proc. Lit.Phil.Soc. Manchester* **77**, 91 (1933); V. Fock and M. Petrashen, *Phys.Zs. Sow.* **6**, 368 (1934); **8**, 547 (1935); D.R. Hartree, "The Calculation of Atomic Structures" (John Wiley and Sons, New York, 1957). See also R.S. Mulliken, *J.Chim.Phys.* **46**, 497, 675 (1949); C.C.J. Roothaan, *Revs. Mod. Phys.* **23**, 69 (1951); G.G. Hall and J.Lennard-Jones, *Proc. Roy. Soc. London* **A202**, 155 (1950); P.O. Löwdin, *Phys.Rev.* **97**, 1490 (1955); R. McWeeny, *Proc. Roy.Soc. London* **A223**, 63, 306 (1954). C. Froese-Fischer, in *Proc. Girona Workshop on Quantum Chemistry 1988* (Ed. R. Carbo, Elsevier, Amsterdam 1989).
- [3] J. Frenkel, "Wave Mechanics, Advanced General Theory" (Clarendon Press, Oxford 1934), particularly p. 460-462; D.R. Hartree, W. Hartree, and B. Swirls, *Phil.Trans.Roy.Soc. (London)* **238**, 229 (1938); J.C. Slater, *Phys. Rev.* **91**, 528 (1953); P.O. Löwdin, *Phys. Rev.* **97**, 1474 (1955).
- [4] J. C. Slater: *Phys. Rev.* **81**, 385 (1951); **82**, 538 (1951); *Revs. Mod. Phys.* **25**, 199 (1953); H. Shull and P. O. Löwdin: *J. Chem. Phys.* **23**, 1362 (1955); S. F. Boys: *Proc. Roy. Soc. (London)*, **A200**, 542 (1950); *Svensk Kem. Tidskr.* **67**, 367 (1955); *Proc. Roy. Soc. (London)*, **A258**, 402 (1960); *Revs. Mod. Phys.* **32**, 296 (1960); see also Boys, Cook, Reeves and Shavitt, *Nature* **178**, 1207 (1956); S. F. Boys and G. B. Cook: *Revs. Mod. Phys.* **32**, 285 (1960). For a simple proof of the CI-expansion theorem, see e.g. P.O. Löwdin, *Phys. Rev.* **97**, 1474 (1955), particularly p. 1478.
- [5] I.M. Gelfand and M.L. Zetlin, *Dokl. Akad. Nauk SSSR* **71**, 825, 1017 (1950); I.M. Gelfand and M.I. Graev, *Izv. Akad. Nauk SSSR. Ser.Mat.* **29**, 1329 (1965); [*Amer.Math.Soc.Transl.* **64**, 116 (1967)]. J.Paldus, *J.Chem.Phys.* **61**, 3321 (1974), *Int. J. Quantum Chem. S* **9**, 165 (1975); J. Paldus and J. Cizek, *Adv. Quantum Chem.* **9** (Academic Press, New York 1975); F.A. Matsen, *Adv. Quantum Chem.* **11**, 223 (1978); I. Shavitt, *Int. J. Quantum Chem. S* **11**, 131 (1977); *S* **12**, 5 (1978); P. Siegbahn, *J. Chem. Phys.* **72**, 1647 (1980). I. Shavitt, in *Proc. Girona Workshop on Quantum Chemistry 1988* (Ed. R. Carbo, Elsevier, Amsterdam 1989).
- [6] P. Hohenberg and W. Kohn, *Phys.Rev.* **136**, B 864 (1964); M. Levy, in "New Horizons in Quantum Chemistry" (Eds. J.Jortner and B. Pullman, Reidel, Dordrecht, Holland 1989). For a survey of the development of this field during the last 25 years, see the thematic volume: *Adv. Quantum Chem.* **21** (Spec. Ed. S. B. Trickey, Academic Press, San Diego 1989).
- [7] J.C. Slater, *Phys.Rev.* **81**, 385 (1951); R. Gaspar, *Acta Phys.Acad. Sci. Hung.* **3**, 263 (1954); W. Kohn and L.J. Sham, *Phys.Rev.* **140**, A1193 (1965); J.C. Slater, *Adv. Quantum Chem.* **6**, 1 (Academic Press, New York 1972) and in the proceedings from the Sanibel Symposia published in the *Int. J. Quantum Chem.* 1965-75.
- [8] See e.g. P.O. Löwdin, *J. Math. Phys.* **24**, 70 (1983).
- [9] For a survey, see e.g. P.O. Löwdin, *Adv. Quantum Chem.* **19**, 88 (1988).
- [10] See e.g. B.A. Lippman and J. Schwinger, *Phys.Rev.* **79**, 469 (1950).
- [11] K. A. Brueckner, C. A. Levinson and H. M. Mahmoud: *Phys. Rev.* **95**, 217 (1954); K. A. Brueckner: *Phys. Rev.* **96**, 508 (1954); **97**, 1353 (1955); **100**, 36 (1955); K. A. Brueckner and C. A. Levinson: *Phys. Rev.* **97**, 1344 (1955); L. S. Rodberg: *Ann. Phys. (N.Y.)* **2**, 199 (1957).
- [12] See also P.O. Löwdin, *J. Math. Phys.* **3**, 1171 (1962).
- [13] R. K. Nesbet: *Proc. Roy. Soc. (London)*, Ser. A, **230**, 312 (1955).
- [14] R.K. Nesbet, *Proc.Roy.Soc. (London)* **A230**, 312 (1955); R.K.Nesbet, *Phys. Rev.* **109**, 1632 (1958); **118**, 681(1960); R.K. Nesbet, *Revs. Mod.Phys.* **33**, 28 (1961).
- [15] O. Sinanoglu, *Proc.Roy.Soc. (London)* **A260**, 379 (1961); O. Sinanoglu, *J.Chem.Phys.* **36**, 706, 3198 (1962); *Adv. Chem.Phys.* **6**, 315 (1968).
- [16] J. Linderberg and Y. Öhrn, *Proc Roy.Soc. (London)* **A285**, 445 (1965); Y. Öhrn and J. Linderberg, **A139**, 1063 (1965); J.Linderberg and Y. Öhrn, "Propagators in Quantum Chemistry" (Academic Press, New York 1973); P. Jørgensen, *Ann. Rev. Phys. Chem.* **26**, 359 (1975); C.W. McCurdy, T. Rescigno, D. Yeager, and V. McKoy, *Mod. Theor. Chem.* **3** (1977); J. Oddershede, *Adv. Quantum Chem.* **11**, 275 (1978); M.F. Herman, K.F. Freed, and D.L. Yeager, *Adv. Chem. Phys.* **48**, 1 (1981); Y. Öhrn and G. Born, *Adv. Quantum Chem.* **13**, 1 (1981); P.O. Löwdin, *Int.J. Quantum.Chem. Symp. QC* **16**, 485 (1983); *Adv. Quantum Chem.* **17**, 285 (1983);
- [17] P.O. Löwdin, *Physica Scripta* **31** (1985).
- [18] P.O. Löwdin, *J. Chem. Phys.* **19**, 1396 (1951); *J. Mol. Spec.* **10**, 12 (1963); **13**, 326 (1964); *J. Math. Phys.* **3**, 969, 1171 (1962); *J. Mol. Spec.* **14**, 112 (1964); *J. Math. Phys.* **6**, 1341 (1965); *Phys. Rev. A* **139**, 357 (1965); *J. Chem. Phys.* **43**, S175 (1965); in *Perturbation Theory and Its Applications in Quantum Mechanics* (Ed. G.H. Wilcox, John Wiley and Sons, New York 1966) p. 255; *Int. J. Quantum Chem.* **2**, 867(1968).
- [19] P.O. Löwdin, *Phys. Rev.* **139**, A357 (1965).
- [20] P.O. Löwdin, *Int. J. Quantum Chem.* **21**, 69 (1982).

- [21] P.O. Löwdin, *Phys. Rev.* **139**, A357 (1965), particularly p. 359. P.O. Löwdin, *Int. J. Quantum Chem.* **4**, 231 (1971); P.O. Löwdin, in *Proc. Girona Workshop on Quantum Chemistry 1988* (Ed. R. Carbo, Elsevier, Amsterdam 1989).
- [22] F. Relich, *Math. Annalen* **113**, 600; 677 (1937); **116**, 555 (1939); **117**, 356 (1940); **118**, 462 (1942); T. Kato: *Progr. Theor. Phys.* (Japan) **4**, 514 (1949); **5**, 95 (1950).
- [23] Calculations of this type have been carried out by W. Jorgensen, M. Karplus, P. Kollman, U. Landmann, and others. For references, see e.g. P. Cieplak, U.C. Singh, and P. Kollman, *Int. J. Quantum Chem. Symp.* **QB 14**, 65 (1987).
- [24] For the classical perturbation theory, see R.W. Zwanzig, *J.Chem. Phys.* **22**, 1420 (1954); for quantum systems, see L. Reichl, *Modern Course in Statistical Physics*, (University of Texas Press, Austin 1980) ; P.O. Löwdin and B. Nagel, *Ivar Waller issue, Int.J. Quantum Chem.*, spring of 1989 (to be published).
- [25] L. Brillouin, *J. Phys. Radium* [7] **3**, 373 (1932); E. Wigner, *Math. u. Naturw. Anz. ungar Akad. Wiss.* **53**, 477 (1935).
- [26] P.O. Löwdin, in "*Acta Valldalensia*" **3** (1958); *Int. J. Quantum Chem. Symp.* **QC 19**, 19 (1985), particularly p. 23.
- [27] H.A. Bethe, *Phys.Rev.* **103**, 1353 (1956); J. Goldstone, *Proc. Roy. Soc. (London)* **A 238**, 511 (1957); H. A. Bethe and J. Goldstone, *ibid.* **A 238**, 551 (1957). See also P.O. Löwdin, *J.Math.Phys.* **3**, 1171 (1962), particularly p. 1180.
- [28] J. Cizek, *J. Chem. Phys.* **45**, 4256 (1966); *Advan. Chem. Phys.* **14**, 35 (1969); J. Paldus; J. Cizek, and I. Shavitt, *Phys. Rev.* **A5**, 50 (1972); R.J. Bartlett and G.D. Purvis, III, *Int. J. Quantum Chem.* **14**, 561 (1978).
- [29] H.P. Kelly, *Advan. Chem. Phys.* **14**, 129 (1969); R.J. Bartlett and D.M. Silver, *Phys. Rev.* **A10**, 1927 (1974); *Chem. Phys. Lett.* **29**, 199 (1974); *Int. J. Quantum Chem. Symp.* **QC 8**, 271 (1974); *J. Chem. Phys.* **62**, 3258 (1975); R.J. Bartlett and I. Shavitt, *Chem. Phys. Lett.* **50**, 190 (1977); J.A. Pople, J.S. Binkley and R. Seeger, *Int. J. Quantum Chem. Symp.* **QC 10**, 1 (1976). R.J. Bartlett, *Ann. Rev. Phys. Chem.* **32**, 359 (1981); R.J. Bartlett, C.E. Dykstra, J. Paldus in *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, (Ed. C.E. Dykstra, Reidel, Dordrecht, 1984); p. 127. For more recent surveys, see e.g. M.R. Hoffman and H.G.F. Schaefer III, *Adv. Quantum Chem.* **18**, 207 (Ed. P.O. Löwdin, Academic Press, San Diego 1986) and S.A. Kucharski and R.J. Bartlett, *Adv. Quantum Chem.* **18**, 281 (1986).
- [30] R.J. Bartlett and J. Noga, *Chem. Phys. Lett.* **150**, 29 (1988).