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The Convergence of the Rayleigh-Ritz Method in Quantum Chemistry

I. The Criteria of Convergence

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Two *sufficient* criteria for the convergence of the Rayleigh-Ritz Method (RRM) with respect to the *eigenvalues* ("E-convergence") of non-relativistic electronic Hamiltonians of molecules are discussed and compared. Moreover, a necessary *and* sufficient criterion is given. By example (Sect. 9) it is shown that the L^2-completeness of the basis is *not* sufficient to guarantee E-convergence. The convergence of the wave *functions* in different norms ("Ψ-convergence") is also investigated. In particular, sufficient conditions for the *one-particle* basis functions (orbitals) are given, such that a CI calculation in this basis is both E- and Ψ-convergent.

Key words: Criteria of convergence - Completeness of basis sets - Energy space - CI calculations

1. Introduction

The *Rayleigh-Ritz Method* (RRM) - mainly in the form of CI calculations - is one of the standard procedures for approximately solving the Schrödinger equation. But even today, the question of "*E-convergence*" of the RRM using the conventional basis sets of Quantum Chemistry is an open problem, i.e. it is not known for which basis sets $\{\Phi_m\}_{m=1}^{\infty}$ the differences between the Mth order Ritz eigenvalues $E_i^{(M)}$ and the exact eigenvalues E_i become arbitrarily small with increasing number M of basis functions used in any state, $i = 0, 1, 2, \ldots$

It should be emphasized that only the *analytical* convergence is investigated. The problem of "*oscillating*" Ritz eigenvalues arising from an "almost linearly dependent" basis set[1] is not the subject of this paper, i.e. numerical stability is always assumed.

General *sufficient* criteria of E-convergence have been proved, especially for non-relativistic electronic *Hamiltonians* of molecules by Kato [1], for *positive definite* operators by Michlin [2] and, in continuation of Michlin's papers for *excited* states, by Bonitz [3].

[1] For "almost linear dependence" see Courant and Hilbert [12], p. 63, and Klahn and Bingel [13].

It is the aim of this paper to give a criterion for *Hamiltonians* analogous to Michlin's criterion and to compare it with Kato's (cf. Fig. 1). Ultimately we show that the basis $\{\Phi_m\}_{m=1}^{\infty}$ must fulfil a *stronger* condition than the L^2-completeness, namely the completeness in the "energy space" H_A or even in the space H_{A^2}.

Moreover, the convergence of the Ritz *functions*[2] (i.e. "Ψ-convergence")

$$u_i^{(M)} = \sum_{m=1}^{M} c_{im}^{(M)} \Phi_m \tag{1}$$

to the exact wave functions u_i in different norms, i.e. the norms of the space L^2 and the energy space H_A, is investigated (cf. Fig. 3). From this we will obtain a *necessary and sufficient* criterion of E-convergence.

We study especially the convergence of *CI calculations*, i.e. of an RRM with Slater determinants as basis functions (Sect. 8): It is shown that one has to demand the H_A- or the H_{A^2}-completeness of the *orbitals* from which the Slater determinants are constructed.

In Part II of this paper [4] we prove the convergence of CI calculations for special orbitals such as *Slater* and *Gauss* functions by means of the criteria discussed here. The convergence of the RRM for special *two-particle* functions is also investigated.

2. Michlin's Criterion of Convergence

Let all the functions under consideration be defined in the Hilbert space L^2 of the quadratically integrable functions, L^2 having the scalar product (f, g) and the corresponding norm $\|f\| = (f, f)^{1/2}$. The measure space of L^2 is, unless otherwise stated, the $3N$-dimensional Euclidian space $\mathbb{R}^{3N}$, where N denotes the number of electrons.

Let B be a positive definite and self-adjoint linear operator with the domain $D_B \subset L^2$ dense in L^2, i.e. there exists a constant $\beta > 0$, such that

$$(f, Bf) \geqslant \beta(f, f), \qquad f \in D_B \tag{2}$$

holds. Furthermore, let us assume that the lower part of the spectrum of B consists of a finite or infinite number of isolated eigenvalues. To solve the eigenvalue problem of the operator B by means of the RRM it seems reasonable to take a basis set $\{\Phi_m\}_{m=1}^{\infty}$ which is *complete* in L^2. Employing such a basis, each eigenfunction of B can be approximated in the mean with any desired accuracy. However, the L^2-completeness of the basis is *not* a sufficient criterion of E-convergence.

To guarantee the E-convergence, we introduce the "energy space" H_B. Let H_B be that Hilbert space which can be obtained as the *closure* of D_B with the B-norm

$$\|f\|_B = (f, Bf)^{1/2}. \tag{3}$$

A theorem of Michlin ([2], p. 79) now says:

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[2] All functions denoted by u are assumed to be normalized to unity.

Theorem 1

Let the basis $\{\Phi_m\}_{m=1}^{\infty}$ be complete in H_B (i.e. relative to the B-norm). Then the RRM for the positive definite operator B converges in this basis to the *lowest* exact eigenvalue E_0.

Bonitz ([3], p. 147) proved the convergence for all *excited* states $i \leqslant l$, on the premises of Theorem 1, provided that E_l is the first *degenerate* exact (isolated) eigenvalue.

The main argument in the proof of Theorem 1 is as follows: If $u^{(M)}$ is any variation function from the linear space D_M spanned by $\{\Phi_m\}_{m=1}^{M}$, the difference between the appropriate expectation value and the exact ith eigenvalue of B is given by [cf. Eq. (19)]

$$(u^{(M)}, Bu^{(M)}) - E_i \leqslant 2E_i\beta^{-1/2}\|u^{(M)} - u_i\|_B + \|u^{(M)} - u_i\|_B^2. \tag{4}$$

This equation holds in particular in the case $u^{(M)} = u_i^{(M)}$, i.e. if $u^{(M)}$ is the Ritz function. The Ritz eigenvalues can be characterized by (cf. Weinstein and Stenger [5], p. 11)

$$E_i^{(M)} = \min_{u^{(M)} \in D_{Mi}} (u^{(M)}, Bu^{(M)}), \tag{5a}$$

where

$$D_{Mi} = \{u \in D_M | \; \|u\| = 1, \quad (u, u_j^{(M)}) = 0 \text{ for } j < i\}, \tag{5b}$$

i.e. $E_0^{(M)}$ is the *minimum* of the expectation value of B for $u^{(M)} \in D_M$. If the RRM does not converge to the ground state, then no sequence $u^{(M)} \in D_M$ exists, the expectation value of which converges to E_0. This, however, is a contradiction to the assumed H_B-completeness of the basis because of Eq. (4). ♦

We note that the H_B-completeness is not required at all for the proof, but only the possibility of approximating the eigenfunction u_0 by a basis expansion in the B-norm.

3. Properties of Hamiltonians

The non-relativistic electronic molecular Hamiltonian is of the well-known form

$$H = T + V, \tag{6}$$

where T and V denote the operators of kinetic and potential energy. In position space with the one-particle vectors $r_k = (x_k, y_k, z_k)$ and the *total* position vector $r = (r_1, \ldots r_N)$ the operator of kinetic energy for N particles is given by

$$T = -\tfrac{1}{2} \sum_{k=1}^{N} \left(\frac{\partial^2}{\partial x_k^2} + \frac{\partial^2}{\partial y_k^2} + \frac{\partial^2}{\partial z_k^2}\right), \tag{7}$$

and in momentum space with the one-particle and *total* momentum vectors $\boldsymbol{p}_k$ and $\boldsymbol{p}$, respectively, by

$$T = \tfrac{1}{2}p^2 = \tfrac{1}{2} \sum_{k=1}^{N} p_k^2. \tag{8}$$

Choosing

$$D_T = \{f(r) \mid (1 + p^2)\hat{f}(p) \in L^2\} \tag{9}$$

as domain of T, where $\hat{f}(p)$ denotes the Fourier transform of $f(r)$, T becomes a self-adjoint operator, for it is a maximal multiplication operator (cf. Kato [6], p. 272). The operator V is the well-known Coulomb potential

$$V = -\sum_{\alpha} Z_\alpha \sum_{i=1}^{N} \frac{1}{r_{i\alpha}} + \sum_{i<j} \frac{1}{r_{ij}}. \tag{10}$$

Here, Z_α is the nuclear charge of nucleus α, $r_{i\alpha}$ the distance between nucleus α and electron i and r_{ij} the interelectronic distance between the electrons i and j. An important property of this operator is its *T-boundedness*, proved by Kato [1], i.e. there exist two positive constants a and b, such that

$$\| Vf \| \leqslant a \| f \| + b \| Tf \|, \qquad f \in D_T \tag{11}$$

holds, also b can be taken arbitrarily small. Because of this equation, criteria of convergence *independent* of V can be proved, and thus, *systematic* statements about the convergence are made possible, *valid for all molecules.*

Because of Eq. (11), the Hamiltonian (6) with the domain D_T is also a self-adjoint operator (cf. Kato [6], p. 287), such that all eigenfunctions of H are elements of D_T.

As a consequence of Eq. (11), the T-boundedness of V in the *quadratic form* can be proved, i.e. choosing two suitable constants a' and b', where b' may be arbitrarily small, the inequality

$$|(f, Vf)| \leqslant a' \| f \|^2 + b' \| T^{1/2} f \|^2, \qquad f \in D_{T^{1/2}} \tag{12}$$

holds (cf. Kato [6], p. 321). Here $T^{1/2}$ is the square root (cf. Kato [6], p. 281) of T, which in momentum space is defined by

$$T^{1/2} = 2^{-1/2} | p | = 2^{-1/2} \left(\sum_{k=1}^{N} p_k^2 \right)^{1/2} \tag{13}$$

having the domain

$$D_{T^{1/2}} = \{f(r) \mid (1 + |p|)\hat{f}(p) \in L^2\}. \tag{14}$$

Obviously, $T^{1/2}$ is a maximal multiplication operator and thus self-adjoint. This is also true for the operator $(1 + T)^{1/2}$ if its domain is $D_{T^{1/2}}$.

It should be noted that Eq. (12) is always a consequence of Eq. (11) even for potentials different from (10). But, in general, the opposite is not true, e.g. for the one-dimensional δ-potential. Thus Eq. (11) is a *stronger* condition on the potential than Eq. (12).

Concerning the potential V of Eq. (10), we never make use of its explicit form but only of its properties (11) or (12), respectively. Therefore, all the statements of this paper hold for any Hamiltonian with a T-bounded potential in the norm [Eq. (11)] or the quadratic form [Eq. (12)] according to which of both equations has been used for the proof; our statements hold therefore for all "*Kato-potentials*" (cf. Simon [7], introduction and p. 32).

4. Michlin's Criterion of Convergence for Hamiltonians

Hamiltonians of molecules are semi-bounded from below, i.e. there exists a positive constant c such that

$$B = c + H, \qquad D_B = D_T \tag{15}$$

is a positive definite operator. Choosing a basis set $\{\Phi_m\}_{m=1}^{\infty}$, which is complete in the energy space $H_B = H_{c+H}$, the convergence of the RRM for such a Hamiltonian follows from Theorem 1.

In order to eliminate the potential from the condition of convergence, we introduce the energy space H_A, which is *independent of* V: Let H_A be the closure of the linear space D_T having the scalar product and norm, respectively

$$(f, g)_A = (f, Ag) = (f, (c + T)g) \tag{16}$$

$$\| f \|_A = (f, Af)^{1/2} = (f, (c + T)f)^{1/2}. \tag{17}$$

Now, because of the T-boundedness of V in the quadratic form [Eq. (12)] and the positive definiteness of B [Eq. (2)], the B-norm (3) and the A-norm (17) can be shown to be *equivalent*, i.e. there are two positive constants c_1 and c_2, such that

$$c_1 \| f \|_A \leqslant \| f \|_B \leqslant c_2 \| f \|_A, \qquad f \in D_T \tag{18}$$

holds (Proof: Klahn [8], p. 37). Consequently, the energy spaces H_A and H_B are the same (cf. Smirnow [9], p. 297). Thus we have the criterion of convergence for Hamiltonians:

Theorem 2 ("Michlin's criterion")

Let the basis $\{\Phi_m\}_{m=1}^{\infty}$ be complete in H_A [i.e. relative to the A-norm, Eq. (17)]. Moreover, let E_l be the first exact degenerate eigenvalue of the Hamiltonian H. Then, in this basis, the RRM converges to the lowest exact eigenvalues of H for $i \leqslant l$.

A direct proof can be given in complete analogy to the proof of Theorem 1. One has only to replace Eq. (4) by the following inequality (Proof: [8], p. 32)

$$(u^{(M)}, Hu^{(M)}) - E_i \leqslant 2\,|E_i|\, c^{-1/2} \| u^{(M)} - u_i \|_A + (2 + 2b' + a'c^{-1}) \| u^{(M)} - u_i \|_A^2 \quad \blacklozenge \tag{19}$$

We notice the energy space H_A to be independent of the choice of the constant $c > 0$. This is true, because two norms, $\| f \|_{A(c)}$ and $\| f \|_{A(d)}$, can be shown to be equivalent if both c and d are positive constants; the reason being the positiveness of T. Furthermore, H_A can be obtained either from its definition given above or from the closure of D_T with the A'-norm, which can be introduced in analogy to Eq. (17)

$$\| f \|_{A'} = (f, A'f)^{1/2} = (f, (c + T^{1/2})^2 f)^{1/2} \tag{20}$$

since the A- and A'-norms are also equivalent (Proof: [8], p. 32).

Moreover, the sets $D_{T^{1/2}}$ and H_A can be shown to be the same; also the space H_A and the Sobolew space $W_2^{(1)}$ are identical, i.e. the space of all elements $f \in L^2$, the generalized first derivatives of which are elements of L^2 (cf. Smirnow [9], p. 537). Therefore, we have the relation between the sets:

$$D_{T^{1/2}} = H_A = W_2^{(1)}. \tag{21}$$

We remember that Theorem 2 requires the investigation of completeness in the energy space H_A. However, one usually studies the question of completeness in the space L^2. We therefore formulate a condition of convergence equivalent to that of Theorem 2 requiring a proof of completeness in L^2:

Lemma 1

The system $\{\Phi_m\}_{m=1}^{\infty}$ is complete in H_A if and only if $\{(c+T)^{1/2}\Phi_m\}_{m=1}^{\infty}$ or $\{(c+T^{1/2})\Phi_m\}_{m=1}^{\infty}$ with $c > 0$ is complete in L^2. ♦

This lemma can be proved by the following (cf. [8], p. 26).

Lemma 2

Let L_ρ^2 be the Hilbert space of all quadratically integrable functions with the weight function $\rho > 0$. Then $\{\Phi_m\}_{m=1}^{\infty}$ is complete in L_ρ^2 if and only if $\{\rho^{1/2}\Phi_m\}_{m=1}^{\infty}$ is complete in L^2. ♦

Thus, Lemma 1 follows immediately, for H_A is a L_ρ^2-space in momentum space. To see this, one has only to choose

$$\rho = c + \tfrac{1}{2}p^2 \tag{22a}$$

or

$$\rho = (c + 2^{-1/2}|p|)^2 \tag{22b}$$

according to the generation of H_A by closure with the A- or A'-norm, respectively.

5. Kato's Criterion of Convergence for Hamiltonians

Another criterion of convergence was given by Kato [1].

Theorem 3 ("Kato's criterion")

Let the system $\{(c+T)\Phi_m\}_{m=1}^{\infty}$, with $c > 0$, be complete in L^2. Then the RRM for the Hamiltonian H converges for all states to the exact eigenvalues of H if $\{\Phi_m\}_{m=1}^{\infty}$ is chosen as a basis set. ♦

The proof is mainly based on the characterization of the Ritz eigenvalues by Eq. (5) with H instead of B and on an inequality analogous to Eqs. (4) and (19), which can be proved using the T-boundedness of the potential [Eq. (11); for the proof of Eq. (23) see [8], p. 22]:

$$(u^{(M)}, Hu^{(M)}) - E_i \leqslant [c^{-1}(a + |E_i|) + b + 1] \, \| u^{(M)} - u_i \|_{A^2}. \tag{23}$$

The A^2-norm, used in Eq. (23), is defined by

$$\| f \|_{A^2} = (f, A^2 f)^{1/2} = \| (c + T) f \|. \tag{24}$$

If one introduces the corresponding Hilbert space H_{A^2}, a second condition of convergence, equivalent to that of Theorem 3, can be given: Let H_{A^2} be the closure of D_T with the A^2-norm. We then have the following:

Lemma 3

The system $\{(c + T)\Phi_m\}_{m=1}^{\infty}$ is complete in L^2 if and only if $\{\Phi_m\}_{m=1}^{\infty}$ is complete in H_{A^2}. ♦

This lemma is a direct consequence of Lemma 2. One has only to realize that H_{A^2} is a L^2_ρ-space in momentum space, where

$$\rho = (c + \tfrac{1}{2}p^2)^2. \tag{25}$$

In complete analogy to Eq. (21) we now have the equation

$$D_T = H_{A^2} = W_2^{(2)}, \tag{26}$$

where $W_2^{(2)}$ denotes the Sobolew space of all elements of L^2, the generalized second derivatives of which are elements of L^2 (cf. Smirnow [9], p. 491).

The different criteria of convergence are summarized in Fig. 1 and the corresponding spaces in Fig. 2.

Kato's condition		Michlin's condition		
$\{\Phi_m\}_{m=1}^{\infty}$ is H_{A^2}-complete	$\longrightarrow$	$\{\Phi_m\}_{m=1}^{\infty}$ is H_A-complete	$\longrightarrow$	$\{\Phi_m\}_{m=1}^{\infty}$ is L^2-complete
$\updownarrow$		$\updownarrow$		
$\{(c + T)\Phi_m\}_{m=1}^{\infty}$ is L^2-complete		$\{(c + T)^{1/2}\Phi_m\}_{m=1}^{\infty}$ is L^2-complete		
		$\updownarrow$		
		$\{(c + T^{1/2})\Phi_m\}_{m=1}^{\infty}$ is L^2-complete		

Fig. 1. Summary of the relations between the different conditions of convergence

$$\begin{array}{ccccc} H_{A^2} & \subset & H_A & \subset & L^2 \\ \| & & \| & & \\ D_T & & D_{T^{1/2}} & & \\ \| & & \| & & \\ W_2^{(2)} & & W_2^{(1)} & & \end{array}$$

Fig. 2. Summary of the relations between the different spaces and sets used. ("$\|$" means equality of the sets)

6. Comparison of the Criteria

Still unanswered is the question: What is the difference between the criteria of Michlin and Kato? We expect Kato's condition to be the stronger one, because its derivation requires the T-boundedness [Eq. (11)], while the derivation of Michlin's condition requires only the T-boundedness in the quadratic form [Eq. (12)], which itself is a consequence of the T-boundedness. Indeed, the following theorem holds:

Theorem 4

Let $\{\Phi_m\}_{m=1}^{\infty}$ be complete in H_{A^2}. Then $\{\Phi_m\}_{m=1}^{\infty}$ is complete in H_A.

Before proving this theorem, we state the inclusion

$$H_{A^2} \subset H_A \subset L^2, \tag{27}$$

which is a consequence of Eqs. (21), (26), (9) and (14). We now have to show that the completeness of $\{(1 + T)^{1/2}\Phi_m\}_{m=1}^{\infty}$ in L^2 follows from that of $\{(1 + T)\Phi_m\}_{m=1}^{\infty}$ in L^2. Therefore we choose $f \in L^2$ with the property

$$(f, (1 + T)^{1/2}\Phi_m) = 0, \qquad m = 1, 2, 3, \ldots \tag{28}$$

and show f to be the zero element[3] of L^2: To f there exists a function $g \in H_A$ with the property[4]

$$f = (1 + T)^{1/2} g. \tag{29}$$

Using the self-adjointedness of $(1 + T)^{1/2}$, from (28) and (29) we obtain

$$(g, (1 + T)\Phi_m) = 0, \qquad m = 1, 2, 3, \ldots \tag{30}$$

Because of the assumed completeness of $\{(1 + T)\Phi_m\}_{m=1}^{\infty}$ and the fact that $g \in H_A \subset L^2$, it follows that $g = \Theta$ and thus $f = \Theta$ by Eq. (29). ♦

Analogously one can prove:

Theorem 5

Let $\{\Phi_m\}_{m=1}^{\infty}$ be complete in H_A. Then $\{\Phi_m\}_{m=1}^{\infty}$ is complete in L^2. ♦

We emphasize that the inverse of Theorems 4 and 5 is *not* true, i.e. there exist basis sets

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[3] The zero element of L^2 and H_A, respectively, is denoted by Θ.

[4] This function is determined by its Fourier transform $\hat{g} = \hat{f}/(1 + p^2/2)^{1/2}$.

which are complete in L^2 but incomplete in H_A or which are complete in H_A but incomplete in H_{A^2} (cf. Sect. 9, Table 1).

Therefore the H_{A^2}-completeness is a sufficient but not a necessary condition of E-convergence. The weaker condition of H_A-completeness is also only sufficient, since it can be sharpened to a necessary *and* sufficient condition (cf. Theorem 6, Sect. 7). Such a sharpening is possible because the H_A-completeness of the basis has not been fully used for the proof of Michlin's criterion, but only the possibility of approximating all the eigenfunctions of H in the A-norm.

A consequence of Theorems 4 and 5 is that both Kato's and Michlin's criterion require the L^2-completeness of the basis. But it can be shown that the L^2-completeness is not a *necessary* criterion because of the *in*completeness of the set $\{u_i\}_{i=0}^{\infty}$ in L^2, since the molecular Hamiltonian always contains a continuous spectrum.

With restriction to non-degenerate exact eigenvalues, Michlin's criterion seems to be completely sufficient for investigating the question of E-convergence. But Kato's criterion is much more easy to handle than Michlin's in such cases, where only a proof of completeness in position space is feasible. The reason is that the operator T in position space is the well-known differential operator defined by Eq. (7), whereas $T^{1/2}$ is a rather inconvenient integral operator.

It should be emphasized that the criteria discussed in this paper do not refer to the *speed* of the convergence. For this property depends decisively on the special molecule under consideration, i.e. on its potential.

7. The Convergence of the Wave Function

If the Ritz eigenvalues converge to the exact eigenvalues with $M \to \infty$, the convergence of the Ritz *functions* in the mean follows - non-degenerate exact eigenvalues assumed - for the *ground* state from Eckart's inequality (Eckart [10])[5]

$$\| u_0^{(M)} - u_0 \|^2 \leqslant 2 \frac{E_0^{(M)} - E_0}{E_1 - E_0} \tag{31}$$

and for *excited* states from its generalization given by Löwdin [11]

$$\| u_i^{(M)} - u_i \|^2 \leqslant 2 \frac{E_i^{(M)} - E_i}{E_{i+1} - E_i} \left\{ 1 + G_i^2 \sum_{j=0}^{i-1} (E_{i+1} - E_j) \right\}, \qquad G_i = \sum_{j=0}^{i-1} (E_i - E_j^{(M)})^{-1/2}. \tag{32}$$

Furthermore, the Ψ-convergence in the A-norm follows from the inequality[6]

$$\begin{aligned} \| u_i^{(M)} - u_i \|_A^2 &\leqslant (E_i^{(M)} - E_i) \{(1 - b')^{-1} + 2(E_{i+1} - E_i)^{-1} H_i\} \\ H_i &= [c + (a' + |E_i|)(1 - b')^{-1}] \left[1 + G_i^2 \sum_{j=0}^{i-1} (E_{i+1} - E_j) \right], \end{aligned} \tag{33}$$

[5] Eqs. (31), (32) and (33) are meaningful only if $u_i^{(M)}$ has been multiplied by a complex phase factor of absolute value 1, such that the overlap integral $(u_i^{(M)}, u_i)$ becomes real and positive.

[6] In Eq. (33), $b' < 1$ is assumed.

which can be proved as follows: With the relation $A = c + T = c + H - V$ [cf. Eq. (17)] and Eq. (12) one obtains for any $f \in H_A$

$$\|f\|_A^2 \leqslant (c + a' - b'c)\|f\|^2 + b'\|f\|_A^2 + |(f, Hf)|. \tag{34}$$

Choosing especially $f = u_i^{(M)} - u_i$, one easily obtains

$$(f, Hf) = E_i^{(M)} - E_i + E_i\|f\|^2. \tag{35}$$

Putting (35) into (34) and solving (34) for $\|f\|_A^2$, one gets

$$\|f\|_A^2 \leqslant (E_i^{(M)} - E_i)(1 - b')^{-1} + [c + (a' + |E_i|)(1 - b')^{-1}]\,\|f\|^2. \tag{36}$$

With (32), Eq. (33) follows at once. ♦

From Eq. (33) we see that the Ψ-convergence in the A-norm is a necessary condition of E-convergence. Thus, combining the inequalities (33) and (19) and employing Eq. (5), we obtain a *necessary and sufficient* criterion for E-convergence:

Theorem 6

The RRM converges to the lowest l (non-degenerate) exact eigenvalues if and only if the basis $\{\Phi_m\}_{m=1}^{\infty}$ is chosen such that the lowest l exact wave functions of the Hamiltonian can be approximated in the A-norm with any desired accuracy. ♦

It should be noted that this condition of convergence is a weaker one than the H_A-completeness of Michlin's criterion; for if a basis is complete in H_A, surely all the exact wave functions can be approximated by a basis expansion in the A-norm with arbitrary accuracy, whereas the reversal is not generally true. But since the H_A-completeness of a basis set is much more easy to prove than the possibility of approximating explicitly unknown wave functions, theorem 6 is rather useless for practical purposes.

No definite statements can be made about the Ψ-convergence in the A^2*-norm*, however. If the basis is H_A-complete but H_{A^2}-incomplete, then

$$\|u_i^{(M)} - u_i\|_{A^2} \to 0 \quad (M \to \infty), \tag{37}$$

in general, does *not* hold even though the RRM is E-convergent. Moreover, it is not clear whether the H_{A^2}-completeness is a *sufficient* criterion for the validity of Eq. (37). Possibly, this is not the case.

We now ask whether the Schrödinger equation is fulfilled in the limit $M \to \infty$, i.e. whether

$$\|(H - E_i^{(M)})u_i^{(M)}\| \to 0 \qquad (M \to \infty) \tag{38}$$

is valid for any E-convergent RRM. The answer is no, since, in general, Eq. (37) does not hold and because of

Lemma 4 (cf. [8], p. 46)

Let the RRM be E-convergent for the ith state.[7] Then Eq. (37) holds if and only if Eq. (38) holds. ♦

[7] This assumption can be shown to be dispensable.

Relations between the statements about the Ψ-convergence relative to different norms can be obtained from the inequality (39), which is a consequence of the positiveness of T [8]

$$\| f \|_{A^2} \geqslant c \, \| f \|_A^2 \geqslant c^2 \| f \|, \qquad f \in H_{A^2}. \tag{39}$$

From this, the Ψ-convergence in the A^2-norm causes that in the A-norm and the latter that in the mean square:

$$\| u_i^{(M)} - u_i \|_{A^2} \to 0 \Rightarrow \| u_i^{(M)} - u_i \|_A \to 0 \Rightarrow \| u_i^{(M)} - u_i \| \to 0 \qquad (M \to \infty). \tag{40}$$

All the statements made in this section about convergence are summarized in Fig. 3.

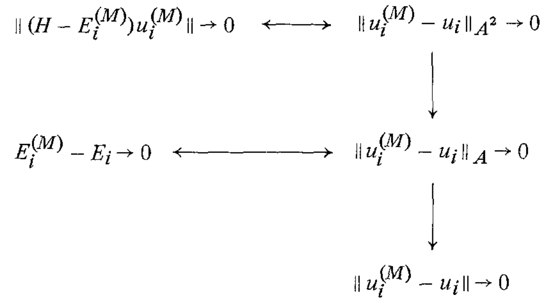

Fig. 3. Convergence scheme for the wave functions. The scheme holds for the lowest l states ($i = 0, \ldots, l-1$), if E_l is the first degenerate eigenvalue

8. The Convergence of CI-Calculations

In Quantum Chemistry, the RRM is often carried out in the form of a CI-calculation, i.e. the N-electron basis functions[9] Φ_m are chosen to be N-dimensional Slater determinants generated from a given set of *one*-particle functions or *orbitals* $\varphi_m(r_1)$. It is therefore desirable to find *conditions for the orbitals*, such that the CI calculation converges.

It is reasonable that the H_A - or H_{A^2}- completeness of the *orbital basis* is a sufficient condition of convergence. We will now show this to be the case.

Since Slater determinants are - apart from the spin functions - linear combinations of N-fold products of the orbitals, we first of all study the completeness properties of such product functions.

As is well known, the following lemma is valid (cf., e.g., Courant and Hilbert [12], p. 56, or Kato [6], p. 255, in a somewhat different formulation):

Lemma 5

Let the orbital basis $\{\varphi_m(r_1)\}_{m=1}^{\infty}$ be complete in $L^2(\mathbb{R}^3)$. Then the set of all N-fold

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[8] More precisely, the second part of Eq. (39) even holds for any $f \in H_A$.

[9] Different from the previous notation, Φ_m now denotes a function including spatial- *and* spin-coordinates.

product functions

$$\left\{\prod_{k=1}^{N} \varphi_{m(k)}(\boldsymbol{r}_k)\right\}_{m(k)=1}^{\infty}$$

is complete in $L^2(\mathbb{R}^{3N})$. ♦

From this we get another lemma, which is the most important step in proving the convergence of CI calculations:

Lemma 6

Let the orbital basis $\{\varphi_m(\boldsymbol{r}_1)\}_{m=1}^{\infty}$ be complete in $H_A(\mathbb{R}^3)$. Then the set of all N-fold product functions

$$\left\{\prod_{k=1}^{N} \varphi_{m(k)}(\boldsymbol{r}_k)\right\}_{m(k)=1}^{\infty}$$

generated from this is complete in $H_A(\mathbb{R}^{3N})$.

Proof (carried out in momentum space)
Because of the assumption and Lemma 1 the system

$$\{(1+|\boldsymbol{p}_1|)\hat{\varphi}_m(\boldsymbol{p}_1)\}_{m=1}^{\infty} \tag{41}$$

is complete in $L^2(\mathbb{R}^3)$. Therefore, with Lemma 5, the completeness of

$$\left\{\prod_{k=1}^{N}(1+|\boldsymbol{p}_k|)\hat{\varphi}_{m(k)}(\boldsymbol{p}_k)\right\}_{m(k)=1}^{\infty} \tag{42}$$

in $L^2(\mathbb{R}^{3N})$ follows. Because of Lemma 1 we have to prove the completeness of

$$\left\{\left[1+\left(\sum_{k=1}^{N} p_k^2\right)^{1/2}\right] \prod_{k=1}^{N} \hat{\varphi}_{m(k)}(\boldsymbol{p}_k)\right\}_{m(k)=1}^{\infty} \tag{43}$$

in $L^2(\mathbb{R}^{3N})$. Thus we choose an element $\hat{f}(\boldsymbol{p}) \in L^2(\mathbb{R}^{3N})$, such that $\hat{f}$ is orthogonal to the set (43), and show that $\hat{f} = \Theta$. From the orthogonality of $\hat{f}$ to the set (43) and with

$$\hat{g}(\boldsymbol{p}) = \frac{1+\left(\sum_{k=1}^{N} p_k^2\right)^{1/2}}{\prod_{k=1}^{N}(1+|\boldsymbol{p}_k|)} \hat{f}(\boldsymbol{p}) \in L^2(\mathbb{R}^{3N}) \tag{44}$$

it follows that

$$\left(\hat{g}, \prod_{k=1}^{N}(1+|\boldsymbol{p}_k|)\,\hat{\varphi}_{m(k)}(\boldsymbol{p}_k)\right) = 0; \qquad m(k) = 1, 2, 3, \ldots \tag{45}$$

As the set (42) is complete in $L^2(\mathbb{R}^{3N})$, we conclude that $\hat{g} = \Theta$ and, because of (44), finally that $\hat{f} = \Theta$. ♦

A corresponding lemma relative to the space H_{A^2} can be proved in a completely analogous way.

Hence, the convergence of the RRM for *arbitrary* molecules follows on account of Michlin's or Kato's criterion, respectively, if the pertaining basis consists of all possible N-fold product functions that can be constructed from an orbital basis complete in H_A or H_{A^2}.

Taking spin into account, the criteria of convergence have to be modified. Instead of requiring the completeness of the pure spatial basis in H_A or H_{A^2}, one now has to investigate the completeness of a basis set including spin functions in the spaces $\tilde{H}_A(N)$ or $\tilde{H}_{A^2}(N)$, respectively. These spaces are defined as the direct product of the spaces $H_A(\mathbb{R}^{3N})$ and $H_{A^2}(\mathbb{R}^{3N})$ with the N-particle spin space S_N of dimension 2^N:

$$\tilde{H}_A(N) = H_A(\mathbb{R}^{3N}) \otimes S_N \tag{46}$$

$$\tilde{H}_{A^2}(N) = H_{A^2}(\mathbb{R}^{3N}) \otimes S_N. \tag{47}$$

As exact wave functions are antisymmetric, it is sufficient for the convergence to take basis sets, which are complete in the subspace of all antisymmetric functions from $\tilde{H}_A(N)$ or $\tilde{H}_{A^2}(N)$.

Now, let $\alpha(s)$ and $\beta(s)$ be the well-known one-particle spin functions spanning S_1. Then the finite set of all possible N-fold product functions of $\{\alpha, \beta\}$ forms a complete set in S_N. If we multiply each of these functions with each one of an N-fold product set generated from an orbital basis $\{\varphi_m\}_{m=1}^{\infty}$, we have constructed all possible N-fold product functions including spin from $\{\varphi_m\}_{m=1}^{\infty}$; this set is called[10] $\{\Phi_K^{(N)}\}$. Moreover, if the orbital basis is complete in $H_A(\mathbb{R}^3)$ or $H_{A^2}(\mathbb{R}^3)$, the set $\{\Phi_K^{(N)}\}$ is complete in $\tilde{H}_A(N)$ or $\tilde{H}_{A^2}(N)$ because of Lemma 6.

Furthermore, if $\mathscr{A}$ is the antisymmetrizer, $\{\Phi_m = \mathscr{A}\Phi_K^{(N)}\}$ is the set of all Slater determinants that can be obtained from $\{\varphi_m\}_{m=1}^{\infty}$. Finally we get

Lemma 7

If the orbital basis $\{\varphi_m\}_{m=1}^{\infty}$ is complete in $H_A(\mathbb{R}^3)$, the set of all possible Slater determinants that can be constructed from this basis is complete in the subspace of all antisymmetric functions of $\tilde{H}_A(N)$.

Proof

Let $f \in \tilde{H}_A(N)$ be antisymmetric and orthogonal to all the Slater determinants $\{\Phi_m\}_{m=1}^{\infty}$ relative to the A-norm, Eq. (16). As $\mathscr{A}$ is a projector - provided it is suitably normalized - it follows that[11]

$$(f, \Phi_K^{(N)})_A = (\mathscr{A}f, \Phi_K^{(N)})_A = (f, \mathscr{A}\Phi_K^{(N)})_A = (f, \Phi_m)_A = 0. \tag{48}$$

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[10] K denotes a super-index characterizing all the *spin-orbital* indices of $\Phi_K^{(N)}$.

[11] The integration of the scalar products has to be carried out over spatial *and* spin variables.

Because $\{\Phi_K^{(N)}\}$ has been shown to be a complete set in $\tilde{H}_A(N)$, from (48) we conclude that $f = \Theta$. ♦

A quite analogous lemma can be proved for the space H_{A^2}.

Finally, we summarize the two criteria of convergence for CI calculations, where $\hat{t}$ denotes the one-particle operator of kinetic energy.

Theorem 7 ("Michlin's Criterion")

Let the orbital basis $\{\varphi_m(r_1)\}_{m=1}^{\infty}$ be complete in $H_A(\mathbb{R}^3)$, which is the case if and only if $\{(c+\hat{t})^{1/2}\varphi_m\}_{m=1}^{\infty}$ or $\{(c+\hat{t}^{1/2})\varphi_m\}_{m=1}^{\infty}$, respectively, with $c > 0$, are complete in $L^2(\mathbb{R}^3)$. Let E_l be the first degenerate exact eigenvalue of the Hamiltonian (within the quadratic form T-bounded potential). Then the CI calculation converges for the states $i = 0, 1, 2, \ldots, l$ to the exact eigenvalues if the set of all Slater determinants that can be constructed from $\{\varphi_m\}_{m=1}^{\infty}$ is taken as a basis. Moreover, the Ritz functions of the l lowest states converge to the exact wave functions both in the mean square and in the A-norm. ♦

Theorem 8 ("Kato's Criterion")

Let the orbital basis $\{\varphi_m(r_1)\}_{m=1}^{\infty}$ be complete in $H_{A^2}(\mathbb{R}^3)$, which is the case if and only if $\{(c+\hat{t})\varphi_m\}_{m=1}^{\infty}$, with $c > 0$, is complete in $L^2(\mathbb{R}^3)$. Then the CI calculation converges for all states of the Hamiltonian (with T-bounded potential) to its exact eigenvalues if the set of all Slater determinants that can be constructed from $\{\varphi_m\}_{m=1}^{\infty}$ is taken as a basis. Moreover, if the lowest l exact eigenvalues are non-degenerate, the Ritz functions of these states converge to the exact wave functions both in the mean square and in the A-norm. ♦

It should be emphasized that because of Theorem 7 the question of E-convergence for *arbitrary* molecules up to the first degenerate exact eigenvalue can be decided by a *single* proof of completeness; using Theorem 8 this is possible even for degenerate states.

9. Example of a Basis Complete in L^2 which Leads to a Non-Convergent RRM

That the L^2-completeness of a basis is *not* a sufficient criterion for E-convergence will now be shown by an example. We give a basis complete in L^2, such that the RRM for the $1s$-state of the hydrogen atom converges to a *wrong* value.

A basis set of this kind is

$$\{\Phi_m = (\tfrac{1}{2} + T)^{1/2} r^m e^{-r}\}_{m=1}^{\infty}. \tag{49}$$

To show its properties in detail we first consider the completeness properties of the functions

$$f_m(r) = r^m \exp(-\xi r), \qquad \xi > 0. \tag{50}$$

For these, the following statements are valid[12]:

a) $\{f_m\}_{m=m'}^{\infty}$ with $m' \geqslant 0$ is complete in $s\text{-}L^2$,

b) $\{f_m\}_{m=0}^{\infty}$ is complete in $s\text{-}H_A$ and $s\text{-}H_{A^2}$,

c) $\{f_m\}_{m=1}^{\infty}$ is incomplete in $s\text{-}H_{A^2}$,

d) $\{f_m\}_{m=1}^{\infty}$ is complete in $s\text{-}H_A$.

Proof:

a) The proof can be seen from the second part, [4], Eq. (26).

b) See [4], Theorem 3.

c) As can be checked easily, for the $s\text{-}L^2$ function

$$g(r) = (\tfrac{1}{2}\xi^2 + T)\exp(-\xi r) = \xi r^{-1} \exp(-\xi r) \tag{51}$$

the following orthogonality relations are valid:

$$(g, (\tfrac{1}{2}\xi^2 + T) f_m) = 0 \qquad \text{for } m \geqslant 1 \tag{52}$$

Thus, the assertion follows from Lemma 3.

d) Let f be an element of $s\text{-}H_A$ with

$$(f, f_m)_A = (f, (\tfrac{1}{2}\xi^2 + T) f_m) = 0 \qquad \text{for } m \geqslant 1. \tag{53}$$

We have to show that[3] $f = \Theta$. Since the system

$$(\tfrac{1}{2}\xi^2 + T) f_0 = g \qquad \text{and} \qquad \{(\tfrac{1}{2}\xi^2 + T) f_m\}_{m=1}^{\infty} \tag{54}$$

is complete in $s\text{-}L^2$ by property b) and Lemma 3, the system $\{(\frac{1}{2}\xi^2 + T)f_m\}_{m=1}^{\infty}$ is complete in $s\text{-}L^2 \ominus \{g\}$ by Eq. (52), i.e. the orthogonal complement of $s\text{-}L^2$ relative to the function g. Because of Eq. (53) f is orthogonal to $s\text{-}L^2 \ominus \{g\}$, i.e. f is equal to g apart from a complex number. However, g is not an element of the space $s\text{-}H_A$, as can be checked most easily in momentum space. Thus, we have $f = \Theta$, since $f \in s\text{-}H_A$ by assumption. ♦

We summarize the properties of the f_m in Table 1: The first two lines correspond to a)–d), the last two lines can be obtained from the first ones applying Lemmas 1 and 3 and Theorems 4 and 5.

From Table 1 we see that the basis (49) is *complete* in $s\text{-}L^2$ but *incomplete* in $s\text{-}H_A$. Therefore, we expect the RRM in the basis (49), e.g. for the ground state of the hydro-

[12] $s\text{-}L^2$, $s\text{-}H_A$ and $s\text{-}H_{A^2}$ denote the subspaces of all s-functions of $L^2(\mathbb{R}^3)$, $H_A(\mathbb{R}^3)$ and $H_{A^2}(\mathbb{R}^3)$.

Basis	$s\text{-}L^2$	$s\text{-}H_A$	$s\text{-}H_{A^2}$
$\{f_m\}_{m=0}^{\infty}$	+	+	+
$\{f_m\}_{m=1}^{\infty}$	+	+	–
$\{(\frac{1}{2}\xi^2 + T)^{1/2} f_m\}_{m=1}^{\infty}$	+	–	–
$\{(\frac{1}{2}\xi^2 + T) f_m\}_{m=1}^{\infty}$	–	–	–

Table 1. Completeness properties of the functions $f_m = r^m \exp(-\xi r)$ in the spaces $s\text{-}L^2$, $s\text{-}H_A$ and $s\text{-}H_{A^2}$. "+" means completeness and "–" incompleteness of the set in question

gen atom, to converge to a wrong value. To prove this, from Eq. (33) the existence of a positive constant K has to be shown, such that

$$\| u_0^{(M)} - u_0 \|_A^2 \geqslant K, \tag{55}$$

i.e. because of $u_0 = \pi^{-1/2} \exp(-r)$ and Eq. (1)

$$\left\| \sum_{m=1}^{M} c_{0m}^{(M)} (\tfrac{1}{2} + T)^{1/2} \Phi_m - (\tfrac{1}{2} + T)^{1/2} \pi^{-1/2} \exp(-r) \right\|^2 \geqslant K. \tag{56}$$

For this purpose, we make an orthogonal decomposition of the function $(\frac{1}{2} + T)^{1/2} u_0$ into

$$h_1 = \frac{4}{3\pi} \left(\frac{2}{\pi}\right)^{1/2} \frac{\exp(-r)}{r} \tag{57a}$$

and

$$h_2 = (\tfrac{1}{2} + T)^{1/2} \frac{\exp(-r)}{\pi^{1/2}} - \frac{4}{3\pi} \left(\frac{2}{\pi}\right)^{1/2} \frac{\exp(-r)}{r}, \tag{57b}$$

which has been chosen, such that h_1 is orthogonal to the set $\{(\frac{1}{2} + T)^{1/2} \Phi_m\}_{m=1}^{\infty}$ [cf. Eq. (52)]. Thus we get

$$\begin{aligned} \| u_0^{(M)} - u_0 \|_A^2 &= \left\| \sum_{m=1}^{M} c_{0m}^{(M)} (\tfrac{1}{2} + T)^{1/2} \Phi_m - h_1 - h_2 \right\|^2 \\ &= \left\| \sum_{m=1}^{M} c_{0m}^{(M)} (\tfrac{1}{2} + T)^{1/2} \Phi_m - h_2 \right\|^2 + \| h_1 \|^2 \\ &\geqslant \| h_1 \|^2 = \frac{64}{9\pi^2} = K, \end{aligned} \tag{58}$$

which proves Eq. (55) and consequently the convergence of the RRM for the ground state of the hydrogen atom in the complete basis (49) to a value $E_0^{(\infty)} > -\frac{1}{2}$, i.e. higher than the exact value.

Moreover, from Eq. (33) the minimal defect for such a calculation can be determined. It turns out that (cf. [8], p. 143)

$$E_0^{(M)} - E_0 > 10^{-3}. \tag{59}$$

The example discussed here may appear to be somewhat artificial. As will be seen in the second part of this paper, the *conventional* basis sets - apart from some restrictions - are indeed complete in H_A or H_{A^2}, if they are complete in L^2.

For *one*-dimensional spaces simpler systems than (49) can be found: For example, the set

$$\{x^m \exp(-\tfrac{1}{2}x^2)\}_{m=1}^{\infty} \tag{60}$$

is complete in $L^2(\mathbb{R})$ but incomplete in $H_A(\mathbb{R})$ (cf. [8], p. 136). Moreover, all the functions of this set are elements of D_T. Thus, a theorem of Luchka [14] is *disproved*, asserting that a basis set complete in L^2 is also complete in H_A if all functions are elements of the domain of A, i.e. in our case of D_T.

Finally we give an example for the curious case that the Schrödinger equation for an indefinitely increasing number of basis functions is not fulfilled in the sense of Eq. (38), even if the RRM is convergent. We consider the set $\{f_m\}_{m=1}^{\infty}$ of Eq. (50) with $\xi = 1$ as a basis, which is complete in s-H_A but incomplete in s-H_{A^2} (cf. Table 1), such that the RRM for the ground state of the hydrogen atom is certainly E-convergent. However, by Eq. (52) we get

$$\begin{aligned} \| u_0^{(M)} - u_0 \|_{A^2}^2 &= \| (\tfrac{1}{2} + T)(u_0^{(M)} - u_0) \|^2 \\ &= \| (\tfrac{1}{2} + T) u_0^{(M)} \|^2 + \| (\tfrac{1}{2} + T) u_0 \|^2 \\ &\geqslant \| (\tfrac{1}{2} + T) u_0 \|^2 = 2, \end{aligned} \tag{61}$$

i.e. the Ritz functions $u_0^{(M)}$ do *not* converge to u_0 in the A^2-norm. Consequently the Schrödinger equation is not fulfilled with $M \to \infty$ by Lemma 4 in spite of the E-convergence.

Note added in proof (for part I of the papers)
After submitting the manuscript for publication a theorem of A. Bongers (private communication) came to our knowledge, which proves the convergence of the RRM on the premises of Michlin's criterion, i.e. H_A-completeness of the basis, even in the case of degenerate exact eigenvalues.

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