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The Convergence of the Rayleigh-Ritz Method in Quantum Chemistry

II. Investigation of the Convergence for Special Systems of Slater, Gauss and Two-Electron Functions

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The convergence of the Rayleigh-Ritz Method (RRM) or of CI calculations, respectively, for the non-relativistic electronic Hamiltonian of molecules is investigated using the conventional basis sets of Quantum Chemistry, such as systems of *Slater, Gauss* and *two-electron* functions. Conditions for the choice of *orbital exponents* with respect to Slater and Gauss orbitals are especially given, such that the convergence is guaranteed. *Inter alia*, in Theorem 10 a proof of the convergence of the RRM for a *Hylleraas* basis in s,t,u-coordinates is presented, a question which is still being debated today.

Key words: Convergence of the RRM/CI calculation - Complete basis sets - Orbital exponents - Two-electron functions

1. Introduction

When solving the electronic molecular Schrödinger equation by means of the *Rayleigh-Ritz Method* (RRM) or a *CI calculation*, the suitable choice of a *basis set* is of the greatest importance. This should be done such that the Ritz eigenvalues converge to the exact ones with an increasing number of basis functions involved ("E-convergence").

To guarantee this, using the conventional basis orbitals of Quantum Chemistry, such as *Slater* and *Gauss* functions, the choice of the basis consists essentially in fixing a suitable sequence of non-linear parameters, the *orbital exponents*. For Slater functions, these are usually chosen according to "Slater's rules" [1] and for Gauss functions according to Huzinaga's "*optimized*" orbital exponents [2]. Such a procedure has turned out to be reasonable; but since no calculation with an indefinitely increasing number of basis functions can be performed, the question of ultimate E-convergence can only be decided by a systematic mathematical investigation. From this, *recipes* for the choice of orbital exponents of *one-* and *more-*centre basis orbitals will result.

Moreover, we investigate Slater and Gauss orbitals with *single* orbital exponents.

Aside from one-electron functions "essential" *two-electron* basis functions have been used for the RRM, i.e. such functions which can *not* be written as a product of two orbitals, but which include the interelectronic distance as a coordinate. Functions of this kind have been employed by Hylleraas [3], Kinoshita [4], Pekeris [5] and others for the computation of the helium ground state. But it is an open question still today, above all with respect to the Hylleraas basis in s,t,u-coordinates, whether in this case the RRM does converge (cf. [6–8]). In this paper we will definitely show this to be the case.

As has been shown in the first part of this paper ([9], cited as I in the following), E-convergence is assured by a proof of *completeness* of the basis set in one of the spaces[1] H_A or H_{A^2}; then convergence obtains for *arbitrary* molecules in *any* state; moreover, the convergence of the *wave functions* in the norms of L^2 and H_A is also ensured[2]. Thus, first of all, we have to deal with the completeness of special sets of functions.

Some of the proofs of completeness and convergence have been omitted to save space. They are contained in the thesis of the first author [13], some copies of which are available upon request.

2. One-Dimensional Complete Basis Sets

Since orbitals are frequently a product of radial functions and spherical harmonics [cf. Eq. (9)] it is useful to first investigate one-dimensional basis sets, which are complete in L^2. As measure spaces of L^2 we consider the whole real axis $\mathbb{R}$, the positive real axis $\mathbb{R}^+$ and the intervals [0,1] and [−1,1].

A fundamental theorem for the proof of completeness is the *Theorem of Müntz*, a generalization of Weierstrass' Approximation Theorem (cf. [10], p. 65). Formulated for the space $L^2(0,1)$ it states (cf. [11], p. 52):

Lemma 1 (Theorem of Müntz)

Let $\{\alpha(n)\}_{n=1}^{\infty}$ be a sequence of real numbers with $\alpha(n) > -\frac{1}{2}$. Then the system $\{x^{\alpha(n)}\}_{n=1}^{\infty}$ is complete in $L^2(0, 1)$, iff (if and only if)

$$\sum_{n=1}^{\infty} [\alpha(n) + \tfrac{1}{2}] / [\alpha^2(n) + 1] = \infty \text{ holds.} \quad \blacklozenge$$

From this lemma the completeness of the systems

$$\{\exp[-\xi(n)x]\}_{n=1}^{\infty} \qquad \text{and} \qquad \{x^{1/2}\exp[-\xi(n)x^2]\}_{n=1}^{\alpha} \tag{1}$$

can easily be obtained by a coordinate transformation (cf. [12], [13] pp. 63 and 64), as shown by

Lemma 2

Let $\{\xi(n)\}_{n=1}^{\infty}$ be a sequence of positive numbers. Then the systems (1) are complete in $L^2(\mathbb{R}^+)$, iff

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[1] For the definition of H_A and H_{A^2} see I.

[2] For details and some restrictions see I.

$$\sum_{n=1}^{\infty} \frac{\xi(n)}{1+\xi^2(n)} = \infty \tag{2}$$

holds. ♦

This lemma can be illustrated by some characteristic examples: The sets (1) are complete in $L^2(\mathbb{R}^+)$,

1) iff in the case of monotonically *increasing* exponents $\xi(n)$ the condition $\sum_{n=1}^{\infty} \xi^{-1}(n) = \infty$ holds,
2) iff in the case of monotonically *decreasing* exponents $\xi(n)$ the condition $\sum_{n=1}^{\infty} \xi(n) = \infty$ holds, or
3) if $\{\xi(n)\}_{n=1}^{\infty}$ has an accumulation point ξ with $0 < \xi < \infty$.

Thus, the sets (1) are complete in $L^2(\mathbb{R}^+)$, if, for example,

$$\xi(n) = n, n^{1/2}, n^{-1}, n^{-1/2} \quad \text{or} \quad 1 + n^{-1}, \tag{3}$$

they are incomplete, if, for example,

$$\xi(n) = n^2, n^3, n^{-2} \quad \text{or} \quad n^{-3}. \tag{4}$$

A special property of the sets (1) is the fact that they are either incomplete or "*over*-complete", but never "*exactly*" complete[3]. As can be seen from the condition of completeness [Eq. (2)], an infinite number of such functions can always be deleted from a complete set (1) without changing the property of completeness.

A consequence of Lemma 2 is the following sufficient criterion of completeness, which is an important foundation for proving the convergence of CI calculations in a basis built up from Slater and Gauss orbitals (Proof: [13], p. 66):

Lemma 3

Let $\{\xi(n)\}_{n=1}^{\infty}$ be a sequence of positive numbers having

1) an accumulation point ξ with $0 < \xi < \infty$, or
2) a monotonically increasing subsequence $\xi(n_i) \to \infty$ with $\sum_{n_i} \xi^{-1}(n_i) = \infty$.

Then the sets

$$\{x^k \exp[-\xi(n)x]\}_{n=1}^{\infty} \qquad \text{and} \qquad \{x^{k+1} \exp[-\xi(n)x^2]\}_{n=1}^{\infty} \tag{5}$$

are complete in $L^2(\mathbb{R}^+)$ for any fixed $k = 0, 1, 2, \ldots$ ♦

By this lemma the question of completeness cannot be decided for arbitrary sequences $\xi(n)$ such as $\{\xi(n) = n^2\}_{n=1}^{\infty}$. But because of Lemma 2, the sets (5) are probably *in*complete for such a sequence of orbital exponents [cf. Eq. (4)].

We now consider systems of functions with a *single* orbital exponent:

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[3] For "overcompleteness" and "exact" completeness see [14].

Lemma 4

Let ξ, k and l be fixed constants with $\xi > 0, k = 1, 2, 3, \ldots$ and $l = 0, 1, 2, \ldots$ Then the system

$$\{x^{n+l}\exp[-\xi|x|^k]\}_{n=0}^{\infty} \tag{6}$$

is complete in $L^2(\mathbb{R})$. ♦

The proof of this lemma in the special case $k = 2$ and $l = 0$ can be seen from the textbook of Achieser and Glasmann [15], p. 33. All other cases are rather trivial generalizations of this special case (cf. [13], pp. 68 and 69).

As a consequence of Lemma 4 we have the useful

Corollary

The system $\{x^{2n+l}\exp(-\xi x^k)\}_{n=0}^{\infty}$ is complete in $L^2(\mathbb{R}^+)$ for any fixed $\xi > 0, l = 0, 1, 2, \ldots$ and $k = 1, 2, 3, \ldots$

This assertion can be understood from the following fact: A system $\{\varphi_n, \psi_n\}_{n=0}^{\infty}$ of even functions φ_n and odd functions ψ_n is complete in the Hilbert space $L^2(-a, a)$ with $a \in \mathbb{R}^+$, iff both $\{\varphi_n\}_{n=0}^{\infty}$ and $\{\psi_n\}_{n=0}^{\infty}$ are complete in $L^2(0, a)$ (Proof: [13], p. 71). Now the corollary follows from Lemma 4, if one identifies $\{\varphi_n\}_{n=0}^{\infty}$ with the set of the corollary and $\{\psi_n\}_{n=0}^{\infty}$ with the set $\{x^{2n+1+l}\exp(-\xi x^k)\}_{n=0}^{\infty}$ for even l and vice versa for odd l. ♦

If one is interested in linear combinations of complete sets, the following lemma is useful, it is valid for arbitrary Hilbert spaces H (Proof: [13], p. 73):

Lemma 5

Let $\{\varphi_n\}_{n=1}^{\infty}$ be a complete system in a Hilbert space H. Moreover, let $a_{n\mu}$ $(1 \leqslant \mu \leqslant n)$ be arbitrary complex numbers with $a_{nn} \neq 0$. Then the system

$$\{\psi_n = \sum_{\mu=1}^{n} a_{n\mu}\varphi_\mu\}_{n=1}^{\infty} \tag{7}$$

is also complete in H. ♦

The orthogonalization of complete basis sets is one of the numerous problems to which Lemma 5 can be applied: if, for instance, $\{\varphi_n\}_{n=1}^{\infty}$ is complete in H, then the appropriate orthonormalized system, obtained from the Schmidt procedure, is also complete in H.

A special application is to the set of Legendre polynomials

$$\{P_n(\cos\vartheta)\}_{n=0}^{\infty} \tag{8}$$

in the Hilbert space $L^2_{\sin\vartheta}(0, \pi)$, i.e. the space of all quadratically integrable functions in the interval $[0, \pi]$ with the weight function $\sin\vartheta$. Since both systems $\{x^{2n}\}_{n=0}^{\infty}$ and $\{x^{2n+1}\}_{n=0}^{\infty}$ are complete in $L^2(0, 1)$ because of Lemma 1, $\{x^n\}_{n=0}^{\infty}$ is complete in $L^2(-1, 1)$. Thus $\{P_n(x)\}_{n=0}^{\infty}$ is complete in $L^2(-1, 1)$ by Lemma 5; finally, by a coordinate transformation ($x = \cos\vartheta$) the completeness of (8) in $L^2_{\sin\vartheta}(0, \pi)$ follows.

3. More-Dimensional Complete Basis Sets

Basis orbitals for the space $L^2(\mathbb{R}^3)$ are frequently of the form

$$\varphi_{nlm}(r) = R_{nl}(r)Y_{lm}(\vartheta, \varphi), \tag{9}$$

where (r, ϑ, φ) are spherical coordinates, Y_{lm} the spherical harmonics (cf. e.g. [16], p. 84) and R_{nl} any set of radial functions, which remains to be defined.

We now ask: Under which conditions on the *radial* functions is the system $\{\varphi_{nlm}\}$ complete in $L^2(\mathbb{R}^3)$? And, above all: Under which conditions does a CI calculation, as described in I, Sect. 8, *converge* in this basis?

With respect to the question of completeness the following lemma is valid:

Lemma 6

Let $\{R_{nl}(r)\}_{n\in I(l)}$ be a system of radial functions, where $I(l)$ denotes a set of indices for each fixed $l = 0, 1, 2, \ldots$ Then the orbital basis

$$\{\varphi_{nlm}(r) = R_{nl}(r)Y_{lm}(\vartheta, \varphi)\}_{n\in I(l)} \quad \text{for all } l \geqslant 0,\ |m| \leqslant l \tag{10}$$

is complete in $L^2(\mathbb{R}^3)$, iff $\{rR_{nl}(r)\}_{n\in I(l)}$ is complete in $L^2(\mathbb{R}^+)$ for *each* l.

Proof

Let $\{rR_{nl}(r)\}_{n\in I(l)}$ be complete in $L^2(\mathbb{R}^+)$ for each l. Then by Lemma 2 of Part I $\{R_{nl}(r)\}_{n\in I(l)}$ is complete in $L^2_{r^2}$, i.e. the space of all quadratically integrable functions in $\mathbb{R}^+$ with the weight function r^2. Thus the completeness of (10) follows from the completeness of the spherical harmonics by a theorem of Rellich ([17], p. 8).

If, on the other hand, $\{rR_{nl}(r)\}_{n\in I(l)}$ is incomplete for a single $l = k$, there exists a $g\in L^2(\mathbb{R}^+)$ orthogonal to this set in the scalar product of $L^2(\mathbb{R}^+)$. Therefore,

$$f(r) = r^{-1}g(r)Y_{k0}(\vartheta, \varphi) \tag{11}$$

is orthogonal to (10) in the scalar product of $L^2(\mathbb{R}^3)$, i.e. (10) is incomplete in $L^2(\mathbb{R}^3)$. ♦

This lemma can easily be generalized to the case of two-particle functions:

Lemma 7

The set

$$\{S_{nl\nu\lambda}(r_1, r_2)\, Y_{lm}(\vartheta_1, \varphi_1)\, Y_{\lambda\mu}(\vartheta_2, \varphi_2)\} \qquad n\in I(l),\ \nu\in I'(\lambda);$$
$$\text{for all } l, \lambda \geqslant 0,\ |m| \leqslant l,\ |\mu| \leqslant \lambda \tag{12}$$

is complete in $L^2(\mathbb{R}^6)$, iff the sets

$$\{r_1 r_2 S_{nl\nu\lambda}(r_1, r_2)\}_{n\in I(l),\, \nu\in I'(l)} \tag{13}$$

are complete in $L^2(\mathbb{R}^+ \times \mathbb{R}^+)$ for each l and λ. ♦

After these completeness investigations we now turn to the problem of *convergence* of CI calculations for the basis (10); here we will make use of the important

Lemma 8

Let the sets of radial functions $\{R_{nl}(r)\}_{n\in I(l)}$ be defined for each $l = 0, 1, 2, \ldots$ such that

$$\left\{A_l(c, r)R_{nl}(r) = r\left[c - \frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{l(l+1)}{2r^2}\right]R_{nl}(r)\right\}_{n\in I(l)} \tag{14}$$

is complete in $L^2(\mathbb{R}^+)$ for any $c > 0$ and each $l = 0, 1, 2, \ldots$ Then the set (10) is complete in $H_{A^2}(\mathbb{R}^3)$ and a CI calculation converges in this basis by Kato's criterion of convergence (cf. I, Theorem 8).

Proof

By Theorem 8 of Part I the completeness of the system $\{(c + \hat{t})R_{nl}Y_{lm}\}$ in $L^2(\mathbb{R}^3)$ has to be shown for $c > 0$, where $\hat{t}$ is the one-particle kinetic energy operator. Since the spherical harmonics are eigenfunctions of the angular momentum operator, we obtain, after a short calculation,

$$(c + \hat{t})R_{nl}Y_{lm} = r^{-1}A_l(c, r)R_{nl}(r)Y_{lm}(\vartheta, \varphi). \tag{15}$$

Thus, the assertion follows from the assumed completeness of (14) by Lemma 6. ♦

Analogously to Lemma 6, a theorem of completeness can be proved which is of great importance with respect to the two-particle basis sets used by Hylleraas. Its proof (cf. [13], p. 74) mainly makes use of the completeness of the Legendre polynomials [Eq. (8)].

Lemma 9

Let L^2_{Hyll} be the Hilbert space

$$\left\{f(r_1, r_2, \vartheta)\,\middle|\, \int_0^\infty\int_0^\infty dr_1 r_1^2\, dr_2 r_2^2 \int_0^\pi d\vartheta\, \sin\vartheta\, |f(r_1, r_2, \vartheta)|^2 < \infty\right\}. \tag{16}$$

With $P_l(x)$ the Legendre polynomials and $I(l)$ sets of indices,

$$\{S_{nl}(r_1, r_2)\, P_l(\cos\vartheta)\}_{n\in I(l)} \qquad \text{for all } l \geqslant 0 \tag{17}$$

is complete in L^2_{Hyll}, iff $\{r_1 r_2 S_{nl}(r_1, r_2)\}_{n\in I(l)}$ is complete in $L^2(\mathbb{R}^+ \times \mathbb{R}^+)$ for each $l = 0, 1, 2, \ldots$ ♦

4. One-Centre Slater-Type Basis Orbitals

The radial functions of one-centre Slater-type orbitals are of the form

$$R_{nl}(r) = r^{\alpha(n)+l}\exp[-\xi(n, l)r] \tag{18}$$

with suitably chosen orbital exponents $\xi(n, l)$ and "generalized" total quantum numbers $\alpha(n)$, mostly fixed to be $\alpha(n) = n$ $(n \geqslant 0)$.

Investigating the convergence of CI calculations it is reasonable to treat two cases separately:

1) We choose a *sequence* of orbital exponents and $\alpha(n) = 0$, or
2) we choose $\alpha(n) = n$ and a *single* orbital exponent for each l $\quad \xi(n, l) = \xi(l)$.

The convergence can be shown for both cases separately. Of course, in order to yield a greater *speed* of convergence one can combine both cases.

The completeness of the basis set

$$\{r^l \exp[-\xi(n, l)r]\, Y_{lm}(\vartheta, \varphi)\} \quad \text{for all } n \geqslant 1, l \geqslant 0, |m| \leqslant l \tag{19}$$

in $L^2(\mathbb{R}^3)$ is immediately seen from Lemmas 3 and 6, if the orbital exponents fulfil the following conditions: Let the positive sequences $\{\xi(n, l)\}_{n=1}^{\infty}$ for each $l = 0, 1, 2, \ldots$ have

1) an accumulation point $\xi(l)$ with $0 < \xi(l) < \infty$, or
2) a monotonically indefinitely *increasing* subsequence $\{\xi(n_i, l)\}_{n_i}$ with $\sum\limits_{n_i} \xi^{-1}(n_i, l) = \infty$.

The *convergence* will be proved under more restrictive conditions for the orbital exponents. Essentially, the proof rests on the identity theorem of analytic functions (cf. [24], p. 87); therefore, only such sequences $\{\xi(n, l)\}_{n=1}^{\infty}$ can be considered, which have at least one finite accumulation point for each l [4].

Theorem 1

Let the sequences of positive numbers $\{\xi(n, l)\}_{n=1}^{\infty}$ have an accumulation point $\xi(l)$ with $0 < \xi(l) < \infty$ for each $l = 0, 1, 2, \ldots$ Then the orbital basis (19) is complete in $H_{A^2}(\mathbb{R}^3)$ and CI calculations in this basis are convergent.

Proof

By Lemma 8 we have to show the completeness of

$$\{A_l(c, r)r^l \exp[-\xi(n, l)r] = [(c - \tfrac{1}{2}\xi^2(n, l))r + (l + 1)\xi(n, l)]\, r^l \exp[-\xi(n, l)r]\}_{n=1}^{\infty} \tag{20}$$

in $L^2(\mathbb{R}^+)$ for each l. Therefore, we choose functions $f_l \in L^2(\mathbb{R}^+)$, which are orthogonal to the set (20) relative to the scalar product of $L^2(\mathbb{R}^+)$ and show that [5] $f_l = \Theta$:

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[4] Otherwise, Weierstrass' factor theorem had to be applied; but in this case the proof of convergence fails.

[5] Θ denotes the zero element of the space L^2.

For this purpose we define the functions[6]

$$g_l(z) = (f_l, [(c - \tfrac{1}{2}z^2)r + (l + 1)z] r^l \exp[-zr])_{\mathbb{R}^+} \tag{21}$$

which are analytic in the positive complex half-plane $\mathrm{Re}(z) > 0$. Because of the definition of f_l we have for each l

$$g_l(\xi(n, l)) = 0, \qquad (n \geqslant 1). \tag{22}$$

As the sequences $\{\xi(n, l)\}$ have an accumulation point in the region of analyticity $\mathrm{Re}(z) > 0$, the $g_l(z)$ vanish identically in $\mathrm{Re}(z) > 0$ by the identity theorem of analytic functions. Thus, their first and second derivatives also vanish identically and we obtain, after a short calculation,

$$-(f_l, r^{l+1} \exp(-zr))_{\mathbb{R}^+} = g_l''(z) + 2zg_l'(z) + (1 + z^2)g_l(z) \equiv 0, \qquad (\mathrm{Re}(z) > 0) \tag{23}$$

Putting $z = \xi(n, l)$ into (23), $f_l = \Theta$ follows from Lemma 3. ♦

The assumptions of this theorem are fulfilled, for instance, if all the $\xi(n, l)$ are numbers in a fixed "*interval of convergence*"

$$0 < \xi_{\min} \leqslant \xi(n, l) \leqslant \xi_{\max} < \infty, \tag{24}$$

since the sequences $\{\xi(n, l)\}_{n=1}^{\infty}$ then have an accumulation point in the interval $[\xi_{\min}, \xi_{\max}]$ by the theorem of Bolzano-Weierstrass.

The conditions of Theorem 1 for the orbital exponents are, however, only sufficient. Thus, a CI calculation might be convergent in the basis (19) even for sequences like $\xi(n, l) = n$ or n^{-1}.

A less usual orbital type is the "anisotropic" Slater function of Eq. (25). The conditions of convergence for such a basis are quite similar to those for the basis (19):

Theorem 2 (Proof: see [13], p. 90)

Let the orbital exponents $\{\xi_i(n)\}_{n=1}^{\infty}$, with $i = x, y, z$, each have a finite accumulation point. Then the system

$$\{(1, x, y, z, xy, xz, yz, xyz) \cdot \exp[-\xi_x(n)\,|x| - \xi_y(m)\,|y| - \xi_z(l)\,|z|]\}_{n,m,l=1}^{\infty} \tag{25}$$

is complete in $H_A(\mathbb{R}^3)$ and CI calculations converge by Michlin's criterion of convergence (cf. I, Theorem 7). ♦

We now consider Slater functions with a single orbital exponent $\xi > 0$:

$$\{r^{n+l} \exp(-\xi r) Y_{lm}\}_{n=n'}^{\infty} \qquad \text{for all } l \geqslant 0, |m| \leqslant l. \tag{26}$$

Because of Lemmas 4 and 6, the basis (26) is complete in $L^2(\mathbb{R}^3)$ for any fixed $n' = 0, 1, 2, \ldots$ The *convergence* is guaranteed by the

[6] The index $\mathbb{R}^+$ of the scalar product says that it is a scalar product of the space $L^2(\mathbb{R}^+)$.

Theorem 3

The Slater basis (26) is complete in $H_{A^2}(\mathbb{R}^3)$ for $n' = 0$ and CI calculations are convergent in this basis.

Proof:

By Lemma 8 the completeness of $\{A_l(c, r)R_{nl}(r)\}_{n=0}^{\infty}$, i.e. of

$$\left\{r^{n+l+1}\exp(-\xi r)\left[c - \frac{1}{2}\xi^2 + \frac{(n+l+1)\xi}{r} - \frac{n(n+2l+1)}{2r^2}\right]\right\}_{n=0}^{\infty} \tag{27}$$

in $L^2(\mathbb{R}^+)$ has to be shown for each $l = 0, 1, 2, \ldots$ Choosing especially $c = \xi^2/2$, this follows at once from Lemmas 4 and 5. ♦

As a consequence of this theorem we can now prove the convergence of CI calculations in the basis

$$\{x^n y^m z^l \exp(-\xi r)\}_{n,m,l=0}^{\infty}, \{rx^n y^m z^l \exp(-\xi r)\}_{n,m,l=0}^{\infty}. \tag{28}$$

The first part of the system (28) is already complete in $L^2(\mathbb{R}^3)$ (cf. [13], p. 94), for convergence both parts have to be taken into account:

Theorem 4

The system (28) with $\xi > 0$ is complete in $H_{A^2}(\mathbb{R}^3)$ and CI calculations in this basis are convergent.

Proof

Because of Part I, Theorem 8, we choose an $f \in L^2(\mathbb{R}^3)$, such that

$$\begin{aligned}&(f, (c+\hat{t})x^n y^m z^l \exp(-\xi r)) = 0\\ &(f, (c+\hat{t})rx^n y^m z^l \exp(-\xi r)) = 0\end{aligned} \tag{29}$$

is valid for all $n, m, l \geqslant 0$ and show that[5] $f = \Theta$. Now, any function of the form $r^{\nu+\lambda}\exp(-\xi r)Y_{\lambda\mu}$ can be written as a finite linear combination of functions of the system (28). Thus, from (29) it follows that

$$(f, (c+\hat{t})r^{n+1}\exp(-\xi r)Y_{lm}) = 0 \qquad \text{for all } n \geqslant 0,\ l \geqslant 0,\ |m| \leqslant l \tag{30}$$

and therefore $f = \Theta$ by Theorem 3. ♦

5. One-Centre Gaussian Basis Orbitals

The many uses of Gauss-type basis orbitals are mainly due to the fact that all molecular integrals, including the 3- and 4-centre forms, can be evaluated analytically. On the other hand, Gaussians have the wrong behaviour for small and large r: For $r \to 0$ they have no *cusp* like an exact wave function (cf. [18]) and for $r \to \infty$ they decrease too quickly. These "unphysical" properties cause a slower convergence of CI calculations as compared with the convergence behaviour using a Slater-type basis.

Firstly, we investigate Gaussians with variable orbital exponents:

$$\{r^l \exp[-\xi(n, l)r^2]\, Y_{lm}(\vartheta, \varphi)\} \qquad \text{for all } n \geqslant 1, l \geqslant 0, |m| \leqslant l. \tag{31}$$

The *completeness* of this system in $L^2(\mathbb{R}^3)$ is ensured by Lemmas 3 and 6 if the orbital exponents fulfil the following conditions for each fixed l: Let $\{\xi(n, l)\}_{n=1}^{\infty}$ have

1) an accumulation point $\xi(l)$ with $0 < \xi(l) < \infty$, or
2) an indefinitely *increasing* subsequence $\xi(n_i, l)$ with $\Sigma_{n_i} \xi^{-1}(n_i, l) = \infty$, or
3) a subsequence $\xi(n_i, l)$ *decreasing* monotonically to zero with $\Sigma_{n_i} \xi(n_i, l) = \infty$.

The case 3), which is not a direct consequence of Lemma 3, can be reduced to case 2) by a Fourier transformation (cf. [13], p. 97).

Now the important theorem concerning the *convergence* with Gaussians is:

Theorem 5 (Proof: see [13], p. 98)

Let the sequences $\{\xi(n, l)\}_{n=1}^{\infty}$ of positive orbital exponents for each l have

1) an accumulation point $\xi(l)$ with $0 < \xi(l) < \infty$, or
2) a subsequence $\xi(n_i, l)$ decreasing monotonically to zero with $\Sigma_{n_i} \xi(n_i, l) = \infty$.

Then the set of Gaussian orbitals (31) is complete in $H_{A^2}(\mathbb{R}^3)$ and CI calculations in this basis are convergent. ♦

Theorem 5 guarantees the convergence of a CI calculation for arbitrary molecules and states in the Gaussian basis (31), provided that the orbital exponents fulfil the conditions of Theorem 5. This is the case, if, for instance,

1) all orbital exponents belong to a fixed interval of convergence [cf. Eq. (24)], or
2) $\xi(n, l) = n^{-1}$ or $n^{-1/2}$.

Of course, it is always possible to add to such a sequence of orbital exponents additional values. These do not destroy the convergence but may be used to increase its speed.

As an example of such a case we consider the "optimized" orbital exponents given by Huzinaga [2] for different atoms. As far as can be seen from such *finite* sets, they can be divided into two sub-sequences, one of which has an accumulation point at zero or near zero, which is responsible for the convergence, while the other increases indefinitely and describes the cusp.

We now turn to Gaussians with single orbital exponents:

$$\{r^{2n+l} \exp[-\tfrac{1}{2}\xi(l)r^2]\, Y_{lm}(\vartheta, \varphi)\} \qquad \text{for all } n \geqslant n', l \geqslant 0, |m| \leqslant l. \tag{32}$$

The *completeness* of (32) in $L^2(\mathbb{R}^3)$ for fixed $n' = 0, 1, 2, \ldots$ and positive $\xi(l)$ follows from Lemma 6 and the corollary of Lemma 4. The *convergence* is guaranteed by the

Theorem 6 (Proof: see [13], p. 101)

The basis of Gaussian orbitals (32) with $n' = 0$ and $\xi(l) > 0$ is complete in $H_{A^2}(\mathbb{R}^3)$ and CI calculations in this basis are convergent. ♦

Through Theorems 5 and 6 the convergence of CI calculations is ensured even if one takes a combination of the two sets (31) and (32) as a basis.

Finally, we consider a system quite analogous to Eq. (28):

$$\{x^n y^m z^l \exp(-\tfrac{1}{2}\xi r^2)\}_{n,m,l=0}^{\infty}. \quad (33)$$

Theorem 7

The orbital basis (33) is complete in $H_{A^2}(\mathbb{R}^3)$ and CI calculations in this basis are convergent.

Proof

The completeness of $\{H_n(x)\exp(-\xi x^2/2)\}_{n=0}^{\infty}$ in $H_{A^2}(\mathbb{R})$ has been proved by Kato [19], $H_n(x)$ being the Hermite polynomials (cf. [10], p. 91). Thus, the completeness of $\{x^n \exp(-\xi x^2/2)\}_{n=0}^{\infty}$ in $H_{A^2}(\mathbb{R})$ follows from Lemma 5, and the assertion of the theorem follows from a lemma mentioned[7] in I. ♦

It should be emphasized that all convergence conditions, especially those concerning the choice of orbital exponents, should only be considered as mathematical guidelines. They should be fulfilled, but even then there is still considerable freedom in their choice leaving room for physical arguments like Slater's rules or optimization procedures.

6. Many-Centre Basis Orbitals

The criteria of convergence of Michlin and Kato (cf. Part I, Theorems 7 and 8) are valid for both atoms and molecules; the number of centres does not play a role in their formulation. Therefore CI calculations converge already in a *one*-centre orbital basis for *arbitrary* molecules if one of the criteria proved above is fulfilled. Once the convergence is assured, adding further orbitals at *other* centres changes nothing. However, in this way, the *speed* of convergence can be considerably enhanced.

Moreover, there are no special conditions of convergence which are characteristic of many-centre orbitals. Let us, for instance, consider a two-centre orbital basis of Slater functions or Gaussians according to Eqs. (19) and (31), $\{\xi_A(n, l)\}_{n=1}^{\infty}$ and $\{\xi_B(n, l)\}_{n=1}^{\infty}$ being their orbital exponents at the two centres A and B each having an accumulation point. Thus the CI calculation is convergent using the *sub*sets at centre A or B alone. Deleting orbital exponents from the sequences $\{\xi_A(n, l)\}_{n=1}^{\infty}$ and $\{\xi_B(n, l)\}_{n=1}^{\infty}$, E-convergence is preserved for *both* subsets as long as both still have an accumulation point. The convergence is also preserved if only *one* sub-sequence,

[7] It is a lemma analogous to Lemma 6 of Part I, where H_A has to be replaced by H_{A^2}.

$\{\xi_A(n, l)\}_{n=1}^{\infty}$ or $\{\xi_B(n, l)\}_{n=1}^{\infty}$, has an accumulation point, but E-convergence is destroyed if *none* of the sub-sequences has an accumulation point. The case that the CI calculation is E-convergent neither in the basis functions of centre A nor of B but *is* E-convergent in the total basis, does not occur.

7. Two-Electron Basis Functions

Using "essential" two-electron functions, high accuracy can be achieved by the RRM already with only a few basis functions. These functions include the interelectronic distance r_{12} as a coordinate; therefore correlation effects are taken into account even by a single function.

Examples of such functions are those which have been used by Hylleraas [3], Kinoshita [4] and Pekeris [5] for the computation of the helium ground state.

However, the question of convergence for these calculations has remained unsolved, if not debatable, even today. Expanding the exact ground-state eigenfunction u in a basis of Hylleraas functions Φ_k [cf. Eq. (48)],

$$u = \sum_k c_k \Phi_k, \tag{34}$$

and putting (34) into the Schrödinger equation, one obtains a recursion formula for the c_k [6] which does not allow them to be determined without contradiction. It was therefore believed that the RRM in the Hylleraas basis $\{\Theta_k\}_{k=1}^{\infty}$ could not be E-convergent. Attempts [7, 8] to prove this convergence have not been successful until now. In the following, this long-standing question will be *positively* resolved.

7.1 Hydrogen-Like Orbitals

To prove the convergence for two-electron basis sets, as a first step we consider once more an orbital basis: the hydrogen-like functions (35).

As is well known, the discrete *eigen*functions of the hydrogen atom do *not* form a complete set in $L^2(\mathbb{R}^3)$ because of the continuous spectrum. They are therefore unsuitable as a basis for the RRM. That is why Hylleraas proposed to use modified hydrogen-like basis functions:

$$\begin{aligned}\{\varphi_{nlm}(r) &= R_{nl}(r) Y_{lm}(\vartheta, \varphi)\\ &= r^l L_{n+l}^{(2l+1)}(\xi r) \exp(-\tfrac{1}{2}\xi r) Y_{lm}(\vartheta, \varphi)\} \qquad \text{for all } n > l \geqslant 0, |m| \leqslant l.\end{aligned} \tag{35}$$

The exact hydrogen eigenfunctions differ from the φ_{nlm} by an orbital exponent $\xi(n) = 2/n$ varying with n. Moreover, the φ_{nlm} are orthogonal with the weight factor r^{-1}.

We next prove

Theorem 8

The set of hydrogen-like functions (35) with $\xi > 0$ is complete in $H_{A^2}(\mathbb{R}^3)$ and CI calculations converge in this basis.

Proof

The radial functions $R_{nl}(r)$, as defined in Eq. (35), fulfil the differential equation (cf. [3], p. 17)

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}-\frac{1}{4}\xi^2+\xi\frac{n}{r}\right]R_{nl}(r)=0. \tag{36}$$

Because of Lemma 8 we have to show the completeness of $\{A_l(c,r)R_{nl}(r)\}_{n=l+1}^{\infty}$ in $L^2(\mathbb{R}^+)$ for each $l=0,1,2,\ldots$, i.e. using Eq. (36) the completeness of

$$\left\{A_l(c,r)R_{nl}(r)=r\left[c-\frac{1}{8}\xi^2+\frac{1}{2}\xi\frac{n}{r}\right]R_{nl}(r)\right\}_{n=l+1}^{\infty}. \tag{37}$$

Choosing especially $c=\xi^2/8$, this can be seen immediately by Lemmas 4 and 5. ♦

From this theorem a useful consequence can be drawn:

Lemma 10

Let the radial functions $R_{nl}(r)$ be defined as in Eq. (35) and $\xi>0$. Then the system

$$\{(nr_2+\nu r_1)R_{nl}(r_1)R_{\nu l}(r_2)\} \qquad \text{for all } n \text{ and } \nu>l \tag{38}$$

is complete in $L^2(\mathbb{R}^+\times\mathbb{R}^+)$ for each fixed $l=0,1,2,\ldots$ ♦

The proof of Lemma 10 makes use of Theorem 8 and Lemma 7 of this paper and Lemma 3 of Part I (cf. [13], p. 108).

7.2 Hylleraas-Basis in r_1, r_2, ϑ-Coordinates

The Helium atom can be described by the following choice of coordinates:

1) the distances r_1, r_2 of both electrons from the nucleus and the angle ϑ subtended by the vectors r_1 and r_2;
2) the three Eulerian angles describing the position of the triangle subtended by (r_1, r_2, ϑ).

If one is interested only in *S-states,* which are independent of the orientation of this triangle, the six-dimensional problem can be reduced to a three-dimensional one: all basis functions in question need only depend on the coordinates r_1, r_2 and ϑ. The norm of such a special function $f\in L^2(\mathbb{R}^6)$ can be written as (cf. [3], p. 19; [21], p. 1737):

$$\|f\|^2=8\pi^2\int_0^\infty dr_1 r_1^2\int_0^\infty dr_2 r_2^2\int_0^\pi d\vartheta\,\sin\vartheta\,|f(r_1,r_2,\vartheta)|^2=\|f\|^2_{\text{Hyll}}. \tag{39}$$

Through this norm a new Hilbert space is induced, namely the space L^2_{Hyll}, defined by Eq. (16), which consists of all S-functions of $L^2(\mathbb{R}^6)$.

In these coordinates the kinetic energy operator takes the form

$$\hat{T}f=-\tfrac{1}{2}(\Delta_1'+\Delta_2')f \qquad \text{for } f\in L^2_{\text{Hyll}} \tag{40}$$

where Δ_i' $(i = 1, 2)$ is the modified Laplacian

$$\Delta_i' = \frac{1}{r_i^2}\frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} + \frac{1}{r_i^2 \sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\frac{\partial}{\partial\vartheta}. \tag{41}$$

Now, Hylleraas used the following set of two-electron S-functions:

$$\{R_{nl}(r_1)R_{\nu l}(r_2)P_l(\cos\vartheta)\} \qquad \text{for all } n, \nu > l \geqslant 0 \tag{42}$$

where the $R_{nl}(r)$ are defined as in Eq. (35) and the P_l are the Legendre polynomials. The *convergence* of the RRM is ensured by

Theorem 9

The Hylleraas basis (42) is complete in the subspace of all S-functions of $H_{A^2}(\mathbb{R}^6)$ and the RRM converges in this basis for any S-state.

Proof

It has to be shown that

$$\{(c + \hat{T})R_{nl}(r_1)R_{\nu l}(r_2)P_l(\cos\vartheta)\} \qquad \text{for all } n, \nu > l \geqslant 0 \tag{43}$$

is complete in L^2_{Hyll}. For convenience we choose $c = \xi^2/4$; using the differential equation of the Legendre polynomials

$$\frac{1}{\sin\vartheta}\frac{d}{d\vartheta}\sin\vartheta\frac{d}{d\vartheta}P_l(\cos\vartheta) = -l(l+1)P_l(\cos\vartheta) \tag{44}$$

and the Eqs. (36), (40) and (41) we obtain after a short calculation

$$(\tfrac{1}{4}\xi^2 + \hat{T})R_{nl}(r_1)R_{\nu l}(r_2)P_l(\cos\vartheta) = \tfrac{1}{2}\xi\left(\frac{n}{r_1} + \frac{\nu}{r_2}\right)R_{nl}(r_1)R_{\nu l}(r_2)P_l(\cos\vartheta). \tag{45}$$

Thus by Lemma 9 the completeness of

$$\left\{r_1 r_2\left(\frac{n}{r_1} + \frac{\nu}{r_2}\right)R_{nl}(r_1)R_{\nu l}(r_2)\right\} \qquad \text{for all } n, \nu > l \tag{46}$$

in $L^2(\mathbb{R}^+ \times \mathbb{R}^+)$ remains to be shown for each $l = 0, 1, 2, \ldots$ This, however, has already been done through Lemma 10 of this paper. ♦

With this theorem any doubts about the convergence of the RRM for S-states in the basis (42) (cf. [3], p. 18) have turned out to be groundless.

7.3. Hylleraas-Basis in s, t, u-Coordinates

Hylleraas [22] obtained much better results for the helium ground state with the coordinates:

$$\begin{aligned} s &= r_1 + r_2 & 0 \leqslant s \leqslant \infty \\ t &= -r_1 + r_2 & 0 \leqslant t \leqslant u \\ u &= r_{12} = (r_1^2 + r_2^2 - 2r_1 r_2 \cos\vartheta)^{1/2} & 0 \leqslant u \leqslant s. \end{aligned} \tag{47}$$

We now show the RRM to be convergent in the Hylleraas basis

$$\{\exp(-\tfrac{1}{2}\xi s)\, s^n t^m u^l\} \qquad \text{for all } n, m, l \geqslant 0. \tag{48}$$

This is already true if only functions with *even* l are used.

Theorem 10

Let ξ be positive. Then $\{\exp(-\frac{1}{2}\xi s)\, s^n t^m u^{2l}\}_{n,m,l=0}^{\infty}$ is complete in the subspace of all S-functions of $H_{A^2}(\mathbb{R}^6)$ and the RRM is convergent in this basis for any S-state.

Proof

Let f be an element of L^2_{Hyll} with the property that[8]

$$(f, (c + \hat{T}) \exp(-\tfrac{1}{2}\xi s) s^n t^m u^{2l})_{\text{Hyll}} = 0 \tag{49}$$

for all $n, m, l \geqslant 0$. By Theorem 3 of Part I $f = \Theta$ has to be shown. For this purpose we go over from s, t, u to r_1, r_2, ϑ-coordinates[9]

$$(f, (c + \hat{T}) \exp[-\tfrac{1}{2}(r_1 + r_2)]\, (r_1 + r_2)^n (-r_1 + r_2)^m (r_1^2 + r_2^2 - 2r_1 r_2 \cos\vartheta)^l)_{\text{Hyll}} = 0. \tag{50}$$

As can be easily seen (cf. [13], p. 182), the functions $r_1^p r_2^q$ can be written for each $p, q = 0, 1, 2, \ldots$ as a finite linear combination of $(r_1 + r_2)^n (-r_1 + r_2)^m$, where $p + q = m + n$. Thus, from (50) we get

$$(f, (c + \hat{T}) \exp[-\tfrac{1}{2}(r_1 + r_2)]\, r_1^p r_2^q (r_1^2 + r_2^2 - 2r_1 r_2 \cos\vartheta)^l)_{\text{Hyll}} = 0. \tag{51}$$

If we write down this equation for $l = 0, 1, 2, \ldots$ and solve it successively, we obtain for each $p, q, k = 0, 1, 2, \ldots$

$$(f, (c + \hat{T}) \exp[-\tfrac{1}{2}(r_1 + r_2)]\, r_1^{p+k}\, r_2^{q+k} \cos^k\vartheta)_{\text{Hyll}} = 0. \tag{52}$$

Since the $R_{nl}(r)$ of Eq. (35) are finite linear combinations of the set

$$\{r^{p+l} \exp(-\tfrac{1}{2}\xi r)\}_{p=0}^{n-1} \tag{53}$$

if follows from Eq. (52) that

$$(f, (c + \hat{T}) R_{nl}(r_1) R_{\nu l}(r_2) P_l(\cos\vartheta))_{\text{Hyll}} = 0 \tag{54}$$

for all $n, \nu > l \geqslant 0$. Consequently, we have $f = \Theta$ by theorem 9. ♦

Although the basis functions (48) with odd l are not necessary for convergence, they are still important. They are responsible for an adequate approximation of the correla-

[8] The index "Hyll" of Eq. (49) indicates that it is a scalar product of the space L^2_{Hyll}.
[9] Strictly, in Eq. (50) $\tilde{f}$ instead of f had to be written, where $\tilde{f}(r_1, r_2, \vartheta) = f(s, t, u)$.

tion cusp[10] and therefore contribute to a high speed of convergence. Schwartz [23] achieved even higher speed using half-integral powers of u in his calculations.

It should be clear that for the computation of ^1S-states only functions with even m and for ^3S-states only those with odd m have to be used.

7.4 Kinoshita Basis

An extension of the Hylleraas basis (48) is Kinoshita's basis

$$\left\{\exp(-\tfrac{1}{2}\xi s)\, s^n \left(\frac{u}{s}\right)^m \left(\frac{t}{u}\right)^l\right\}_{n,m,l=0}^{\infty}. \tag{55}$$

The Hylleraas basis (48) is a subset of (55) restricted to $n \geqslant m \geqslant l \geqslant 0$. Therefore the RRM is convergent in the basis (55) as well as by Theorem 10.

As Kinoshita has shown, the exact wave function u can be expanded in his basis (55) according to Eq. (34), i.e. the expansion coefficients can indeed be determined without any contradiction, different from the case of the Hylleraas basis (48). Thus we conclude that there is no direct correspondence between the questions of expansion of wave functions and E-convergence.

7.5 Pekeris Basis

The basis functions of Pekeris [5] are written in "perimetric" coordinates:

$$\begin{aligned} x &= \tfrac{1}{2}(u-t) = \tfrac{1}{2}(r_{12}+r_1-r_2) \\ y &= \tfrac{1}{2}(u+t) = \tfrac{1}{2}(r_{12}-r_1+r_2) \qquad 0 \leqslant x, y, z \leqslant \infty \\ z &= s-u \quad = r_1+r_2-r_{12} \end{aligned} \tag{56}$$

The basis set is of the form

$$\{L_n(x)L_m(y)L_l(z)\exp[-\tfrac{1}{2}\xi(x+y+z)]\}_{n,m,l=0}^{\infty}, \tag{57}$$

L_n being the Laguerre polynomials of degree n. The convergence is guaranteed by

Theorem 11 (cf. [13], p. 116)

Let ξ be positive. Then the Pekeris basis (57) is complete in the subspace of all S-functions of $H_{A^2}(\mathbb{R}^6)$ and the RRM is convergent in this basis for any S-state. ♦

The proof of this theorem can be reduced to Theorem 10 by taking the fact into account that the Pekeris functions of Eq. (57) can be written as finite linear combinations of the Hylleraas functions of Eq. (48).

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10 For the correlation cusp of molecular wave functions see [18].

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References

1. Slater, J. C.: Phys. Rev. **36,** 57 (1930)
2. Huzinaga, S.: J. Chem. Phys. **42,** 1293 (1965)
3. Hylleraas, E. A.: Advan. Quantum Chem. **1,** 1 (1964)
4. Kinoshita, T.: Phys. Rev. **105,** 1490 (1957); **115,** 336 (1959)
5. Pekeris, C. L.: Phys. Rev. **112,** 1649 (1958); **115,** 1216 (1959)
6. Bartlett, J. H., Gibbons, J. J., Dunn, C. C.: Phys. Rev. **47,** 679 (1935)
7. Coolidge, A. S., James, H. M.: Phys. Rev. **51,** 855 (1937)
8. Kato, T.: Trans. Am. Math. Soc. **70,** 212 (1951)
9. Klahn, B., Bingel, W. A.: Theoret. Chim. Acta (Berl.), Part I, preceding paper
10. Courant, R., Hilbert, D.: Methods of mathematical physics, Vol. I, 1st English edition. New York: Interscience 1953
11. Schönhage, A.: Approximationstheorie. Berlin: de Gruyter 1971
12. Crum, M. M.: J. Lond. Math. Soc. **31,** 433 (1956)
13. Klahn, B.: Thesis, Göttingen 1975
14. Klahn, B., Bingel, W. A.: to be published in Intern. J. Quantum Chem.
15. Achieser, N. I., Glasmann, I. M.: Theorie der linearen Operatoren im Hilbert-Raum, 5th Ed. Berlin: Akademie-Verlag 1968
16. Eyring, H., Walter, J., Kimball, G. E.: Quantum chemistry, 11th Ed. New York: Wiley 1963
17. Rellich, F.: Eigenwerttheorie partieller Differentialgleichungen, Vorlesungsmanuskript Teil II. Göttingen 1953
18. Bingel, W. A.: Theoret. Chim. Acta (Berl.) **8,** 54 (1967)
19. Kato, T.: Trans. Am. Math. Soc. **70,** 195 (1951)
20. Hylleraas, E. A.: Z. Phys. **48,** 469 (1928)
21. Morse, P. M., Feshbach, H.: Methods of theoretical physics. New York: McGraw-Hill 1953
22. Hylleraas, E. A.: Z. Phys. **65,** 209 (1930)
23. Schwartz, M. H.: Phys. Rev. **103,** 110 (1956); **120,** 483 (1960); **128,** 1146 (1962); **130,** 1029 (1963)
24. Knopp, K.: Theory of functions, Part I. New York: Dover Publications 1945

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