Theoret. chim. Acta (Berl.) 16, 126—144 (1970)

Electronic Wave Functions for Atoms

II. Some Aspects of the Convergence of the Configuration Interaction Expansion for the Ground States of the He Isoelectronic Series*

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Received June 18, 1969

Several specialized configuration interaction (CI) calculations for the ground states of the He isoelectronic series have been carried out with the purpose of defining successive orders of approximation to the wave function, so that reliable patterns of convergence can be investigated for the energy, some one-electron expectation values, and the wave function itself. We advocate the use of a sequence of wave functions to extrapolate expectation values and to find the extrapolation error = final error bound. As a direct consequence of this study, we show what the utmost limitations of CI expansions are for these systems and what is to be expected in similar situations (electron pairs in many-electron wave functions). Finally, a comparison is made between CI and interparticle coordinates wave functions.

Für die isoelektronische Reihe des He werden eine Reihe spezieller CI-Rechnungen für die Grundzustände ausgeführt mit dem Ziel, eine Folge von Näherungen an die Wellenfunktion definieren zu können. Auf diese Weise können zuverlässige Kriterien für das Konvergenzverhalten für die Energie, einige Ein-Elektronen-Erwartungswerte und für die Wellenfunktion untersucht werden. Wir befürworten den Gebrauch einer Folge von Wellenfunktionen, um die Erwartungswerte extrapolieren zu können und den Fehler der Extrapolation (= die endgültige Fehlergrenze) zu finden. Darausfolgend zeigen wir für diese Systeme die Grenzen von CI-Reihen und was in ähnlichen Fällen (Elektronenpaaren in Mehr-Elektronen-Wellen-Funktionen) zu erwarten ist. CI Funktionen und Funktionen, die die Relativkoordinaten der Teilchen enthalten, werden verglichen.

On a effectué plusieurs calculs d'interaction de configuration spécialisés pour les états fondamentaux de la série isoélectronique à He, en vue de déterminer la fonction d'onde avec différents degrés d'approximation pour étudier avec sûreté la convergence de l'énergie, de certains observables monoélectroniques et de la fonction d'onde elle même. Nous avons recours à une suite de fonctions d'onde pour extrapoler les valeurs moyennes et trouver la limite d'erreur. Cette étude a pour conséquence directe de montrer que les limitations les plus sévères du traitement d'I.C. apparaissent pour ces systèmes et sans doute pour ceux présentant une situation analogue (paires électroniques dans des fonctions d'onde polyélectroniques). Finallement, on compare l'I.C. et les fonctions d'onde contenant les coordonnées interparticulaires.

1. Introduction

Accurate and extensive calculations for the ground states of the He isoelectronic series have been carried out by Pekeris [1, 2] and also by Scherr and Knight [3, 4]. It is a most notable characteristic of Pekeris' wave functions that

* This work was supported by grants from the National Science Foundation and the US Air Force Office of Scientific Research.

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successive orders of approximation can be uniquely determined, so that expectation values, the energy included, converge in a simple and well defined way towards their exact values[1]. Unfortunately, at the present time, there are no such powerful practical methods to deal with larger systems. Thus, it is of interest to investigate the possibility of making meaningful calculations of electronic structures by means of the less accurate, but quite manageable, configuration interaction (CI) method. By meaningful calculations we understand those in which accurate expectation values are reported together with their error bounds, and in which the approximations in the wave function are quantitatively estimated.

In this work, the convergence patterns for wave functions and expectation values are studied; they provide error bounds to expectation values as well as information on the limitations of CI expansions, and they permit the assessing of the accuracy of recent CI calculations [6–8].

The CI expansions are considered in terms of natural spin-orbitals [9, 10] (NSO's). In spite of the fact that there are many works on CI expansions for these systems [10–19], and that several NSO's analyses of them are available [10, 14, 18, 20, 21], new calculations are in order, for our purposes. In Sect. 2 the wave functions employed are described together with the method used for the extrapolation of energies. Next the patterns of convergence for energies and eigenvector components are shown. The results obtained for some one-electron expectation values are analized likewise.

It is also of interest to study which sort of admixture of CI and interparticle coordinates methods is the most likely to be adopted so that more or less definitive *ab initio* energy results for many-electron systems can be guaranteed in the future. A preliminary view of this problem is given in Sect. 4.

2. Wave Functions and Extrapolation Method

The wave functions we consider are of the form

$$\Psi(1,2) = \sum_{l=0}^{l_{\max}} \Phi_l(r_1, r_2)\, P_l(\cos\gamma)\, A_l \cdot \text{spin part} \tag{1}$$

$$= \sum_{l=0}^{l_{\max}} \left\{ \sum_{i=1}^{I(l)} \sum_{j=i}^{I(l)} (1+P_{12})\, R_{il}(r_1)\, R_{jl}(r_2)\, B_{ijl} \right\} P_l(\cos\gamma) \cdot \text{spin part} \tag{2}$$

$$= \sum_i \chi_i^*(1)\, \chi_i(2)\, D_i \tag{3}$$

$$= \sum_{l=0}^{l_{\max}} \left\{ \sum_{i=1}^{I(l)} \varphi_{il}(r_1)\, \varphi_{il}(r_2)\, C_{il} \right\} P_l(\cos\gamma) \cdot \text{spin part} \tag{4}$$

with

$$|C_{il}| \geqq |C_{i+1,l}|\,. \tag{5}$$

The right hand members in Eqs. (1) and (2) are finite CI expansions for two-electron systems, ^1S states [22]. Eq. (3) gives their representations in terms of NSO's. Eq. (4) is similar to Eq. (3); it defines the functions φ_{il}, which are called natural radial orbitals (NRO's) of $\Psi(1,2)$. The orthonormal sets $\{R_{il}\}$ and $\{\varphi_{il}\}$ are

1 Some off-diagonal matrix elements escape to this behaviour; see [5].

linear combinations of Slater-type orbitals S_{jl}:

$$\varphi_{il} = \sum_{j=1}^{J(l)} S_{jl} a_{jli}, \tag{6}$$

$$S_{jl} = N_{jl} r^{(n_{jl}+l)} e^{-Z_{jl} r} \tag{7}$$

where N_{jl} is a normalization constant and

$$J(l) \geqq I(l). \tag{8}$$

At this point it is necessary to define the partial energy contributions $\Delta E'_{il}$ and $\Delta E''_{il}$. For this, we consider the wave functions Ψ' and Ψ'':

$$\Psi'(1,2) = \sum_{l=0}^{l'_{\max}} \left\{ \sum_{i=1}^{I'(l)} \sum_{j=i}^{I'(l)} (1+P_{12}) \varphi_{il} \varphi_{jl} E_{ijl} \right\} P_l(\cos\gamma) \cdot \text{spin part}, \tag{9}$$

$$\Psi''(1,2) = \sum_{l=0}^{l'_{\max}} \left\{ \sum_{i=1}^{I'(l)} \varphi_{il} \varphi_{il} G_{il} \right\} P_l(\cos\gamma) \cdot \text{spin part} \tag{10}$$

with

$$l'_{\max} \leqq l_{\max},$$
$$I'(l) \leqq I(l).$$

The functions above are truncations of the Ψ of Eqs. (1)–(4) in which the linear coefficients have been reoptimized. We denote by E'_{il} the energy obtained from Ψ' of Eq. (9) when $l = l'_{\max}$ and $i = I'(l)$, while E''_{il} is defined analogously from Eq. (10). The partial energy contributions are then

$$\Delta E'_{il} = E'_{il} - E'_{i-1,l}, \tag{11}$$

$$\Delta E''_{il} = E''_{il} - E''_{i-1,l}. \tag{12}$$

If Ψ is the best variational approximation when the CI expansion is truncated at $l = l_{\max}$, we think of it as an "exact" 012...l-limit wave function, i.e., for $l_{\max} = 2$, Ψ is an "exact" spd-limit wave function. We can also talk about "exact" $E'_{il}(l_{\max})$ values.

In dealing with accurate wave function one finds in practice, for He, that

$$\Delta E'_{il} = \Delta E''_{il} \pm 0.05 \Delta E''_{il}; \tag{13}$$

moreover, with increasing nuclear charge and i values this agreement is even better. It turns out that this small discrepancy between $\Delta E'_{il}$ and $\Delta E''_{il}$ values makes the study of the patterns of convergence for the energy, independent of the distinction between them. In what follows, the values reported are $\Delta E'_{il}$'s and the primes are dropped.

Now let us consider the function Ψ' given by Eq. (9) and let $\Psi'(-il)$ denote a Ψ' from which orbital (il) has been deleted. Then, we find, in practice, the following relationship:

$$\Delta E_{il} = \langle \Psi' | H | \Psi' \rangle - \langle \Psi'(-il) | H | \Psi'(-il) \rangle \pm 0.002 \Delta E_{ij}, \tag{14}$$

for

$$l < l'_{\max},$$
$$i = I'(l)$$

which means that the "energy contributions" of an orbital (il) are practically independent of the presence of higher harmonics in the wave function. Eq. (14) also tells us that, for accurate angular limit wave functions, the small energy errors in each of the angular components add up to the total energy error. In addition, although for small i values the E'_{il}'s show a slight dependence on the $l_{\max}$ which defines Ψ, this is not the case for $E'_{\infty l}$ values. Of course, $E''_{\infty l}$ values *are* affected under the same circumstances, i.e. $E''_{\infty 0}$ for He is about -2.87896 a.u. (He), even though Eq. (14) is still valid.

In practice it is not difficult to determine whether or not a $\Delta E'_{il}$ has converged to its exact value: the STO set is manipulated to make every E'_{il} a minimum, i.e. further STO's are added until the $\Delta E'_{il}$'s remain stationary. For He, the ΔE_{i0} values, up to $i=5$, are believed to be accurate to seven decimals; ΔE_{60} may be off by a few units in the seventh decimal and the error of ΔE_{70} is probably not greater than 10 per cent, while ΔE_{80}, ΔE_{90} and $\Delta E_{10,0}$ are certainly far from correct. When $l>0$, the computed E_{il} values are affected by the same errors resulting from the lower harmonic contributions, and thus the ΔE_{il}'s can always be computed accurately.

We shall proceed to write the basic equations for the extrapolation of the energy. Let us denote by $E_0^c, E_1^c, \ldots$ etc., the calculated angular energy limits. Then, from (14) it follows that

$$E_{\infty l} = E_l^c + l\text{-type corrections}\,, \tag{15}$$

$$l\text{-type corrections} = (l-1)\text{-type corrections} + (E_{hl}^c - E_l^c) + \sum_{i=h+1}^{\infty} \Delta E_{il} \tag{16}$$

where the subscript h in E_{hl}^c, represents the highest i value for which the corresponding ΔE_{il} is trustworthy, as determined in the process of building up the STO basis. The superscript c in the E_{il}'s indicates that these are computed quantities, i.e.

$$E_{hl} = E_{hl}^c + (l-1)\text{-type corrections}\,. \tag{17}$$

The ΔE_{il}'s for $i>h$ are found from empirical relationships, suggested by an analysis of their convergence patterns when $i \leq h$ (see Section 3):

Let us refer now to the construction of the STO set. (The choice of STO functions over Gaussian functions is obvious [23].) The search for adequate STO parameters creates several problems which can be faced in many possible ways. The path that we take (which we do not claim to be the only desirable one) is as follows: a large non-optimized STO set is employed to compute a He wave function which includes radial terms only. We obtain the NSO's of this function, and the one with the largest occupation number is written as a sum of a positive function plus a negative function. These functions are then "eye fitted" to two STO's with the help of an STO table. The new STO set is then conveniently enlarged, while particular attention is being given to the spatial distribution of the additional STO's relative to the first two. The process is then repeated, and this time the first two NSO's are decomposed and fitted. When we reach the stage in which the fourth NSO is to be fitted, we find that the positive and negative functions are nearly identical, and thus the whole process is broken. In this way, after five minutes of computer time[2], 6 STO's are obtained from which we get a wave function with an eigenvalue $E = -2.879001$ a.u. (He). Supplementary STO's, evenly distributed through the relevant spatial regions, are then introduced, but now priority is given to the energy improvements and to the stability of the ΔE_{il}'s, as pointed out before in the discussion on the extrapolation method. Some of the former STO's are slightly modified to "make room" for the new ones. After obtaining the first ten s-type STO's for He, we proceed to add p-type STO's in a similar fashion, while keeping the S_{j0}'s fixed. Then the S_{j0}'s are varied again in the hope of getting an improved sp-energy limit but without success; the original $\{S_{j0}\}$ set is finally kept intact. The S_{j2}'s are found likewise. (We have also considered functions S_{j3}, but only in order to test the stability of quantities related to the convergence patterns for the eigenvector components and some one-electron expectation values.) Similar energy results and patterns of convergence are obtained when instead of proceeding as above, the sets $\{S_{j1}\}$ and $\{S_{j2}\}$ are constructed from $\{S_{j0}\}$ in the following manner

$$Z_{j1} = 1.6 Z_{j0}\,; \quad n_{j1} = n_{j0}\,; \quad j = 1, 2, \ldots 8\,, \tag{18}$$

$$Z_{j2} = 2.6 Z_{j0}\,; \quad n_{j2} = n_{j0}\,; \quad j = 1, 2, \ldots 6\,. \tag{19}$$

The only reason for having less STO's for higher l-values is the lack of additional computer storage. In fact, as we shall see in the next section, in order to get energy errors smaller than 10^{-7} a.u. for each harmonic contribution, an increasing number of STO's is needed as l becomes larger. The empirically determined factors 1.6 and 2.6 of Eqs. (18) and (19) are not exempt of meaning. As pointed out by Shull and Löwdin [14], if the radial basis employed consists of associated Laguerre functions of order $(2l+2)$, the orbital exponent Z_l for the lth angular type as determined by a maximum overlapping criterion, is shown to be $Z_0(2l+3)/3$. The parameters Z_{j0} for He are, in the order in which they have been obtained: 1.30; 3.15; 1.30; 2.23; 3.25; 6.05; 7.80; 3.70; 5.25; and 3.40, and the n_{j0}'s are: 0; 1; 1; 0; 2; 0; 2; 4; 3, and 5, respectively. The Z_{j1}'s, n_{j1}'s, Z_{j2}'s and n_{j2}'s are obtained from Eqs. (18) and (19).

For the other members of the isoelectronic series with a nuclear charge Z, the STO sets are found by scaling the set for He, as has been done by Davis in his studies of the radial limits [17]:

$$Z_{jl}(Z) = A(Z) \cdot Z_{jl}(2)/3.25\,; \quad n_{jl}(Z) = n_{jl}(2) \tag{20}$$

with $A(Z) = 5.31$; 7.3; 9.3; 11.2; 13.1, and 15.0 for $Z = 3$ through 8, respectively. The validity of this procedure has been successfully tested for $Z = 8$.

It remains to be said how the spd-limit wave functions are obtained from the STO basis. Because of storage requirements of the computer program employed, we cannot handle the full [10s, 8p, 6d] orbital basis. Thus, [10s, 8p] wave functions are computed and the resulting NSO basis is truncated into an [8s, 7p] orbital basis. This set is now combined with six d-type STO's to compute spd-limit wave functions and NSO's.

2 We have employed the CDC 3600/3400 computer at Indiana University, with an effective storage capacity of 41000 words. The computer programs are those used in previous calculations (Refs. [7, 8]) and the computations are carried out in double precision arithmetic.

The truncation effected on the sp orbital basis slightly disturbs the patterns of convergence for the E_{i0}'s when these are studied with spd-limit wave functions. Similar considerations apply to the determination of the electronic density at the nucleus.

3. Patterns of Convergence for Energies and Expansion Coefficients

A. Radial Energy Limit

In Table 1 we have grouped the radial energy limits for He, as calculated and estimated by various authors, in order to fix in the reader's mind the kind of energy accuracy we shall be dealing with.

Table 2 shows the calculated E_{i0} values for He and O^{6+}. We find that the radial energy limit for He can be estimated from the empirical relationship

$$\Delta E_{i0} = -A_0 \cdot (b_0 + i)^{-6} \pm \delta_0 \Delta E_{i0} \quad \text{for} \quad 2 \leqq i \leqq 7 \tag{21}$$

where $A_0 = 0.322$, $b_0 = -0.35$ and $\delta_0 = 0.13$. Eq. (21) gives each ΔE_{i0} for He, $i = 2, 3, \ldots, 7$, with no more than 13 per cent of error. Assuming that each ΔE_{i0}, $i \geqq 8$, calculated from (21), has an error not greater than 25 per cent, taking into consideration possible errors of up to 15 per cent for ΔE_{70}, and using Eqs. (15) and (16), the exact radial energy limit of He is estimated to be

$$E_{\infty 0} = -2.8790284 \pm 0.0000012 \text{ a.u. (He)}.$$

We see that, according to Eq. (21), $\Delta E_{12,0} \approx 10^{-7}$ a.u., and that the remainder of the infinite sum (from $i = 13$ through infinity) does not exceed $3 \cdot 10^{-7}$ a.u.

B. Higher Angular Energy Limits

Similarly as in the case of the radial limit, the ΔE_{il}'s are given by

$$\Delta E_{il} = -A_l (b_l + i + l)^{-6} \pm \delta_l \Delta E_{il}, \quad i \geqq 2, \tag{22}$$

which is also valid for $i = 1$ when $l = 2$. It may be said at this point that the -6 power in Eq. (22) is quite a fact: a -5 or a -7 power would increase δ_l to 0.40 and even higher. The results of an application of Eq. (22) for He are given in Table 3.

Table 1. *Radial energy limit for* He

	Calculated[a]	Estimated
Weiss[b]	−2.878956	—
Shull and Löwdin[c]	−2.878970	−2.87900 ± 0.00003
Handler and Joy[d]	−2.8790190	—
Davis[e]	−2.8790248	−2.8790280 ± 0.0000018
This work[f]	−2.8790255	−2.8790284 ± 0.0000012
Schwartz[g]	−2.8790264	−2.879028 ± 0.000001

[a] Energies in a.u. (He).
[b] Ref. [15]; 5 basic fuctions.
[c] Ref. [14]; 6 basic functions.
[d] Ref. [19]; 11-terms expansion.
[e] Ref. [17]; 11 basic functions.
[f] 10 basic functions.
[g] Ref. [16]; 45-terms expansion.

Table 2. *Calculated E_{i0} values for* He *and* O^{6+}

i	$E_{i0}(\mathrm{He})^{a}$	$-\Delta E_{i0}{}^{b}$	$E_{i0}(\mathrm{He})^{c,d}$	$-\Delta E_{i0}$	$E_{i0}(O^{6+})^{c}$	$-\Delta E_{i0}{}^{e}$
1	−2.861531		−2.861651		−59.111141	
2	−2.87792920	1639820	−2.87790016	1624916	−59.12483994	1369894
3	−2.87884420	91500	−2.87883670	93654	−59.12582586	98592
4	−2.87898022	13602	−2.87897668	13998	−59.12597988	15402
5	−2.87901204	3182	−2.87900996	3328	−59.12601636	3648
6	−2.87902065	861	−2.87901944	948	−59.12602619	983
7	−2.87902479	414	−2.87902381	437	−59.12603121	502
8	−2.87902509[f]	30	−2.87902480[f]	99	−59.12603148[f]	27
9	−2.87902547[f]	38				
10	−2.87902548[f]	1				

[a] The NOS's are taken from an *s*-limit wave function.
[b] In units of 10^{-8} a.u. (He).
[c] The NSO's are taken from an *spd*-limit wave function.
[d] The differences between this column and the first one are explained at the end of Sect. 2.
[e] In units of 10^{-8} a.u. (O).
[f] These values differ appreciably from the exact ones; see discussion preceeding Eq. (15).

Table 3. *Values of* $(-\Delta E_{i2})$ *for* He, *according to Eq. (22)*

i	$-\Delta E_{i2}$
6	0.000006360
7	3162
8	1692
9	960
10	586
11	355
12	229
13	151
14	103
15	72
16	51
17	37

The E_l^c's from our *spd*-limit wave functions are given in Table 4, the parameters corresponding to Eq. (22) in Table 5. The A_l's and b_l's for Li^{+} through N^{5+} can be readily interpolated from those given in Table 5, if one assumes a linear dependence with respect to Z, in which case the corresponding δ_l values oscillate between 0.05 and 0.20.

Accurate angular energy limits for He through O^{6+}, obtained using Eqs. (15), (16), and (22), are presented in Table 6; their probable errors are 10^{-6} a.u. for the $E_{\infty 0}$'s, $4 \cdot 10^{-6}$ a.u. for the $E_{\infty 1}$'s and 10^{-5} a.u. for the $E_{\infty 2}$'s. Also, we find that $\Delta E_{14,1} \approx \Delta E_{14,2} \approx 10^{-7}$ a.u., and that in general, the rate of convergence of the radial expansions associated with each l-value deteriorates with increasing l. This behaviour was conjectured long ago by Schwartz [16] on the basis of similar results obtained by second order perturbation theory.

Table 4. *E_l^c values from our spd-limit wave functions, in a.u. (atom)*

l	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}
0	−2.8790248	−7.2524881	−13.6268554	−22.0015097	−32.3762915	−44.7511413	−59.1260315
1	−2.9005069	−7.2758835	−13.6511042	−22.0262422	−32.4013359	−44.7764031	−59.1514533
2	−2.9027492	−7.2786498	−13.6541429	−22.0294477	−32.4046533	−44.7798012	−59.1549127

Table 5. *Parameters of Eq. (22) for the Extrapolation of $E_{\infty l}$'s*

l	A_l (He)	b_l (He)	δ_l (He)	A_l (O^{6+})	b_l (O^{6+})	δ_l (O^{6+})
0	0.322	−0.35	0.13	0.416	−0.25	0.16
1	1.03	−0.05	0.06	1.57	−0.05	0.10
2	1.80	0.10	0.03	3.29	0.20	0.08

Table 6. *Estimated $E_{\infty l}$ values for* He *through* O^{6+}

l	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}
0	−2.8790284	−7.2524917	−13.6268590	−22.0015134	−32.3762952	−44.7511450	−59.1260350
1	−2.900520	−7.275897	−13.651118	−22.026257	−32.401350	−44.776418	−59.151469
2	−2.902774	−7.278677	−13.654172	−22.029479	−32.404686	−44.779836	−59.154950

C. A Golden Rule

The most interesting empirical relationship governing the ΔE_{il}'s seems to be

$$-\Delta E_{il} > -\Delta E_{i,l+1} > -\Delta E_{i+1,l} \tag{23}$$

which, if permanently confirmed, might well be called the *golden rule* for the extrapolation of CI energies. The same rule holds also in the case of first row atoms, when the ΔE_{il}'s are conveniently redefined [8]. It would be interesting to investigate if there is any theoretical hint regarding the general applicability of (23), at least for the systems we consider in this work. In Table 7 we illustrate this behaviour for He.

From Eq. (23) we can get the following upper bounds U_{l+i} to the energy contributions ε_{l+i}:

$$U_{l+1} = \sum_{i=2} \Delta E_{il} > \sum_{i=1} \Delta E_{i,l+1} = \varepsilon_{l+1}\,, \tag{24a}$$

$$U_{l+2} = \sum_{i=3} \Delta E_{il} > \sum_{i=2} \Delta E_{i,l+1} > \sum_{i=1} \Delta E_{i,l+2} = \varepsilon_{l+2}\,, \tag{24b}$$

. . . .

$$U_{l+q} = \sum_{i=q+1} \Delta E_{il} > \cdots > \sum_{i=1} \Delta E_{i,l+q} = \varepsilon_{l+q}\,, \tag{24c}$$

and, as a corollary,

$$E^U_{l+q} = E_{\infty l} + \sum_{l'=l+1}^{l+q} U_{l'} > E_{\infty, l+q}\,, \tag{25}$$

$$E^U = E_{\infty l} + \sum_{l'=l+1}^{\infty} U_{l'} > E(\text{exact})\,. \tag{26}$$

Table 7. *Calculated* $(-\Delta E_{il})$ *values for* He

i \ l	0	1	2
1	2.861651	0.01942906	0.00171935
2	1624916	167169	36964
3	93654	28155	10124
4	13998	6869	3471
5	3328	2207	1455
6	948	615[a]	285[a]
7	437	384[a]	
8	99[a]		

[a] These values differ appreciably from the exact ones, see discussion preceding Eq. (15).

Table 8. *Values of* E_l^U *for* He *and illustration of* l^{-4} *behaviour*

	E_l^U	$-U_l$	$0.043\,l^{-4}$
3	−2.903307	0.000533	0.000533
4	−2.903470	163	168
5	−2.903532	62	69
6	−2.903560	28	33
7	−2.903574	14	18
8	−2.903582	80	105
9	−2.903587	49	66
10	−2.903590	32	43

Table 9. *Upper bounds* E_l^U *for* He *through* O^{6+}

l	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}
3	−2.903307	−7.279405	−13.654967	−22.030304	−32.405531	−44.780691	−59.155813
4	−2.903470	−7.279634	−13.655219	−22.030567	−32.405800	−44.780963	−59.156087
5	−2.903532	−7.279724	−13.655319	−22.030671	−32.405906	−44.781071	−59.156196
6	−2.903560	−7.279764	−13.655364	−22.030718	−32.405954	−44.781120	−59.156245
E_{exact}[a]	−2.903724	−7.279913	−13.655566	−22.030972	−32.406247	−44.781445	−59.156595

[a] Ref. [1].

The results of an application of Eq. (25) are displayed in Table 8, together with the l^{-4} asymptotic behaviour for the successive harmonic contributions to the energy [16].

We can define Δ_{l+1} by

$$\Delta_{l+1} = (\varepsilon_{l+1} - U_{l+1})/\varepsilon_{l+1}\ ; \tag{27}$$

it is likely that the inequality

$$\Delta_{l+i+1} \geqq \Delta_{l+i} \tag{28}$$

holds true, although it does not strictly follow from (24). If Eq. (28) is correct, then the ε_l's might show an even better l^{-4} behaviour than the U_l's, as suggested by comparing the various entries of Table 8. In Table 9, upper bounds E_l^U for He through O^{6+} are presented.

Table 10. *Parameters of Eq. (29) for the extrapolation of C_{il}'s*

l	A_l(He)	b_l(He)	n_l(He)	δ_l(He)	$A_l(O^{6+})$	$b_l(O^{6+})$	$n_l(O^{6+})$	$\delta_l(O^{6+})$
0	0.267	−0.60	4	0.01[a]	0.0872	−0.40	4	0.01[a]
1	5.98	0.50	5	0.02	1.87	0.60	5	0.01
2	11.66	0.90	5	0.005	3.538	0.95	5	0.002

[a] Except for C_{20}, where the error of Eq. (29) is of 12 per cent.

If instead of wishing to obtain upper bounds E_l^U one is interested in more plausible approximations to the ε_l's, one might attempt to extrapolate the parameters A_l and b_l of Eq. (22) for higher l values. For instance, for He, one can set $A_3 = 2.6$ and $b_3 = 0.2$, which give an ε_3(calculated) $= -0.00062$ a.u. A good estimate for ε_3 is -0.000553 a.u. (see Sect. 4), and thus the energy error in the extrapolation above is more than ten per cent. However, if we take the latter value for ε_3 and postulate an l^{-4} behaviour for the ε_l's with $l \geqq 4$, we obtain $E = -2.90366$ a.u. (He), which is still an upper bound, and within 0.00006 a.u. of the exact energy value. A more empirical procedure to get ε_l values, $l \geqq 3$, consists in adjusting the constant of the l^{-4} law, so that the energy converges towards its exact value.

D. *Expansion Coefficients*

We consider the *spd*-limit wave functions in their natural form. The coefficients C_{il} of Eq. (4) are found to satisfy

$$C_{il} = -A_l(b_l + i + l)^{-n_l} \pm \delta_l C_{il}, \tag{29}$$

except for C_{10}. The parameters of Eq. (29) are given in Table 10. We see that these δ_l's are considerably smaller than those of Eq. (22). The trend of decreasing δ_l's with increasing l-values is maintained. The powers -4 for the *s*-components, and -5 for the *p*-'s and higher ones, are quite definite.

An inequality similar to our *golden rule* holds true:

$$|C_{il}| > |C_{i,l+1}| > |C_{i+1,l}|. \tag{30}$$

E. *Z-Dependent Trends*

The trends to be discussed below are derived from the *spd*-limit wave functions. A similar behaviour is observed when either *s*-limit or *sp*-limit wave functions are considered. In this subsection, the algebraic operations are carried out as if all atoms were of infinite mass, and the results are later interpreted in the appropriate atomic units: a.u. (atom).

A crude expression for $E_{10}(Z)$ is

$$E_{10}(Z) = -(Z - 5/16)^2 - 0.0137 \pm 0.0003. \tag{31}$$

Eq. (31) can be improved as follows:

$$E_{10}(Z) = -(Z - 5/16)^2 - A(Z) \tag{32a}$$

$$A(Z) = A(2) + (A(\infty) - A(2))(1 - 1/Z - 2/Z^2) \pm 0.00001 \tag{32b}$$

with $A(2) = 0.013995$ and $A(\infty) = 0.013425$.

Assuming $Z \geqq Z'$, we find the important relationship for the $\Delta E_{il}(Z)$'s (not valid for $\Delta E_{20}(Z)$):

$$\Delta E_{il}(Z) = \Delta E_{il}(Z') + (\Delta E_{il}(\infty) - \Delta E_{il}(Z'))(1-(Z'/Z)^2) \pm 0.1\, h_{il}\, \Delta E_{il}(Z)\,, \tag{33a}$$

$$h_{il}/2 = (\Delta E_{il}(Z_{\max}) - \Delta E_{il}(Z_{\min}))/(\Delta E_{il}(Z_{\max}) + \Delta E_{il}(Z_{\min})) \tag{33b}$$

where $Z_{\max}$ and $Z_{\min}$ define the interval in which Eq. (33a) is valid; the greater the interval, the greater the percentage of error involved in Eq. (33a). For $Z_{\max} = 8$, $Z_{\min} = 2$, we find $h_{il} \leqq 0.3$, so that (33a) gives at most an error of 3 per cent. We see that all ΔE_{il}'s decrease with increasing Z values, except for ΔE_{20} which increases. This increment of ΔE_{20} more than compensates the lowering of the other ΔE_{i0}'s ($i \geqq 3$), and thus the overall s-type contributions to the correlation energy becomes smaller for larger Z values.

The equations regulating the Z-dependence of the expansion coefficients $C_{i0}(Z)$ are very simple:

$$C_{10}(Z) = C_{10}(Z') + (1 - C_{10}(Z'))(1-(Z'/Z)^2) + \Delta\,, \tag{34a}$$

$$\Delta \leqq 0.0002 \cdot (Z'/Z) \cdot C_{10}(Z)\,, \tag{34b}$$

and

$$C_{i0}(Z) = a_i \cdot (Z'/Z) \cdot C_{i0}(Z') \pm 0.01\, C_{i0}(Z), \qquad i \geqq 3\,, \tag{35a}$$

$$a_i = 1.00 \pm 0.05\,. \tag{35b}$$

An equation analogous to Eq. (35) holds for $C_{20}(Z)$ and also for $C_{i1}(Z)$ and $C_{i2}(Z)$, but the percentage of error is somewhat larger.

F. Results for some One-Electron Expectation Values

It is of interest to see if "energy methods" can be channeled to yield not only good extrapolated energies, but also other quantities of physical interest. What follows are preliminary results which point out the main difficulties.

The expectation value of an operator

$$f = \sum_{i=1}^{N} f_i$$

can be expressed as

$$\langle \Psi | f | \Psi \rangle \equiv f = \sum_{j=1}^{M} n_j \cdot f_j \tag{36}$$

where

$$f_j = \langle \chi_j(1) | f_1 | \chi_j(1) \rangle\,, \tag{37}$$

$$\gamma(1|1')\, \chi_j(1) = n_j \cdot \chi_j(1)\,, \tag{38}$$

$$\gamma(1|1') = N \int \Psi^*(1', 2, \ldots N)\, \Psi(1, 2, \ldots N)\, \mathrm{d}(2, 3 \ldots N)\,. \tag{39}$$

We refer to the eigenvalues n_j as occupation numbers, the χ_j's are the NSO's of Ψ, and $\gamma(1|1')$ is the reduced first order density matrix. The constant M in

Eq. (36) is equal to the dimension of the NSO space. When Ψ has ^1S symmetry, the χ_j's are symmetry adapted [24]

$$\chi_j(1) = \varphi_{il} Y_{lm_l}(\theta, \varphi) \begin{cases} \alpha & \text{or} \\ \beta \end{cases} \tag{40}$$

and also

$$n_j = n_{il} \quad \text{(independent of } m_l \text{ and spin)}. \tag{41}$$

Further, if $f_j = f_j(r)$, then we have

$$f_j = f_{il} \quad \text{(independent of } m_l \text{ and spin)} \tag{42}$$

and thus, Eq. (36) may be rewritten in the form

$$f = \sum_{l=0}^{l_{\max}} \sum_{i=1}^{I(l)} 2(2l+1) \cdot n_{il} \cdot f_{il} \tag{43}$$

$$= \sum_{l,i} F_{il}, \tag{44}$$

$$F_{il} = 2(2l+1) \cdot n_{il} \cdot f_{il}. \tag{45}$$

The one-electron operators we consider are

$$f = \delta(\boldsymbol{r}) \equiv (\delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2))/2$$

and

$$f = r^n \equiv (r_1^n + r_2^n)/2$$

where n is an integer. When $n = -3$ or -4, the summation in Eq. (43) is understood to start with $l = 1$.

Upon inspection of the results obtained with s-, sp-, spd-, and (spd-limit + one f orbital) wave functions, it is clear that there exist convergence patterns for the f_{il}'s, n_{il}'s and F_{il}'s. Let us denote by g_{il} any one of these quantities; then we have

$$g_{il} = g_{il}(l_{\max}). \tag{46}$$

One alternative for the solution of our problem is to calculate $g_{il}(\infty)$'s. Except for $\{g_{10}(l_{\max})\}$, the sequences of values $\{g_{il}(l_{\max})\}$ converge rapidly and simply in all the cases considered. However, these sequences are quite sensitive to a good description of the lth type radial functions. Thus, even if there are patterns of convergence, these may lead to extrapolated values which differ from the exact ones by more than the error inherent in the extrapolation itself. In other words, the stability of the ΔE_{il}'s does not guarantee that of the g_{il}'s. (Of course, one might then look for g_{il}'s defined in a manner analogous to the ΔE_{il}'s, but this does not work; in particular there does not exist an equation similar to Eq. (14).)

Let us illustrate this shortcoming with $\delta(\boldsymbol{r})$. In Table 11 we list $F_{i0}(l_{\max})$ values. Our extrapolated result for He is 1.810401 ± 0.000005, while Pekeris finds calculated and extrapolated values of 1.810419 and 1.810427, respectively [2]. Our result is encouraging (it agrees with Pekeris' to four decimals) and it is not (the apparent extrapolation error is five times too small). The main reason for this

Table 11. *Pattern of convergence for the average value of* $\delta(\boldsymbol{r})$

i	$F_{i0}(0)$	$F_{i0}(1)$	$F_{i0}(2)$	$F_{i0}(3)$[a]	$F_{i0}(\infty)$
1	1.7989685	1.7944311	1.7948152	1.7948075	1.794810
2	162829	150811	149478	149342	14933
3	6477	5816	5734	5722	572
4	841	722	706	703	702
5	183	143	135	134	134
6	253	183	172	170	17
7	69	74	67	67	7
$\delta(\boldsymbol{r})$	1.816008	1.810183	1.810423	1.810400	1.810401

[a] Calculated with a (*spd*-limit + energy opt. *f* orbital) wave function.

discrepancy has been tracked to insufficient stability of the $F_{i0}(2)$'s, which in turn arises as a consequence of a truncation of the NSO basis employed, in going from the *sp*-limit wave function to the *spd*-limit wave function (see end of Section 2). It is apparent that some weak stability of the F_{il}'s has to be accepted as a practical fact in CI calculations. However, it is imperative to control these fluctuations and to give an estimate of their magnitude: work in this direction is in progress.

The angular convergence of some one-electron expectation values is illustrated in Table 12. It is likely, although this has not yet been investigated thoroughly enough, that accurate *s*-limit wave functions give lower bounds to the r^n values computed with the exact radial limit wave functions, when n is positive. The same may be said about 01 ... l-limit wave functions *if* the first $(l-1)$ harmonic contributions are represented exactly. Such a behaviour might give a clue for setting up an adequate method to compute these expectation values: after a reasonable STO basis is obtained, the orbital exponents Z_{jl} are varied to make r^n a maximum, while the linear coefficients of the CI expansion are always determined through the eigenvalue equation for the energy. Of course, such a procedure must be carried out without penalizing the energy.

In Table 13 we collect *spd*-limit results for Li^+ through N^{5+}. The average value of r^{-1}, which is related to the diamagnetic shielding of the nucleus by the electrons, seems to converge towards $(Z-5/16)$ for high Z, which is the same value one would obtain if the computation were made with the optimized hydrogenic Ψ

$$\Psi = N e^{-1/2\cdot(Z-5/16)\cdot(r_1+r_2)} \cdot \text{spin part}.$$

The behaviour of r^{-3} is found to be linear with Z, to within 0.2 per cent.

A most successful series of CI calculations for the two-electron atomic species has been carried out by Weiss [15]: he combines optimized STO parameters with an energetically optimum distribution of STO's among the different harmonic functions. We have obtained the corresponding 14-terms NSO expansion from Weiss' STO basis (g orbitals omitted). The angular limits results are shown in Table 14. We have also explored another definition of the successive orders of approximation, as shown in Table 15. In any case, the $\{g_{il}(l_{\max})\}$ sequences still exhibit convergence patterns, but they are not stable

Table 12. *Angular convergence of some one-electron expectation values for* He *and* O^{6+}

l	$\delta(r)$	r^{-2}	r^{-1}	r	r^2	r^3	r^4	r^5	r^{-3}	r^{-4}
Helium										
0	1.816008	6.021120	1.686177	0.934513	1.211035	2.021007	4.137424	10.043413		
		(6.020600)[a]	(1.686177)	(0.934523)	(1.211089)					
1	1.810183	6.015657	1.687730	0.930264	1.196048	1.975352	3.995613	9.574064	0.017048	0.071671
2	1.810423	6.016731	1.688107	0.929733	1.194323	1.970385	3.980927	9.527832	0.016982	0.070648
3[b]	1.810400	6.016732	1.688149	0.929645	1.194022	1.969505	3.978316	9.519630	0.016929	0.070429
Exact[c]	1.810427	6.0174080	1.688316798	0.929472293	1.19348299					
O^{6+}										
2	149.8050	119.49518	7.687547	0.196774	0.051957	0.017230	0.006882	0.003215	0.098118	1.803861
3[b]	149.8084	119.49518	7.687561	0.196773	0.051956	0.017230	0.006882	0.003215	0.098250	1.800764

[a] Ref. [19].
[b] See footnote in Table 11.
[c] Ref. [2].

Table 13. *Some spd-limit results for* Li^+ *through* N^{5+}

Z	$\delta(r)$	r^{-2}	r^{-1}	r	r^2	r^3	r^4	r^5	r^{-3}	r^{-4}
3	6.851694	14.927184	2.687818	0.572832	0.446397	0.441481	0.529954	0.748383	0.030384	0.198387
4	17.196808	27.839801	3.687686	0.414304	0.232099	0.164258	0.140607	0.141264	0.043885	0.390561
5	34.755253	44.753233	4.687620	0.324566	0.141981	0.078270	0.052093	0.040634	0.057423	0.647167
6	61.436349	65.667037	5.687583	0.266800	0.095744	0.043232	0.023541	0.015012	0.070972	0.967933
7	99.149756	90.581048	6.687561	0.226496	0.068907	0.026351	0.012142	0.006548	0.084548	1.354029

Table 14. *Some angular limit results for* He, *obtained with Weiss'* STO *basis*

l	$\delta(r)$	r^{-2}	r^{-1}	r	r^2	r^3	r^4	r^5	r^{-3}	r^{-4}
0	1.821196	6.022864	1.686183	0.934253	1.209263	2.011867	4.094224	9.843353		
1	1.815328	6.017243	1.687708	0.930042	1.194477	1.967274	3.957836	9.401359	0.017046	0.071556
2	1.815442	6.018222	1.688079	0.929500	1.192704	1.962121	3.942449	9.352292	0.017005	0.070928
3	1.815499	6.018482	1.688170	0.929369	1.192277	1.960893	3.938803	9.340721	0.016939	0.070650

Table 15. *Some results for* He, *obtained with Weiss'* STO *basis*

NSO's	$\delta(r)$	r^{-2}	r^{-1}	r	r^2	r^3	r^4	r^{-3}	r^{-4}	Energy
$3s2p1d$	1.813635	6.013439	1.687334	0.929893	1.193596	1.963978	3.946449	0.016532	0.064436	−2.901694
$3s2p1d1f$	1.813367	6.012987	1.687319	0.929849	1.193443	1.963549	3.945252	0.016465	0.064163	−2.902072
$3s2p2d1f$	1.813779	6.014242	1.687545	0.929692	1.193031	1.962547	3.942668	0.016468	0.064056	−2.902433
$3s3p2d1f$	1.814390	6.015891	1.687794	0.929565	1.192732	1.961881	3.941055	0.016759	0.067020	−2.902689
$4s3p2d1f$	1.814551	6.016329	1.687855	0.929549	1.192732	1.961989	3.941647	0.016753	0.066996	−2.902756
$4s3p2d2f$	1.814688	6.016761	1.687934	0.929495	1.192593	1.961657	3.940814	0.016737	0.066886	−2.902876
$4s3p3d2f$	1.814927	6.017394	1.688032	0.929442	1.192462	1.961357	3.940071	0.016757	0.066982	−2.902975
$4s4p3d2f$ [a]	1.815221	6.018053	1.688121	0.929395	1.192256	1.961070	3.939303	0.016941	0.070669	−2.903042

[a] The next entry, $(5s4p3d2f)$, is omitted, as it coincides with the $spdf$-limit shown in Table 14.

under further improvements of the wave function and thus the extrapolated values are worthless. (Obviously, this does not prevent them of approaching the exact values in some cases.)

Finally, it should be mentioned that there exists a *golden rule* for the F_{il}'s

$$F_{il}(l_{\max}) > F_{i,l+1}(l_{\max}) > F_{i+1,l}(l_{\max}). \tag{47}$$

Unfortunately, Eq. (47) is not sufficient to estimate the angular convergence of the expectation values considered, if the CI expansion is truncated at $l_{\max} = 2$, because at this stage of approximation, the value of $F_{10}(\infty)$ remains uncertain. This points out to the bottleneck of the problem: the determination of $F_{10}(\infty)$.

4. CI vs. Interparticle Coordinates

It has been held for many years that Hylleraas-type wave functions for many-electron systems are too cumbersome, while CI expansions converge slowly. It is impossible to assess the present validity and importance of this old complaint without discussing the physical problems which are at stake. But it is always important to expose and to understand the weak points in each of the methods employed.

Fifteen years ago, Green *et al.* [12] transformed the famous 3- and 6-parameters wave functions of Hylleraas [25] (to be denoted $\Psi_{3\mathrm{Hy}}$ and $\Psi_{6\mathrm{Hy}}$ respectively) into CI expansions where the functions $\Phi_l(r_1, r_2)$ of Eq. (1) are replaced by functions $\Phi_l(r_<, r_>)$[3]. The same type of analysis has later been extended [13] to Chandrasekhar's 3-parameters wave function [27], to be denoted Ψ_{Ch}. In Table 16 we have listed the calculated ε_l^c values obtained from various wave functions together with our "exact" estimates ε_l. (Green and collaborators report unnormalized ε_l^c values which we have here normalized; also, if the coefficients of the resulting CI expansion are reoptimized, only ε_1^c of Ψ_{Ch} shows variations in the fifth decimal, with respect to the normalized values.)

The implications of the results exhibited in Table 16 are remarkable. First, we notice that ε_2^c derived from $\Psi_{6\mathrm{Hy}}$ agrees quite well with ε_2. The *sp*-limit energy error of $\Psi_{6\mathrm{Hy}}$ is shown to be -0.00048_2 a.u.; if we add this value to the total energy for $\Psi_{6\mathrm{Hy}}$ we get the exact energy! The obvious conclusion is that

Table 16. *Energy analysis of interparticle coordinates wave functions for* He

l	$-\varepsilon_l(\Psi_{\mathrm{CH}})$	Error	$-\varepsilon_l(\Psi_{3\mathrm{Hy}})$	Error	$-\varepsilon_l(\Psi_{6\mathrm{Hy}})$	Error	$-\varepsilon_l$[a]
0	2.87757_4	0.00146	2.87828_7	0.00074	2.87867_4	0.00036	2.879028[b]
1	0.02087	0.00062	0.02117	0.00032	0.02136_4	0.00013	0.021492[b]
2	0.00209	0.00016	0.00208	0.00017	0.00225_5	0.00000	0.002254[b]
3	0.00051	0.00004	0.00051	0.00004	0.00055_3[b]	—	—
Sum 4 to ∞	0.00038	0.00001	0.00039_3	0.00000	0.00039_4[b]	—	—
Calc. energy	−2.90142		−2.90244		−2.90324		

[a] Obtained from the data of Table 6.
[b] These values are considered to be "exact".

3 Similar functions have later been employed by Schwartz [16], and by Byron and Joachain [26].

$\Psi_{6\mathrm{Hy}}$ gives $\varepsilon_3^c, \varepsilon_4^c, \ldots$ etc., with more than 6 decimals of accuracy and that all its energy error is due to an inadequate representation of the *sp* basis. Thus, one should be able to compute He wave functions with energy errors smaller than 10^{-6} a.u. just by adding a suitable *sp* basis to the 6-dimensional set which defines $\Psi_{6\mathrm{Hy}}$, or even better, by using the direct product of both sets as basis. A similar reasoning on Ψ_{Ch},

$$\Psi_{\mathrm{Ch}} = N(e^{-Z_1 r_1} e^{-Z_2 r_2} + e^{-Z_2 r_1} e^{-Z_1 r_2})(1 + \alpha r_{12})$$

leads us to predict that the admixture of a $(1 + \alpha r_{12})$ factor into an *sp* basis, should bring the energy of He to a value in error by no more than 0.00019 a.u. This clearly indicates the interest there is in setting up a refined computer program to explore the possibility of using such a restricted basis in computations for states of first row atoms.

5. Discussion

Let us summarize what has been accomplished in this work. First, we have shown (empirically) the existence of patterns of convergence for the CI energy, expansion coefficients and some one-electron expectation values. The basic equations for the extrapolation of the energy, Eqs. (15) and (16), are based on Eq. (14), which has been assumed by other authors for a long time [28]; here we have carried out a nearly exhaustive test of it, and its consequences have been exploited in an empirical study of the (practical) asymptotic behaviour of suitably defined energy contributions. The convergence of the radial expansions is shown to deteriorate with increasing l-values, and for $l \geqq 3$, the successive harmonic contributions to the energy follow, approximately, an l^{-4} type of law. The various implications of such convergence behaviour can best be assessed by examining Tables 2, 3, 7, 8 and 16.

A *golden rule* for the extrapolation of CI energies is proposed. Other alternatives are discussed in relation to the atomic states considered.

The convergence patterns for the expansion coefficients throw light into the convergence of the CI wave functions itself.

The Z-dependent trends found for various quantities are didactically valuable because of their simplicity.

The channeling of "energy methods" to obtain other quantities of physical interest is considered, and possible alternatives and improvements are discussed. The existence of patterns of convergence alone does not legitimate the extrapolation of the quantities involved, unless such patterns are shown to be stable under further improvement of the wave function. On the way, we have noticed that CI is the natural method to compute the average value of $\delta(r)$. Other methods, like those of Chandrasekhar and Herzberg [29], or that of Kinoshita [30], are relatively inferior in this respect[4], in spite of their superiority with regard to the energy.

4 These wave functions give average $\delta(r)$ values of 1.8102 and 1.8106 respectively; $\Psi_{3\mathrm{Hy}}$ and $\Psi_{6\mathrm{Hy}}$ give 1.7984 and 1.8167 respectively, see [31]. The values reported in Refs. [2, 4] are the most accurate ones.

The analysis of Green *et al.* has been combined with our estimated angular energy limits and, in this way, the source of the energy errors in various interparticle coordinates wave functions is quantitatively discussed [5]. It is shown that an sp basis with a correlation factor of the type $(1+\alpha r_{12})$ can give wave functions with energy errors smaller than 0.0002 a.u.

All previous considerations regarding the energy also apply to the pertinent "portions" of many-electron wave functions (K shell expansions) as in the "pair correlations" theory of Sinanoğlu and coworkers [32], and some of the results in this paper have been already utilized to estimate K shell energy errors [7, 8].

Clearly, the highest dividend paid by this type of investigation is the discovery of the methodological problems one has to face in the determination of CI wave functions, as well as the exposure of the inherent limitations of a given type of expansion. The determination of rigorous upper and lower bounds to computed expectation values is a separate problem.

Acknowledgements. I am indebted to Professor H. Shull for his continuous interest and criticism, and for financial support. It is a pleasure to thank my wife Annik for several corrections and improvements on the manuscript. The valuable colloboration of the machine operators and other staff members and users of the Research Computing Center at Indiana University is gratefully acknowledged.

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