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'Partitions' in the perturbation theory of n -electron systems: III. The third-order energy

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Abstract. In the perturbation theory of the general n -electron system, $H(n) = \sum^n f(i) + \lambda \sum^n g(i, j)$, the subsystem method provides a finite decomposition (termed 'partition') in each order of the perturbation eigenfunctions and energies. The present paper shows that the third-order energy $E^{(3)}(n)$ is a weighted sum of third-order energies $E^{(3)}(n_1)$ belonging to electronic states (most of them highly excited) of the $n_1 =$ four-, three- and two-particle subsystems. The proof uses a parentage expansion of the second-order n -electron eigenfunction. The energy partitions can be regarded as the rigorous derivation of the important 'atomic energy relations' intuitively derived by Bacher and Goudsmit.

1. Introduction

It is the goal of this paper to prove an additional part of the conjecture that the solution to the n -electron eigenvalue problem, within each order of the perturbation expansion, can be built up from the solutions of finitely many *self-contained* n_1 -electron eigenvalue problems, where $n_1 = 1, 2, 3, \dots$. The n_1 -electron problems belong to the *subsystems* obtained from the full system by removing electrons. The maximal n_1 to enter at perturbation order $r = 0, 1, 2, \dots$, is prescribed by the 'non-separability' condition for the component eigenfunctions and energies, respectively. The order $r = 3$ being considered here requires subsystems of size $n_1 \leq 4$.

The idea of the subsystem analysis, and its connection to the perturbation expansion in powers of the interelectronic interaction, have both been described by Bacher and Goudsmit (1934). Their method has been broadened mathematically and extended to also include the eigenfunctions up to first order (Racah 1943, Sinanoğlu 1961, Chisholm and Dalgarno 1966). The first-order eigenfunction is built up from $\sim \binom{n}{2}$ symmetry-adapted first-order pair functions. This theorem, unlike Bacher and Goudsmit's method which focuses on the valence electrons, has found frequent application to the *ab initio* calculation of second-order (Knight 1982) and third-order energies of ten-electron and larger atoms (Jankowski *et al* 1982, Jankowski and Rutkowski 1988).

Two earlier papers (Schmidt 1983, Schmidt *et al* 1986, hereafter referred to as I and II, respectively) were intended to give a thorough mathematical framework to the subsystem method, covering energies as well as eigenfunctions. We have used the term 'partitions' for the finite decompositions that are typical for the method. The present paper treats the third-order energy $E^{(3)}(n)$. In §§ 2 and 3 the given n -electron state will be assumed 'strictly non-degenerate'. Section 4 also treats the more general case of a closed-shell atomic state.

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The structure of $E^{(3)}(n)$ can be regarded as a consequence of either the pair structure of the first-order eigenfunction (compare (3b)) or, equivalently, of the pair and three-electron structure of the second-order eigenfunction (compare (3a)). The mutual coupling of the coordinates of the pairs (or three-electron functions) and the $1/r_{ij}$ interaction generates various types of integrals. It is easy to separate $E^{(3)}(n)$ into a sum of pair energies $E^{(3)}(2)$, and a complicated remainder consisting of non-separable three- and four-electron integrals and of factorising integrals. On the other hand, if the partition exists, the totality of all contributions can be ordered (in principle by addition and subtraction) to form *entire* perturbation energies $E^{(3)}(4)$, $E^{(3)}(3)$, $E^{(3)}(2)$ without any terms remaining that do not have this quality. As a matter of fact, one knows the probable final result to which the process should lead: this equation occurs (rather as an ansatz than as a rigorous statement) in Bacher and Goudsmit's (1934) method and in Trees' (1954) extension thereof. The form of the partition sought can also be guessed from analogy with the available partitions of $E^{(1)}$ and $E^{(2)}$ (I). The proof of the $E^{(3)}$ partition turns out to be far more complicated than that for the second-order energy.

2. The partition of $E^{(3)}$

As in I and II, consider an n -electron system with Hamiltonian

$$H(f, g; n) = \sum_{1 \leq i \leq n} f(x_i) + \lambda \sum_{1 \leq i < j \leq n} g(x_i, x_j). \quad (1)$$

The one-particle operator f contains the kinetic energy and the potential of the external forces.. The 'subsystems' of (1) are defined as $H(f, g; m)$ for particle numbers $m = 1, 2, \dots, n$. It is important that the f and g operators be the same for the whole family of systems. This is naturally fulfilled if g is the full interelectronic interaction:

$$g(x_i, x_j) = 1/r_{ij}. \quad (2a)$$

The present theory first addresses this case, i.e. for atoms the $1/Z$ expansion (Hirschfelder *et al* 1964). The Hartree-Fock-based perturbation expansion (McWeeny and Steiner 1965) where the interaction is screened:

$$g(x_i, x_j) = 1/r_{ij} - \frac{1}{n-1} [v(x_i) + v(x_j)] \quad (2b)$$

is, in principle, contained in the results of this paper since the occurrence of the one-particle potentials v in (2b) does not alter the 'non-separability' (compare I (2.14)) of $1/r_{ij}$. However, since f and g become dependent on the particular n -electron state being considered, the subsystems $H(f, g; m)$ will be of a much more formal character than in the case of (2a).

An eigenstate of $H(f, g; m)$ (any $m \leq n$) will be written as $\psi(f, g; m)$ or $\psi(m)$, and its energy as $E(f, g; m)$ or $E(m)$. The configuration labelling the state is added as a subscript: π, ρ, σ, K denote two-, three-, four- and n -electron configurations, respectively. For each $\psi(m)$ and $E(m)$ the (formal) Rayleigh-Schrödinger perturbation expansion in powers of λ is assumed. The full (not intermediate) normalisation (Hirschfelder *et al* 1964) for the perturbation wavefunctions $\psi^{(r)}$ ($r = 0, 1, 2, \dots$) is used. The third-order perturbation energy can be expressed in terms of the $\psi^{(r)}$ in

different ways:

$$E^{(3)} = \text{Re} \langle \psi^{(0)} | G - E^{(1)} | \psi^{(2)} \rangle \quad (3a)$$

$$E^{(3)} = \langle \psi^{(1)} | G - E^{(1)} | \psi^{(1)} \rangle \quad (3b)$$

where G is the sum of the $g(x_i, x_j)$ in (1). Since the partition of $\psi^{(2)}$ is available (II), the expression (3a) is the more convenient point of departure for deriving the $E^{(3)}$ partition: $E^{(3)}$ requires setting up parent wavefunctions of four, three and two electrons. In $\psi^{(2)}$, part of the necessary coupling is already realised.

The $E^{(3)}$ partition is treated here for the technically simple case of the zero-order energy $E_K^{(0)}(n)$ being *strictly non-degenerate* (as defined in I, appendix B). This means that the $\psi^{(0)}$ functions for both the full n -electron state, and for each relevant parent state of four, three, and two electrons, have the form of a single Slater determinant and that no further symmetry adaptation is required.

Theorem. Consider the eigenstate of configuration K of the n -electron Hamiltonian $H(f, g; n)$. Under the above assumptions, the third-order perturbation energy has the partition:

$$E_K^{(3)}(f, g; n) = \sum_{\sigma \subset K} E_{\sigma}^{(3)}(f, g; 4) - (n-4) \sum_{\rho \subset K} E_{\rho}^{(3)}(f, g; 3) + \binom{n-3}{2} \sum_{\pi \subset K} E_{\pi}^{(3)}(f, g; 2). \quad (4)$$

Each third-order energy on the right-hand side belongs to the appropriate subsystem and state as indicated. The number of terms in the σ , ρ and π sums is $\binom{n}{4}$, $\binom{n}{3}$, $\binom{n}{2}$, respectively.

Remark. Equation (4) holds for $n \geq 2$. For $n=2, 3$ and 4 it expresses the non-separability of $E^{(3)}(f, g; n)$. For $n=3$, for example, the σ sum is empty and the π sum is cancelled by the prefactor $(n-3)(n-4)/2$.

The smallest particle number so that $E^{(3)}(n)$ has a genuine decomposition is $n=5$. As an illustration of the partition, consider the ground state of the five-electron system. Its configuration $K = (1, 2, 3, 4, 5)$ consists of the five lowest one-particle levels (eigenvalues of f in (1)). Equation (4) expresses $E_K^{(3)}$ in terms of the $E^{(3)}$ energies for the substates or 'parent states' belonging to the subconfigurations of K . These are $\binom{5}{4} = 5$ four-electron states, $\binom{5}{3} = 10$ three-electron and $\binom{5}{2} = 10$ two-electron states. The prefactors in (4) are 1, -1, 1, respectively. Some of the parent states are ground or low-lying states, but most of them are doubly or multiply excited. For example, $\sigma = (2, 3, 4, 5)$ is similar to a core-ionised state.

3. Proof

The derivation of (4) to be given here departs from the expression (3a) for each of the third-order energies. The n -electron second-order function $\psi^{(2)}(f, g; n)$ is used in the form of its partition (II, (8)).

First an elementary procedure for deriving (4) will be described since it shows clearly the process of grouping of primitive parts into entire perturbation energies $E^{(3)}(m)$ ($m=4, 3, 2$) and entire 'V expressions' (see appendix 1). The same grouping is made in the construction of the parentage expansion of $\psi^{(2)}(n)$ which forms the main step of the systematic proof. This proof can afterwards be given very compactly.

The eigenfunction $\psi^{(2)}(n)$ contains, apart from orbitals, wavefunctions $\psi^{(2)}(2)$, $\psi^{(2)}(3)$ and products $\psi^{(1)}(2)\psi^{(1)}(2)$. By inserting $\psi^{(2)}(n)$ into (3a), ten types of primitive integrals A_1, A_2, \dots, C_4 arise. They are listed on the left-hand side of table 1. For example, a particular integral of B_2 type is

$$(B_2)_{\rho k} = \langle \psi_{\rho+k}^{(0)}(x_1, \dots, x_4) | g(x_3, x_4) | \psi_{\rho}^{(2)}(x_1, x_2, x_3) \psi_k^{(0)}(x_4) \rangle \quad (5)$$

where k and ρ are configurations of one and three electrons, respectively. The integral (5) is a fragment of the perturbation energy $E_{\sigma}^{(3)}(4)$ with $\sigma = \rho + k$ (notation as in I, (B6)). The total $E_{\sigma}^{(3)}(4)$ contains further B_2 integrals as well as the A_1, A_2, A_3, B_1, C_2 types and also integrals of the factorising type C_1 . Table 1 shows which integral types enter a given $E^{(3)}(m)$ or a given V expression. In the construction of the partition (4), it is the first step to form the four-electron energies $E^{(3)}(4)$. Each of them must appear with weight 1. It is interesting that factorising integrals (A_3 and C_1) also occur in $E^{(3)}(4)$. The next steps provide the $E^{(3)}(3)$ and $E^{(3)}(2)$. The factorising integrals which remain at the end are absorbed by V expressions.

The more systematic way of obtaining the partition (4) begins with the parentage expansion of $\psi^{(2)}$ (see appendix 2). In this expansion the structure of $E^{(3)}$ is being prepared on the level of the wavefunctions. Rewrite $E_K^{(3)}(n)$ thus:

$$E_K^{(3)}(n) = \binom{n}{2} \text{Re} \langle g(x_1, x_2) \psi_K^{(0)} - \theta_K^{(1)} | \psi_K^{(2)} \rangle \quad (6)$$

where

$$\theta_K^{(1)} = \sum_{\pi \in K} a_{\pi} E_{\pi}^{(1)} \psi_{\pi}^{(0)}(x_1, x_2) \psi_{\pi}^{(0)}(x_3, \dots, x_n).$$

Inserted into (6), the parentage expansion (A2.1) produces six terms corresponding to each of (A2.2)-(A2.7), namely the four-, three- and two-electron parts of (4) and vanishing V expressions of the types $V(3, 2)$, $V(2, 2)$ and $V(2, 2, 2)$, respectively. This completes the proof of (4).

Table 1. The types of primitive integrals occurring in the third-order energy $E^{(3)}(n)$ for $n \geq 6$. The crosses indicate how the individual types contribute to the non-separable energies $E^{(3)}(m)$ ($m = 4, 3, 2$) and to the vanishing V expressions defined in appendix 1.

Primitive integral			Is a fragment of					
Integrand†	(i, j)	Type	$E^{(3)}(4)$	$E^{(3)}(3)$	$E^{(3)}(2)$	$V(3, 2)$	$V(2, 2)$	$V(2, 2, 2)$
$g(x_i, x_j) \psi^{(2)}(x_1, x_2)$	(1, 2)	A_1	×		×			
	(2, 3)	A_2	×					
	(3, 4)	A_3	×					
$g(x_i, x_j) \psi^{(2)}(x_1, x_2, x_3)$	(1, 2)	B_1	×	×			×	
	(3, 4)	B_2	×					
	(4, 5)	B_3				×		
$g(x_i, x_j) \psi^{(1)}(x_1, x_2)$ $\times \psi^{(1)}(x_3, x_4)$	(1, 2)	C_1	×			×	×	
	(2, 3)	C_2	×					
	(4, 5)	C_3				×		
	(5, 6)	C_4						×

† For particle number $n = 5$, C_4 and $V(2, 2, 2)$ do not occur. The remainder of the table is the same.

‡ The one-electron functions in the integrand do not affect the integral type and have been omitted. For a complete integral see (5).

4. Discussion

In this paper, it has been shown that the third-order energy of an n -electron state can be expressed solely in terms of third-order energies belonging to the *parent states* (Racah 1943) of four, three and two electrons. The parent states, most of which are highly excited, arise by removing all but four, three or two electrons from the original system.

There is a particular interest in the subsystem method: the partitions of $E^{(1)}$, $E^{(2)}$ (compare I), and of $E^{(3)}$, exhibit a *physical aspect* as each of them represents a relation between the energies of the isoelectronic series (i) of a stable many-electron state, and (ii) of a set of high-lying, usually autoionising, few-electron states (compare Komninos *et al* 1986). Following Bacher and Goudsmit (1934), the energy partitions can, in principle, be empirically examined using the measured spectra of an atom and its ions. The partition (4) can also be used as a computational tool in the *ab initio* calculation of $E^{(3)}(n)$ (if, as usual, n is not very large). Adopting the variation-perturbation procedure of Knight (1982) or Jankowski and Rutkowski (1988), one would evaluate each component energy in terms of first-order pair functions. Some of the physical and computational aspects of the energy partitions will be examined in more detail in a later paper.

The proof of the partition has employed a parentage expansion of the second-order eigenfunction and the device of the vanishing V expressions. The latter make transparent the mutual cancellation of the factorising integrals in $E^{(3)}(n)$. The V expressions are a counterpart of the disconnected graphs of the diagrammatic perturbation theory (Paldus and Čizek 1975). A thorough comparison might shed some light on new aspects of the connected-graph theorem (Hurley 1976, Hubač 1980, Kutzelnigg 1984).

The $E^{(3)}$ partition has the form of (4) for a strictly non-degenerate n -electron state. The derivation is, however, transferable to the case of an atom with completely closed shells. For the $1/Z$ expansion of atoms, the f and g operators in (1) are (Hirschfelder *et al* 1964):

$$f(x_i) = -\frac{1}{2}\nabla_i^2 - 1/r_i \quad (7)$$

and $g = 1/r_{ij}$. For the ground state $K = 1s^2 2s^2 2p^6(^1S)$ of the ten-electron atom, the partition is

$$E_K^{(3)}(\text{Ne}) = \sum_{\sigma} p_{\sigma} E_{\sigma}^{(3)}(\text{Be}) - 6 \sum_{\rho} p_{\rho} E_{\rho}^{(3)}(\text{Li}) + 21 \sum_{\pi} p_{\pi} E_{\pi}^{(3)}(\text{He}). \quad (8)$$

In (8) the subscripts K , σ , ρ , π are to specify atomic states (terms) rather than the mere configurations of (4). The σ sum contains the $E^{(3)}$ energies for those states (terms) of the beryllium isoelectronic series which are parents to K . Each $E_{\sigma}^{(3)}$ appears with a weight p_{σ} equal to the multiplicity of the term. The total sum of the p_{σ} is $\binom{n}{4} = 210$. Similarly, the ρ and π sums refer to terms of the lithium and helium isoelectronic series. Table 2 summarises a few of the terms and their multiplicities.

The concept of the energy partitions is related, apart from the method of Bacher and Goudsmit (1934), to the decomposition given by Knight (1969, 1982) for the $1/Z$ second-order energy of atoms. Knight employs three-electron contributions which are not whole three-electron perturbation energies; his decomposition appears therefore to be less systematic than the 'partition' of $E^{(2)}(n)$. Knight's (1982) fractional-parentage-like weight factors have significance for the generalisation of (8) to open-shell states.

Table 2. $E^{(3)}$ partition for the $1/Z$ expansion of the ten-electron atom ground state (closed shells). The table gives a few of the parent states entering (8). The weights p_σ , p_ρ and p_π are equal to the multiplicity of the respective term.

σ	Four electrons		Three electrons		Two electrons	
	p_σ	ρ	p_ρ	π	p_π	
$1s^2 2s^2 (^1S)$	1	$1s^2 2s (^2S)$	2	$1s^2 (^1S)$	1	
$1s^2 2s 2p (^1P)$	3	$1s^2 2p (^2P)$	6	$1s 2s (^1S)$	1	
$1s^2 2s 2p (^3P)$	9	$1s 2s 2p (^2P)$	6	$1s 2s (^3S)$	3	
...			
$2p^4 (^1D)$	5	$2p^3 (^2D)$	10	$2p^2 (^1D)$	5	

Finally, it should be noted that in recent years a different subsystem method has been developed by Valdemoro and coworkers (Lain *et al* 1988). The method approximates the two-particle density matrix of an n -electron state by a sum of density matrices describing groups of p electrons at a time, where $p = 2, 3, 4, \dots$, are the stages of the approximation. Although the formulation differs from that of the present paper, it is evident that a common foundation exists for both methods.

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Appendix 1. The vanishing V expressions

The existence of the $E^{(3)}$ partition stems partly from the vanishing of certain symmetrical combinations of scalar products which will be referred to as ' V expressions'. An individual V -expression summarises a few of the factorising integrals which occur in $E_K^{(3)}(n)$, $n \geq 4$, and it forms the smallest vanishing unit of its kind.

Consider the scalar products

$$P_{\mu\mu_1}^{(r)} = \langle \psi_\mu^{(0)} | \psi_{\mu_1}^{(r)} \rangle \quad (\text{A1.1})$$

$$Q_{\mu\mu_1}^{(r)} = \langle \psi_\mu^{(0)} | G(m) - E_{\mu_1}^{(1)} | \psi_{\mu_1}^{(r-1)} \rangle \quad (\text{A1.2})$$

for the order $r = 1$ or $r = 2$ and for perturbation wavefunctions of m electrons where $m = 2$ or $m = 3$. μ, μ_1 are any two m -electron configurations contained in the overall configuration K . $G(m)$ is the sum of the $g(x_i, x_j)$ for the m particles similar to (1). For example $G(2) = g(x_1, x_2)$. Let π, ν, λ , as well as π_1, ν_1, λ_1 , denote two-electron configurations in K and ρ, ρ_1 three-electron configurations in K .

A V expression of the first type is

$$V(3, 2) = Q_{\rho\rho_1}^{(2)} P_{\pi\pi_1}^{(1)} + P_{\rho\rho_1}^{(2)} Q_{\pi\pi_1}^{(1)} \quad (\text{A1.3})$$

and $V(3, 2) = 0$ holds if $\rho + \pi = \rho_1 + \pi_1$ and $\rho \neq \rho_1$. '+' denotes the union of disjoint configurations as in I, (B6). Another V expression, to be called $V(2, 2)$, is obtained

from (A1.3) by replacing ρ, ρ_1 by the pair ν, ν_1 of two-electron configurations. $V(2, 2) = 0$ if $\nu + \pi = \nu_1 + \pi_1$ and $\nu \neq \nu_1$. The last type of V expression occurring for the third perturbation order is

$$V(2, 2, 2) = Q_{\lambda\lambda_1}^{(1)} P_{\nu\nu_1}^{(1)} P_{\pi\pi_1}^{(1)} + P_{\lambda\lambda_1}^{(1)} Q_{\nu\nu_1}^{(1)} P_{\pi\pi_1}^{(1)} + P_{\lambda\lambda_1}^{(1)} P_{\nu\nu_1}^{(1)} Q_{\pi\pi_1}^{(1)}. \quad (\text{A1.4})$$

One has $V(2, 2, 2) = 0$ if $\lambda + \nu + \pi = \lambda_1 + \nu_1 + \pi_1$ (no further condition). For brevity, the configuration subscripts, such as $\rho\rho_1\pi\pi_1$ which specify a V expression, have not been written on the left-hand side of (A1.3)–(A1.4). The fact that the V expressions vanish follows immediately from the perturbation equations by suitable scalar multiplication.

Appendix 2. Parentage expansion of $\psi^{(2)}(n)$

The proof of the $E^{(3)}$ partition employs the following parentage expansion of the second-order eigenfunction. This expansion is more general than in the case of the first-order eigenfunction (I, § 4) since it uses wavefunction products with two, three and four factors:

$$\psi_K^{(2)}(x_1, x_2, \dots, x_n) = \mathcal{A}'[\Omega_4 + \Omega_3 + \Omega_2 + \Omega_{3,2} + \Omega_{2,2} + \Omega_{2,2,2}] \quad (\text{A2.1})$$

where \mathcal{A}' is the antisymmetriser for the variables x_3, x_4, \dots, x_n and

$$\Omega_4 = \binom{n-2}{2} \sum_{\sigma} a_{\sigma} \psi_{\sigma}^{(2)} \cdot \psi_{\bar{\sigma}}^{(0)} \quad (\text{A2.2})$$

$$\Omega_3 = -(n-2)(n-4) \sum_{\rho} a_{\rho} \psi_{\rho}^{(2)} \cdot \psi_{\bar{\rho}}^{(0)} \quad (\text{A2.3})$$

$$\Omega_2 = \binom{n-3}{2} \sum_{\pi} a_{\pi} \psi_{\pi}^{(2)} \cdot \psi_{\bar{\pi}}^{(0)} \quad (\text{A2.4})$$

$$\Omega_{3,2} = \binom{n-2}{3} \sum_{\pi, \rho} b_{\pi\rho} [3\psi_{\rho}^{(1)} \cdot \psi_{\pi}^{(1)} + \psi_{\pi}^{(0)} \cdot \psi_{\rho}^{(2)}] \cdot \psi_{\overline{\pi+\rho}}^{(0)} \quad (\text{A2.5})$$

$$\Omega_{2,2} = -3 \binom{n-2}{3} \sum_{\pi, \nu} b_{\pi\nu} [\psi_{\pi}^{(1)} \cdot \psi_{\nu}^{(1)} + \psi_{\pi}^{(0)} \cdot \psi_{\nu}^{(2)}] \cdot \psi_{\overline{\pi+\nu}}^{(0)} \quad (\text{A2.6})$$

$$\Omega_{2,2,2} = 3 \binom{n-2}{4} \sum_{\pi, \nu, \lambda} c_{\pi\nu\lambda} \psi_{\pi}^{(0)} \cdot \psi_{\nu}^{(1)} \cdot \psi_{\lambda}^{(1)} \cdot \psi_{\overline{\pi+\nu+\lambda}}^{(0)}. \quad (\text{A2.7})$$

The same shorthand notation has been used as in II, § 3. The subscripts π, ν, λ denote two-electron configurations, ρ and σ denote three- and four-electron configurations, respectively. The configurations appearing in a given product are mutually disjoint and their union is K . All parentage coefficients result from the definition I, (C6) or from successive application of it:

$$a_{\pi} = a(\pi, \bar{\pi}, K) \quad (\text{A2.8})$$

$$b_{\pi\nu} = a_{\pi} \cdot a(\nu, \overline{\pi + \nu}, \bar{\pi}) \quad (\text{A2.9})$$

$$c_{\pi\nu\lambda} = b_{\pi\nu} \cdot a(\lambda, \overline{\pi + \nu + \lambda}, \overline{\pi + \nu}). \quad (\text{A2.10})$$

a_{σ}, a_{ρ} and $b_{\pi\rho}$ follow from (A2.8) and (A2.9) by replacing the appropriate subscripts.

The phases of the wavefunctions in (A2.1)–(A2.7) derive uniquely from the once chosen phases of the non-separable components $\psi^{(0)}(n=1), \psi^{(1)}(n=2), \psi^{(2)}(n=2)$ and $\psi^{(2)}(n=3)$; see I, § 3. In terms of these phases the parentage expansion (A2.1) and the partition II, (8) represent identical functions.

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