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'Partitions' in the perturbation theory of n -electron systems: II. The second-order eigenfunction

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Abstract. In the perturbation theory of the general n -electron system, $H(n) = \Sigma^n f(i) + \lambda \Sigma^n g(i, j)$, we understand by a 'partition' of the r th-order eigenfunction a finite decomposition into eigenfunctions of subsystems $H(n_1)$, $n_1 < n$.

Under the assumption of 'strict non-degeneracy', we prove the existence of a 'partition' for the second-order eigenfunction $\psi^{(2)}(n)$. The components are $\psi^{(2)}(n_1 = 2)$, $\psi^{(2)}(n_1 = 3)$, $\psi^{(1)}(n_1 = 2)$; they belong to the (highly excited) two- and three-electron states which arise by multiple ionisation of the given n -electron state. The smallest system such that $\psi^{(2)}(n)$ possesses a non-trivial 'partition' has four electrons.

1. Introduction

The quantum mechanical eigenvalue problem for a system of n electrons is related in a natural way to the eigenvalue problems arising from the subsystems with less than n electrons. (The 'subsystems' are obtained by removing electrons from the original system.) This relationship does not exist for the entire n -electron eigenfunction $\psi(n)$ nor the entire energy $E(n)$, but only for their coefficients in the perturbation expansion with respect to powers of the electron interaction

$$G = \sum_{i < j}^n g(i, j). \quad (1)$$

Only the perturbation expansion is able to expose this structure in terms of subsystems and to express it in the form of mathematical statements. We are primarily interested in that partitioning of the n -electron Hamiltonian where no screening potential is used, i.e. where $g(i, j) = 1/r_{ij}$. For the mathematical treatment the more general assumption (1) suffices.

It is true that the well known 'cluster expansions' (Sinanoğlu 1963, Primas 1865) are guided by the same physical idea of a description in terms of subsystems. However, a cluster expansion is applied to the *entire* eigenfunction $\psi(n)$ and is a more practical method of extracting parts of $\psi(n)$ having some desired product structure. Since such an expansion always contains a remainder term depending on the cluster of all n electrons, the *existence* of the expansion is obvious and the component functions in it can be fixed by various additional requirements.

The diagrammatic many-body theory (Brueckner 1955, Goldstone 1957, Lindgren and Morrison 1982), on the other hand, although it is a perturbation expansion in

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powers of G , chooses a very special procedure for representing the n -particle quantities. Only one-particle states are used, so that no account is taken of any subsystems other than the one-particle subsystem. Sinanoğlu (1961) and Chisholm and Dalgarno (1966) showed that the first-order perturbation eigenfunction $\psi^{(1)}(n)$ for n electrons can be decomposed into a *finite* number of products $\psi_{\pi}^{(1)}(2)\psi_a^{(0)}(1) \dots \psi_b^{(0)}(1)$, where $\psi_{\pi}^{(1)}(2)$ is a two-electron eigenfunction and the $\psi^{(0)}(1)$ are one-electron functions. In this decomposition all component wavefunctions are fully adapted to the underlying physical symmetries so that every product is weighted by a Racah parentage coefficient (Racah 1943, see also Lindgren and Morrison 1982). In a recent paper (Schmidt 1983, to be referred to as I), these natural decompositions (or 'partitions') were defined for the eigenfunction and the energy of any perturbation order r . The 'partition' for the second-order energy was given explicitly.

The problem of whether there exists a partition for every order r and for systems of arbitrary symmetry appears to be complicated and cannot be solved in one step. In the present paper we derive the partition of the second-order eigenfunction $\psi^{(2)}(n)$. Up to now, only a few descriptions of $\psi^{(2)}(n)$ in terms of several-particle components have been given. Musher and Schulman (1968) have found that second-order functions of two and three electrons and first-order functions of two electrons are needed as components. However, they assume these functions to be non-symmetrised and do not relate them to the subsystems. Sanders (1973) discusses the difficulty of using symmetrised components.

If the partition of $\psi^{(2)}(n)$ exists, it is a specific decomposition into a finite number of wavefunctions, each of which is 'non-separable' and arises from the perturbation expansion of some eigenstate of an n_1 -electron subsystem (cf definition in I, § 1). The subsystems with $n_1 = 1, 2$ and 3 are needed. We call a function of several one-particle variables 'non-separable' (see I, equation 2.13) if, roughly, it is not possible to express this function in terms of finitely many functions which all depend on fewer than n variables. This assumption ensures that the decomposition contains no arbitrariness, since a component wavefunction can then never be resolved into other components of smaller particle number. We note that other n -electron theories understand by 'separability' the requirement that, when the system is separated into non-interacting subsystems, the energy and the eigenfunction show the correct physical behaviour (Kutzelnigg 1977). Our definition is similar, because it implies separability for the fully antisymmetrised wavefunction of non-interacting subsystems.

The partition of $\psi^{(2)}(n)$ requires each component wavefunction to have the complete physical symmetry of the respective subsystem. For this reason, the solution will be easiest for an n -electron Hamiltonian which has none but permutational symmetry. The eigenfunctions of the total system and of all subsystems must then comply only with the Pauli principle. This paper will therefore be confined to the case of 'strict non-degeneracy' (see I, appendix B), even though this case is hardly ever realised for actual n -electron systems. The closed-shell assumption, which is commonly used in n -electron theory as a simplification, would guarantee non-degeneracy only for the eigenvalue $E^{(0)}(n)$ of the *total* system. We may however say that our approach is already directed towards the later implementation of angular momentum symmetry because the proof is based on 'parentage expansions' both for the zeroth-order (Racah 1943) and first-order (I, § 4) eigenfunctions.

In § 2 we present the partition for $\psi^{(2)}(n)$. In § 3 we prove that this aggregate of wavefunctions satisfies the second-order perturbation equation and the normalisation condition. In § 4 we illustrate the partition for the four-electron system. In § 5 we

summarise the result and discuss it as a step towards a more general theory of the partitions.

2. The partition of $\psi^{(2)}(n)$

As in I, we consider the n -electron Hamiltonian

$$H(n) = F(n) + \lambda G(n) = H(f, g; n) \tag{2}$$

where

$$F(n) = \sum_{1 \leq i \leq n} f(x_i) \quad G(n) = \sum_{1 \leq i < j \leq n} g(x_i, x_j) \tag{2a, b}$$

and

$$g(x_i, x_j) = |r_i - r_j|^{-1}. \tag{3}$$

x_i denotes space and spin variables for particle i . The one-particle operator f contains the kinetic energy and all forces acting on each electron separately. g is the two-particle interaction; for the derivation below only the 'non-separability' of g is needed. We write an eigenstate of (2) as $\psi(f, g; n)$ or $\psi(n)$ and the corresponding energy as $E(f, g; n)$ or $E(n)$. Their Rayleigh-Schrödinger perturbation expansions are

$$\psi(n) = \psi^{(0)}(n) + \lambda \psi^{(1)}(n) + \lambda^2 \psi^{(2)}(n) + \dots \tag{4}$$

$$E(n) = E^{(0)}(n) + \lambda E^{(1)}(n) + \lambda^2 E^{(2)}(n) + \dots \tag{5}$$

$\psi^{(r)}(n)$ and $E^{(r)}(n)$ satisfy the well known perturbation equations (Hirschfelder *et al* 1964); the equation for the second-order eigenfunction is

$$(F - E^{(0)})\psi^{(2)} + (G - E^{(1)})\psi^{(1)} - E^{(2)}\psi^{(0)} = 0. \tag{6}$$

We assume the total eigenfunction (4) to be fully normalised, i.e. $\langle \psi(n) | \psi(n) \rangle = 1$ for all λ ; therefore $\psi^{(2)}(n)$ satisfies

$$2 \operatorname{Re} \langle \psi^{(0)} | \psi^{(2)} \rangle + \langle \psi^{(1)} | \psi^{(1)} \rangle = 0. \tag{7}$$

A function of n one-particle variables $U(\mathcal{N}) = U(x_1, \dots, x_n)$ is called 'separable' (see I, equation 2.13) if it can be expressed as a *finite* sum of products $U'(\mathcal{N}_1)U''(\mathcal{N}_1)$ (where U' and U'' depend on mutually disjoint (non-trivial) subsets \mathcal{N}_1 and $\bar{\mathcal{N}}_1$ of variables. If $U(\mathcal{N})$ is separable, it can clearly be expressed after similar decompositions of U' , U'' , etc, finally in terms of non-separable functions. $\psi^{(2)}(n)$ is easily seen to be separable for $n \geq 4$ and non-separable for $n = 3$ and $n = 2$ (cf I, table 1).

If, moreover, $\psi^{(2)}(n) = \psi^{(2)}(f, g; n)$ for $n \geq 4$ possesses a 'partition' (see I, p 553) then the non-separable component functions in it can be chosen to have the form of $\psi^{(r_1)}(f, g; n_1)$, $\psi^{(r_2)}(f, g; n_2)$, etc, i.e. to be perturbation eigenfunctions of subsystems of $H(f, g; n)$. It is necessary that $r_1 + r_2 + \dots = r = 2$. So, at most three *types of products* will appear in $\psi^{(2)}(n)$, namely $\psi^{(2)}(n_1)\psi^{(0)}(1)\psi^{(0)}(1) \dots$ for $n_1 = 2$ and 3 and $\psi^{(1)}(2)\psi^{(1)}(2)\psi^{(0)}(1)\psi^{(0)}(1) \dots$ (Compare the first-order eigenfunction $\psi^{(1)}(n)$ which contains just one type of product.) Each of the non-separable components $\psi^{(2)}(3)$, $\psi^{(2)}(2)$, etc, can occur in the partition for finitely many electronic states.

We derive the partition of $\psi^{(2)}(n)$ for the technically simplest case where the zeroth-order eigenvalue $E^{(0)}(n)$ is 'strictly non-degenerate'. This is a requirement to be fulfilled by the one-particle operator f in (2a). f must have so little symmetry that

(i) each of its eigenvalues (orbital energies) e_k , $k \in K$ (K is the configuration being considered) is non-degenerate, i.e. cannot be occupied more than once, (ii) that each sum $e_{k_1} + e_{k_2}$ with $k_1, k_2 \in K$ is a non-degenerate eigenvalue of the two-electron operator $f(x_1) + f(x_2)$, etc. (For the complete definition see I, appendix B.) The strict non-degeneracy of $E^{(0)}(n) = E_K^{(0)}(n)$ implies that the given n -electron state and all of its parent states are uniquely labelled only by their configurations, and that all zeroth-order eigenfunctions (of n and less electrons) are single determinants and need not be adapted to other symmetries.

Theorem. Let $E_K(n)$ be the eigenvalue of $H(f, g; n)$ with n -electron configuration K ($n \geq 2$). Let $E_K^{(0)}(n)$ be strictly non-degenerate. Then the second-order eigenfunction $\psi_K^{(2)}(n)$ has the following partition:

$$\psi_K^{(2)}(x_1, x_2, \dots, x_n) = \mathcal{A}[\phi_3 + \phi_2 + \phi_{2,2}] \quad (8)$$

where

$$\phi_3 = \binom{n}{3} \sum_{\rho \subset K} a(\rho \bar{\rho} K) \psi_\rho^{(2)}(x_1, x_2, x_3) \psi_{\bar{\rho}}^{(0)}(x_4, \dots, x_n) \quad (8a)$$

$$\phi_2 = -(n-3) \binom{n}{2} \sum_{\pi \subset K} a(\pi \bar{\pi} K) \psi_\pi^{(2)}(x_1, x_2) \psi_{\bar{\pi}}^{(0)}(x_3, \dots, x_n) \quad (8b)$$

$$\phi_{2,2} = 3 \binom{n}{4} \sum_{\substack{\pi, \pi' \\ \pi \cap \pi' = \emptyset}} a(\pi \bar{\pi} K) a(\pi' \overline{\pi + \pi'} \bar{\pi}) \psi_\pi^{(1)}(x_1, x_2) \psi_{\pi'}^{(1)}(x_3, x_4) \psi_{\overline{\pi + \pi'}}^{(0)}(x_5, \dots, x_n). \quad (8c)$$

Each component $\psi^{(r)}(\dots)$ arises from the perturbation expansion of some eigenstate of a subsystem $H(f, g; n_1)$, e.g. $\psi_\pi^{(1)}$ and $\psi_\pi^{(2)}$ from the eigenstate $\psi_\pi(2)$ of $H(f, g; 2)$; all $\psi^{(r)}(\dots)$ are antisymmetric with respect to their variables. ρ is a three-electron subconfiguration of K , π and π' are mutually disjoint two-electron subconfigurations of K . A bar indicates the complementary configuration with respect to K (cf I, appendix B). $a(\rho \dots)$ and $a(\pi \dots)$ are the three- and two-particle parentage coefficients; their values are given by I, equation (C6). \mathcal{A} is the antisymmetriser for all n variables.

Remarks. (i) For convenience equations (8a)–(8c) are written in terms of the *separable* zeroth-order functions $\psi_{\bar{\rho}}^{(0)}(n-3)$, etc. In order to correspond precisely to the definition of the partition, one would have to write them explicitly as antisymmetrised products of one-electron states.

(ii) Equation (8) holds for $n \geq 2$. For $n=2$ and $n=3$ one automatically obtains the non-separability of $\psi^{(2)}(n)$ through the integer-valued prefactors in (8a)–(8c).

(iii) The phases of the components $\psi^{(r)}(\dots)$ in equations (8a)–(8c) can be chosen according to a convention similar to that used for $\psi^{(1)}(n)$ (cf I, p 558, remark (2)).

It is important to note that the partition (8) contains no arbitrariness since none of the component functions $\psi^{(2)}(3)$, $\psi^{(2)}(2)$, $\psi^{(1)}(2)$, can be resolved into functions of smaller particle number in the form of a *finite* sum.

3. Proof

We have to prove that the right-hand side of (8) satisfies the perturbation equation (6) and the normalisation condition (7), provided that each of the non-separable components $\psi_\pi^{(2)}(2)$ and $\psi_\rho^{(2)}(3)$ satisfies (6) and (7). The antisymmetry of the right-hand

side of (8) is obvious. We describe here only the method for treating the perturbation equation; the procedure for proving the normalisation is similar.

The various n -electron expressions in (6) will be decomposed into sums over three- and two-electron configurations such that we arrive at (15). We make use of the partitions of $E^{(1)}$, $E^{(2)}$ and $\psi^{(1)}$, and of the parentage expansions of $\psi^{(0)}$ and $\psi^{(1)}$ from I. $\psi^{(0)}$ and $\psi^{(1)}$ are also applied in the forms to be given by (9) and (10). We use the following simplified notation. Since in all products of wavefunctions the variables appear in the order x_1, x_2, \dots, x_n , it suffices to indicate the configuration (and thus the particle number) of each factor, e.g. $\psi_\rho^{(1)}\psi_{\bar{\rho}}^{(0)}$ stands for $\psi_\rho^{(1)}(x_1, x_2, x_3)\psi_{\bar{\rho}}^{(0)}(x_4, \dots, x_n)$. Where indication of the variables is necessary, they appear as $1, 2, \dots, n$ instead of x_1, x_2, \dots, x_n . Further let

$$a(\lambda\bar{\lambda}K) = a_\lambda \quad a(\pi\bar{\pi}K) = a_\pi \quad a(\rho\bar{\rho}K) = a_\rho$$

and

$$\binom{n}{3} = \alpha \quad -(n-3)\binom{n}{2} = \beta \quad \binom{n}{2} = \gamma.$$

We have

$$\psi_K^{(0)} = \binom{n}{n_1} a_\lambda \mathcal{A}[\psi_\lambda^{(0)}\psi_{\bar{\lambda}}^{(0)}] \quad (9)$$

where $1 \leq n_1 \leq n-1$ and λ stands for some fixed n_1 -electron subconfiguration of K . Compare with I, equation (C8).

$$\psi_K^{(1)} = \mathcal{A} \left[\alpha \sum_{\pi \subset \rho \subset K} a_\rho \psi_\rho^{(1)}\psi_{\bar{\rho}}^{(0)} + \beta a_\pi \psi_\pi^{(1)}\psi_{\bar{\pi}}^{(0)} + \gamma a_\pi \psi_\pi^{(0)}\psi_{\bar{\pi}}^{(1)} \right] \quad (10)$$

where π is some fixed two-electron subconfiguration of K . The sum runs over all three-electron configurations $\rho \subset K$ which comprise π ; this sum has $(n-2)$ terms. All parentage coefficients a_π , etc, are those defined by (I, (C6)). The expansions (9) and (10) are counterparts of the parentage expansions (I, (C5)) and (I, (4.7)), respectively. These earlier ones leave a particular set of one-electron variables fixed (cf I, § 4); the present ones leave a set of one-electron states, i.e. a subconfiguration of K , fixed.

The first expression on the left-hand side of (6) may be decomposed as follows:

$$\begin{aligned} [F - E_K^{(0)}]\psi_K^{(2)} &= \mathcal{A}\alpha \sum_\rho a_\rho [F(1, 2, 3) - E_\rho^{(0)}]\psi_\rho^{(2)}\psi_{\bar{\rho}}^{(0)} \\ &+ \mathcal{A} \sum_\pi a_\pi [F(1, 2) - E_\pi^{(0)}][\beta\psi_\pi^{(2)}\psi_{\bar{\pi}}^{(0)} + \gamma\psi_\pi^{(1)}\psi_{\bar{\pi}}^{(1)}] \end{aligned} \quad (11)$$

where $\psi_K^{(2)}$ symbolises the right-hand side of (8). The third part of (11) (containing γ) is obtained using the partition of $\psi_{\bar{\pi}}^{(1)}$ and the relation (I, (C10)) between two-particle parentage coefficients.

Using the parentage expansion (I, (4.7)) one finds

$$G\psi_K^{(1)} = \mathcal{A}\alpha \sum_\rho a_\rho G(1, 2, 3)\psi_\rho^{(1)}\psi_{\bar{\rho}}^{(0)} + \mathcal{A} \sum_\pi a_\pi g(1, 2)[\beta\psi_\pi^{(1)}\psi_{\bar{\pi}}^{(0)} + \gamma\psi_\pi^{(0)}\psi_{\bar{\pi}}^{(1)}]. \quad (12)$$

The partition (I, (3.3)) for $E_K^{(1)}$, as well as for $E_\rho^{(1)}$, together with (10) lead to

$$E_K^{(1)}\psi_K^{(1)} = \mathcal{A}\alpha \sum_\rho a_\rho E_\rho^{(1)}\psi_\rho^{(1)}\psi_{\bar{\rho}}^{(0)} + \mathcal{A} \sum_\pi a_\pi E_\pi^{(1)}[\beta\psi_\pi^{(1)}\psi_{\bar{\pi}}^{(0)} + \gamma\psi_\pi^{(0)}\psi_{\bar{\pi}}^{(1)}]. \quad (13)$$

The partition of $E_K^{(2)}$, (I, (5.2)), together with (9) for $n_1 = 3$ and 2 give

$$E_K^{(2)} \psi_K^{(0)} = \mathcal{A} \left[\alpha \sum_{\rho} a_{\rho} E_{\rho}^{(2)} \psi_{\rho}^{(0)} \psi_{\rho}^{(0)} + \beta \sum_{\pi} a_{\pi} E_{\pi}^{(2)} \psi_{\pi}^{(0)} \psi_{\pi}^{(0)} \right]. \tag{14}$$

Let $L_K^{(2)}(1, \dots, n)$, $L_{\rho}^{(2)}(1, 2, 3)$, $L_{\pi}^{(2)}(1, 2)$ denote the left-hand side of (6), taken for the respective n -, three- or two-particle state and $L_{\pi}^{(1)}(1, 2)$ denote the left-hand side of the first-order equation (I, (2.7)) for this two-particle state. Then equations (11)–(14) yield

$$L_K^{(2)}(1, 2, \dots, n) = \mathcal{A} \left[\alpha \sum_{\rho} a_{\rho} L_{\rho}^{(2)}(1, 2, 3) \psi_{\rho}^{(0)}(4, \dots, n) + \beta \sum_{\pi} a_{\pi} L_{\pi}^{(2)}(1, 2) \psi_{\pi}^{(0)}(3, \dots, n) + \gamma \sum_{\pi} a_{\pi} L_{\pi}^{(1)}(1, 2) \psi_{\pi}^{(1)}(3, \dots, n) \right]. \tag{15}$$

Since, according to the assumption, each component wavefunction satisfies its perturbation equation, the individual $L_{\rho}^{(2)}$, $L_{\pi}^{(2)}$ and $L_{\pi}^{(1)}$, and thus $L_K^{(2)}$, vanish (which was to be proved).

4. Example: the partition of $\psi^{(2)}(n = 4)$

We wish to consider in detail the partition (8) for the ground state of the four-electron system. $n = 4$ is the smallest particle number such that $\psi^{(2)}(n)$ has a non-trivial partition. At the same time, the ($n = 4$) partition exhibits already all product structures that appear in the general case.

The Hamiltonian of the system is now $H(f, g; 4)$; see equation (2). Its ground state has the configuration $K = (1, 2, 3, 4)$, i.e. in zeroth order the electrons occupy the four lowest one-particle levels, as in figure 1. (Because of the assumed ‘strict non-degeneracy’ these levels cannot be occupied more than once.) The term (8a) in the partition (8) involves the three-electron ‘parent states’. Each of these belongs to a configuration $\rho = (k_1, k_2, k_3) \subset K$. There are four such states. They result from the removal (ionisation) of an electron from level 1, 2, 3 or 4. $\rho = (1, 2, 3)$ is the ground state, the others being different excited states of $H(f, g; 3)$. Similarly, the terms (8b) and (8c) in the partition refer to the six possible two-electron ‘parent states’ labelled by $\pi = (k_1, k_2) \subset K$. Table 1 lists all of these three- and two-particle configurations

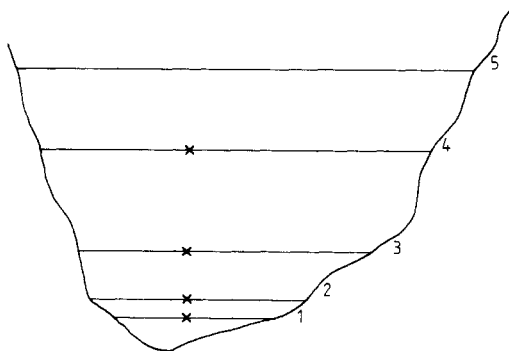


Figure 1. Ground state (in zeroth perturbation order) of the four-electron system for the case of strict non-degeneracy. The three- and two-electron parent states result by removing one or two electrons, respectively.

Table 1. Three- and two-electron subconfigurations of $K = (1, 2, 3, 4)$ which arise in the partition (16).

ρ	$\bar{\rho}$	ε_ρ	π	$\bar{\pi}$	ε_π
(1, 2, 3)	(4)	+1	(1, 2)	(3, 4)	+1
(1, 2, 4)	(3)	-1	(1, 3)	(2, 4)	-1
(1, 3, 4)	(2)	+1	(1, 4)	(2, 3)	+1
(2, 3, 4)	(1)	-1	(2, 3)	(1, 4)	+1
			(2, 4)	(1, 3)	-1
			(3, 4)	(1, 2)	+1

together with their complements $\bar{\rho} = K \setminus \rho$ and $\bar{\pi} = K \setminus \pi$, respectively, and gives the sign $\varepsilon_\rho, \varepsilon_\pi$ of the appropriate parentage coefficient. (The values of the parentage coefficients follow from (I, (C6)).) Thus the partition of the second-order four-electron eigenfunction is

$$\psi_K^{(2)}(x_1, \dots, x_4) = \mathcal{A} \left[2 \sum_\rho \varepsilon_\rho \psi_\rho^{(2)}(x_1, x_2, x_3) \psi_{\bar{\rho}}^{(0)}(x_4) - \sqrt{6} \sum_\pi \varepsilon_\pi \psi_\pi^{(2)}(x_1, x_2) \right. \\ \left. \times \psi_{\bar{\pi}}^{(0)}(x_3, x_4) + \frac{1}{2} \sqrt{6} \sum_\pi \varepsilon_\pi \psi_\pi^{(1)}(x_1, x_2) \psi_{\bar{\pi}}^{(1)}(x_3, x_4) \right]. \tag{16}$$

5. Discussion

In this paper we have proved the following mathematical statement. The second-order eigenfunction $\psi^{(2)}(n)$ of an *n*-electron system can be decomposed without remainder into a finite number of eigenfunctions belonging to the subsystems of one, two and three electrons. (These subsystems arise by removing electrons from the original system.) This decomposition ('partition') involves the 'parent states' (Racah 1943) of the given *n*-electron state, namely *n* orbitals, $\binom{n}{2}$ two-electron states (of first and second order) and $\binom{n}{3}$ three-electron states (of second order).

The present form and derivation of the partition assumes strict non-degeneracy. For the more general (and more practical) case where degeneracy of the parent states arises, one would expect the following.

The *structure* of the partition remains the same as in equations (8)-(8c) and the only thing to be altered is the labelling of the electronic states. This also means altered labels and values for the parentage coefficients. Quantum numbers like spin and orbital angular momentum will be needed in addition to the mere configurations appearing now. In order to *prove* the generalised partition, however, one must proceed carefully since different types of degeneracy (cf Kutzelnigg and Smith 1968) will have to be considered individually.

Starting from the partition of $\psi^{(2)}(n)$, equation (8), one can set up the partition of the *third-order energy* $E^{(3)}(n)$. (This is to be published shortly.) The components are the third-order energies $E^{(3)}(n_1)$ of all parent states of $n_1 = 4, 3$ and 2 electrons. These results indicate that a partition is likely to exist for each of the quantities $\psi^{(r)}(n)$ and $E^{(r)}(n)$ of any order *r*. This would be an important mathematical and physical aspect of the perturbation theory of *n*-electron systems which heretofore has been dealt with almost exclusively in the specialised form of the diagrammatic expansions.

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References

- Brueckner K A 1955 *Phys. Rev.* **100** 36-45
Chisholm C D H and Dalgarno A 1966 *Proc. R. Soc. A* **292** 264-71
Goldstone J 1957 *Proc. R. Soc. A* **239** 267-79
Hirschfelder J O, Byers Brown W and Epstein S T 1964 *Adv. Quantum Chem.* **1** 255-374
Kutzelnigg W 1977 *Methods in electronic structure theory* ed H F Schaefer (New York: Plenum) pp 129-88
Kutzelnigg W and Smith V H Jr 1968 *Int. J. Quantum Chem.* **2** 531-52
Lindgren I and Morrison J 1982 *Atomic many-body theory* (Berlin: Springer)
Musher J I and Schulman J M 1968 *Phys. Rev.* **173** 93-107
Primas H 1965 *Modern Quantum Chemistry, Istanbul Lectures* vol 2, ed O Sinanoğlu (New York: Academic)
Racah G 1943 *Phys. Rev.* **63** 367-80
Sanders F C 1973 *Phys. Rev. A* **7** 1870-5
Schmidt H M 1983 *Int. J. Quantum Chem.* **24** 551-70
Sinanoğlu O 1961 *Phys. Rev.* **122** 493-9
— 1963 *Adv. Chem. Phys.* **6** 315-412, §§ 9-12