



## Molecular Physics

An International Journal at the Interface Between Chemistry and Physics

ISSN: 0026-8976 (Print) 1362-3028 (Online) Journal homepage: <http://www.tandfonline.com/loi/tmph20>

# The history and evolution of configuration interaction

ISAIAH SHAVITT

To cite this article: ISAIAH SHAVITT (1998) The history and evolution of configuration interaction, *Molecular Physics*, 94:1, 3-17

To link to this article: <https://doi.org/10.1080/002689798168303>



Published online: 06 Dec 2010.



Submit your article to this journal [↗](#)



Article views: 287



View related articles [↗](#)



Citing articles: 21 View citing articles [↗](#)

# The history and evolution of configuration interaction

By ISAAH SHAVITT

Department of Chemistry, Ohio State University, Columbus, OH 43210-1185, USA

The configuration interaction (CI) method dates back to the earliest days of quantum mechanics, and is the most straightforward and versatile approach for dealing with electron correlation. The earliest applications typically involved 2–10 terms, while modern molecular CI calculations often employ many millions of configuration state functions (CSFs). In addition to the enormous increase in computer power over the last fifty years, many theoretical developments have contributed to the evolution of the CI approach, including the development of efficient algorithmic tools for the various computational steps and the exploration and optimization of the choices of basis sets, orbitals, and the structure of the CI expansion. Among the milestones in these developments have been the introduction of efficient matrix eigenvalue methods, the introduction of multireference CI expansions, the formulation of various corrections and modifications to overcome the major fault of CI, its lack of extensivity, and particularly the introduction of direct CI, which greatly increased the length of accessible CI expansions by eliminating the need to store the Hamiltonian matrix. Unitary group and related methods have helped make direct CI calculations particularly efficient. Specialized computer programs for full CI calculations have become very efficient and are producing benchmark results which are extremely useful for evaluating other methodologies. Although it has lost ground to the very attractive coupled cluster methods, CI still has an important role to play in quantum chemistry.

## 1. Origins

Configuration interaction (CI) is the most straightforward and general approach for the treatment of electron correlation in atoms and molecules. If we interpret the term in a very broad sense, as applying to any linear expansion of the wavefunction in which the linear coefficients are determined by the Ritz variational approach [1], then the earliest *ab initio* CI calculations would probably be Kellner's 1927 calculations for He and  $\text{Li}^+$  [2], using a four-term expansion in functions of the lengths of the two vectors from the nucleus to the electrons and of the angle between the vectors. A similar 11-term expansion for He was reported by Hylleraas in 1928 [3]. This latter paper included a calculation using a six-term expansion in products of radial functions of the two electrons, presumably the first *ab initio* CI calculation in a narrower sense, not involving interelectron coordinates. These were followed by new Hylleraas treatments of the He atom in 1929 and 1930 [4], using the interelectronic distance instead of the intervector angle as one of the coordinates, and the similar treatment of the  $\text{H}_2$  molecule by James and Coolidge in 1933 [5]. The broad definition would also include some valence bond (VB) calculations, such as the 1933 'VB + ionic' treatment of  $\text{H}_2$  by Weinbaum [6], which is equivalent to a minimal basis molecular orbital-based CI calculation, and the 1936 VB + ionic treatment of  $\text{H}_3$

by Hirschfelder, Eyring, and Rosen [7]. However, in modern usage the name configuration interaction is applied only to linear expansions of the wavefunction in terms of Slater determinants or in terms of 'configuration state functions' (CSFs), which are spin- and symmetry-adapted linear combinations of Slater determinants. The rest of this review deals with CI in this restricted sense.

The term configuration interaction (CI) and its variations were introduced in atomic electronic structure theory to deal with electronic states which could not be characterized adequately by single-configuration wavefunctions, and implied perturbation of an electronic configuration by neighbouring configurations. Two key papers with the same title, 'The theory of complex spectra', provided the initial framework for the treatment of atomic electronic states. The first, a 1929 paper by Slater [8], introduced the Slater determinant and showed how to derive multiplet structures originating in given electron configurations. It also showed how to calculate some matrix elements between Slater determinants, and derived electronic term energies expressed in terms of radial integrals. The second paper, by Condon [9], appeared in 1930. It completed the derivation of the rules (now known as the Slater–Condon rules) for the calculation of Hamiltonian matrix elements between pairs of Slater determinants con-

structed from a set of orthonormal orbitals, and extended Slater's treatment to include the 'interaction of neighbouring configurations'.

Early applications of the theory treated the Slater radial integrals as adjustable parameters, determining their values by least-squares fitting to reproduce spectroscopic line positions. Two 1933 papers of this type included the terms 'interaction of configurations' [10] and 'configuration interaction' [11] in their titles.

## 2. The early years

An early five-configuration *ab initio* CI calculation on  $H_2$ , using elliptical orbitals, was reported by Nagamiya [12] in 1936. A two-configuration CI calculation with numerically determined orbitals on the excited  $^2P$  state of  $O^+$ , using the  $2s^2 2p^3$  and  $2p^5$  configurations, was reported by Hartree, Hartree and Swirles [13] in 1939. That work included the first *ab initio* MCSCF calculation, and compared the use of orbitals optimized specifically for the two-configuration wavefunction with the use of single-configuration SCF orbitals in the same two-configuration wavefunction. Hartree disliked the name configuration interaction because of its perturbation theory implications, and introduced the alternative name 'superposition of configurations'.

Before the introduction and wide-spread use of Gaussian-type (GTO) basis functions, *ab initio* calculations for polyatomic molecules were hampered by the difficulty of calculating multicentre integrals over Slater-type (STO) basis functions. Some  $\pi$ -electron CI calculations were carried out with integral approximations in the late forties and early fifties. A two-configuration calculation on several electronic states of ethylene was reported by Parr and Crawford [14] in 1948, and included a study of the variation in the energy with twisting of the  $CH_2$  groups. A calculation on six  $\pi$ -electron states of benzene, using up to six CSFs per state and ignoring all multicentre integrals, was reported in 1950 by Craig [15]. A more elaborate treatment of benzene, this time using the Sklar approximation [16] for the multicentre integrals, covering 14 electronic states and using 3–12 CSFs per state, was reported later that year by Parr, Craig and Ross [17].

Fully *ab initio* CI calculations involving more than two electrons started appearing in increasing numbers in the fifties. In 1950 appeared the first of a series of papers by Boys developing general procedures for CI calculations and applying them to several atoms and molecules. The first paper [18] included the proposal for the use of Gaussian basis sets in molecular calculations. The second paper in this series [19] appeared in the same year, and reported a calculation on the ground state of the Be atom using 10 CSFs with a (3s1p) STO-basis. In 1952, following several methodological papers

dealing mostly with procedures for vector coupling and matrix element calculations for atoms, appeared a paper by Bernal and Boys [20] reporting CI calculations on the ten-electron series  $Na^+$ , Ne, and  $F^-$ . This work used a quite respectable STO basis set, (5s4p1d), significantly larger than any that had been attempted up to that time, and included 17 CSFs. It was followed in 1953 by two papers by Boys reporting calculations on three electronic states of Be [21] using a (4s4p2d) basis and 7–13 CSFs per state, and calculations on three states of boron and five states of carbon [22] using a (4s4p1d) basis and 12–18 CSFs per state. Among other atomic CI calculations in the early fifties we note the calculations on He by Taylor and Parr [23] in 1952 and by Shull and Löwdin [24] in 1955. The latter paper used an expansion in terms of natural spin orbitals.

An early molecular CI calculation was the 1951 treatment of linear symmetric  $H_3$  by Walsh and Matsen [25], who used a minimal STO basis and three of the four CSFs which can contribute to the ground state in this case. It was followed in 1953 by a calculation on HF with a minimal STO basis and 6 CSFs by Kastler [26], and a calculation on two states of the open-shell  $O_2$  molecule by Meckler [27], using a minimal GTO basis and 9–12 CSFs. Meckler used a computer (the Whirlwind at Massachusetts Institute of Technology) for the solution of the matrix eigenvalue problem, but the rest of the work was done with desk calculators.

Another series of atomic CI calculations was reported by Boys and Price [28] in 1954. These calculations, on ground and excited states of Cl,  $Cl^-$ , S, and  $S^-$ , used a (6s5p2d) STO basis and 23–32 CSFs per state, included relativistic corrections, and obtained very good results for excitation energies and electron affinities. The electronic computer EDSAC was used for the calculation of the basis set integrals and the integral transformations.

Reports of molecular CI calculations started appearing in increasing numbers in the mid fifties. Among these was a minimal-STO-basis calculation on  $H_2O$  by Ellison and Shull [29] using three CSFs, and extended-STO-basis calculations on BH,  $H_2O$  and  $H_3$  reported by Boys and co-workers [30] in 1956. These latter calculations were fully automated, using the EDSAC computer for symbolic manipulations and formula derivations as well as numerical computations. Several minimal-STO-basis CI calculations were reported in 1957 and 1958, including an  $NH_3$  calculation by Kaplan [31] using 13 CSFs, a treatment of several states of  $O_2$  and  $O_2^-$  by Kotani and co-workers [32], full-valence CI calculations for ten electronic states of BH by Ohno [33], and a series of calculations for several states of CH, NH and OH by Krauss and Wehner [34], using 8–18 CSFs per state.

We close this survey of early CI calculations by mentioning the landmark calculation on three states of  $\text{CH}_2$  by Foster and Boys, reported at the first Boulder conference on theoretical chemistry in 1959 and published in 1960 [35]. That calculation obtained bending potential energy curves for the  $^3\text{B}_1$ ,  $^1\text{A}_1$  and  $^1\text{B}_1$  states, and was the first to show a bent ground-state geometry for this radical.

### 3. Infrastructure development

A ‘conventional’ CI calculation involves the following computational steps [36]

- (i) calculation of basis set integrals;
- (ii) determination of orbitals, e.g., by an SCF calculation;
- (iii) transformation of basis set integrals to orbital integrals;
- (iv) calculation and storage of the Hamiltonian matrix elements;
- (v) solution of the matrix eigenvalue problem for the desired state.

Also, procedures for spin- and symmetry-adaptation of the CSFs have to be chosen, and methods for the calculation of Hamiltonian matrix elements between the CSFs have to be implemented [36]. In addition, several choices need to be made for each calculation [36]

- (a) Choice of the basis set;
- (b) choice of the type of orbital to use (e.g., SCF, MCSCF, or natural orbitals);
- (c) choice of the configuration state functions (CSFs) to include in the CI expansion.

Before *ab initio* CI calculations could be carried out efficiently and routinely, effective algorithmic tools had to be developed for the computational steps, and the various choices had to be explored and optimized. We shall not discuss basis set integral calculation, since it is common to all algebraic *ab initio* methods, and shall touch upon only aspects of basis set choice which are particularly relevant to correlated calculations. Matrix element calculation will be considered only as part of the issues of spin and symmetry adaptation. The other choices and computational steps will be discussed in the next few subsections.

#### 3.1. Structure of the configuration interaction expansion

In the early CI calculations, such as those discussed in the previous section [12–35], the number of CSFs included in the CI expansion was very small, and these CSFs were generally selected individually on the basis of physical considerations or by trial and error. More systematic choices became possible as computer power increased and theoretical methods improved.

The ideal CI calculation would be ‘full CI’ (FCI), in which the full many-electron function space of the appropriate spin and symmetry generated by the basis set is used in the wavefunction expansion. Such a calculation provides the most complete solution of the non-relativistic Schrödinger equation within that function space, but is rarely feasible, because the number of CSFs in FCI goes up factorially with the basis set size. Therefore in most applications it is necessary to truncate the CI expansion space in some way to make the calculation practical. Nevertheless, a substantial number of FCI calculations of progressively increasing size have been reported [37–49] and are extremely useful as benchmarks for the assessment of various correlation methods.

Most configuration interaction expansions can be classified as single reference (SRCI) or multireference (MRCI). In the first case, the expansion is based on one dominant CSF, usually the Hartree–Fock configuration constructed from the SCF orbitals, and includes CSFs on the basis of their ‘excitation level’, i.e., the number of electrons occupying orbitals which are empty in the Hartree–Fock configuration [50, 51]. For practical reasons, such calculations usually are limited to single and double excitations (CISD, or SR-CISD), though higher excitations have been included in some cases (see, e.g., Sherrill and Schaefer [52]). In the multireference case, the expansion is based on a set of ‘reference configurations’ [53–56] and again the most common approach is to limit the expansion to single and double excitations (MR-CISD), i.e., to CSFs which are no more than doubly excited with respect to at least one of the reference CSFs. In both single-reference and multireference expansions, excitations from inner-shell orbitals usually are omitted (‘frozen-core CI’), since they contribute little to the description of chemical processes, and since a meaningful treatment of inner-shell correlation requires a greatly expanded basis set [57].

In early MRCI applications, very few reference CSFs were used, and these were chosen individually, on the basis of physical considerations, such as the proper description of dissociation or of a set of electronic states [56], or on the basis of their contributions to the wavefunction or energy, often obtained by perturbation estimates or iteratively in a series of CI calculations [53–55, 58, 59]. In later work more systematic approaches to reference configurations selection were used, mostly based on the idea of an ‘active space’, a set of orbitals having variable occupancy in the reference configurations. Typically, the active space is composed of the valence shell orbitals (corresponding to the molecular orbitals generated from the atomic valence orbitals in a minimal-basis calculation) or a

subset of them. The total orbital space may include all or some of the following subspaces:

- (i) Frozen orbitals (usually inner-shell orbitals), which are doubly occupied in all CSFs;
- (ii) inactive occupied orbitals, doubly occupied in all the reference CSFs but correlated in the MRCI expansion;
- (iii) active orbitals, varying in occupancy between the reference CSFs;
- (iv) virtual (excited) orbitals, unoccupied in any of the reference CSFs, but used in the MRCI expansion;
- (v) discarded orbitals, usually of very high orbital energy, which are completely left out of the CI expansion.

A highly desirable, but not always practical, form of the reference space is the ‘complete active space’ (CAS) [60] which consists of a full CI expansion within the active orbitals. However, when all the valence orbitals are included in the active space [61], the CAS is often quite large and generates an impractically large number of CSFs in the MRCI expansion. Effective alternatives include the ‘restricted active space’ (RAS) [42, 62], in which occupancy restrictions are placed on various subsets of the active orbitals, and the GVB-type active space, generated from a generalized valence bond form of the wavefunction [63, 64].

The number of CSFs in the MRCI expansion sometimes is reduced by systematic restrictions, such as limitation to CSFs which have nonzero Hamiltonian matrix elements with at least one reference CSF (interacting-space limitation [55, 65]), or by individual selection methods. An MRCI calculation with a complete valence active space and all CSFs with up to one electron or up to two electrons in the virtual orbitals space is sometimes referred to as ‘first-order CI’ (FOCI) or ‘second-order CI’ (SOCI), respectively [52, 66] though these names are misleading, since this type of expansion does not consist of the set of terms that contributes to the corresponding order of the perturbation theory wavefunction or energy. Individual selection, in which CSFs are screened and selected on the basis of approximate energy contribution [20–22, 36, 51, 53, 54, 58, 59, 67, 68] (usually estimated by perturbation-based methods) were quite common in conventional CI, in which the Hamiltonian matrix was computed in a systematic order and stored before the eigenvalue computation. In the modern ‘direct CI’ approach, in which matrix elements are calculated as part of each iteration of the eigenvalue determination, particularly as used on vector computers, individual configuration selection usually is not employed, because it interferes with the smooth flow of the calculation.

### 3.2. Spin adaptation

A variety of approaches has been used for the construction of complete sets of  $S^2$  eigenfunctions and for the calculation of Hamiltonian matrix elements between them. The principal approaches can be classified as follows.

Symmetric group methods, which were pioneered by Wigner [69], Weyl [70], Dirac [71] and Waller and Hartree [72], and developed further by Serber [73], Yamanouchi [74], Kotani *et al.* [75], Matsen [76], Ruedenberg [77], and others.

Projection operator methods (Löwdin [78]), including genealogical construction (see, e.g., Pauncz [79]) and the use of ‘Sanibel coefficients’ (Manne [80], Smith and Harris [81]).

‘Bonded functions’, which are Rumer-like pairwise spin couplings [82], introduced in molecular CI calculations by Boys and Reeves (see Reeves [83]) and independently by Sutcliffe [84] and by Cooper and McWeeny [85].

Unitary group methods, introduced in quantum chemistry by Paldus [86] and adapted for efficient CI calculations by Shavitt [87].

The methods in most common use today are based on the unitary group approach or the related symmetric group approach [88], or else avoid spin adaptation and rely on expansions in terms of Slater determinants. However, it should be remembered that spin and symmetry adaptation are important not just for increased efficiency of the calculation, but also to ensure that the resulting wavefunction describes an electronic state of the desired multiplicity and symmetry type and is not contaminated by contributions of the wrong type.

### 3.3. Spatial symmetry adaptation

Symmetry adaptation is particularly important in atomic calculations. The use of full spin and spatial symmetry in atomic CI calculations can reduce the length of the CI expansion by orders of magnitude compared with expansions in Slater determinants, and is important in focusing the calculation on the desired electronic states and in fully characterizing these states. The process of CSF construction for atomic calculations has been called ‘vector coupling’, and was addressed in the early work on multiplet structure by Wigner [69, 89], Slater [8] and Condon [9], and later for *ab initio* CI calculations by Boys [90], Nesbet [91], Salmon and Ruedenberg [92], Bunge and Bunge [93], Sasaki [94], and Munch and Davidson [95], among others.

Symmetry adaptation is trivial in the case of molecules described by Abelian point-group symmetry. In such cases it is necessary only to use symmetry-adapted

orbitals in the construction of the CSFs, and to limit the CI expansion to terms of the desired overall symmetry. Taking advantage of non-Abelian point group symmetry in molecular CI calculations leads to significant complications, and is often eschewed, settling instead for the use of an Abelian subgroup of the full molecular symmetry group. A procedure for utilizing axial point group symmetry (primarily for  $C_{nv}$  and  $D_{nh}$ ) using complex molecular orbitals was developed by Gershgorin and Shavitt [96] and implemented in a conventional CI program by Pipano and Shavitt [97], but was abandoned in later direct CI programs. Projection operator techniques have been developed for the general case (e.g., Wigner [69], Nesbet [98], Simons and Harriman [99]), but have not seen extensive use.

### 3.4. Basis sets

The basis set requirements of correlated calculations are much more demanding than those for SCF treatments. Here we shall focus only on basis set developments of particular interest for correlated treatments (for a recent review on Gaussian basis sets see Shavitt [100]).

A very important advance in basis set technology for high-level calculations was the introduction of ‘generally contracted’ Gaussian basis sets [101]. General contraction can produce significantly more efficient basis sets than the usual ‘segmented’ contraction, because generally contracted basis functions can be chosen to reproduce atomic Hartree–Fock orbitals or atomic natural orbitals, or other desired choices. Correlated calculations typically expend most of their computational effort in the steps following the basis set integrals evaluation and SCF or MCSCF calculation. Furthermore, the effort in the post-SCF stages increases more steeply with basis set size (typically with the sixth power of the number of basis functions) than does the integral evaluation and SCF effort (which is proportional at most to the fourth power). Therefore it is important to derive the maximum benefit from whatever number of contracted basis functions is used, e.g., by employing larger primitive Gaussian sets as well as general contraction, even at the cost of increased integral computation time.

Two types of generally contracted Gaussian basis set specifically designed for correlated calculations have been introduced in recent years. The first type is the atomic natural orbital (ANO) basis sets introduced by Almlöf and Taylor [102]. A particularly effective variation of this approach is the use of ANO basis sets generated by diagonalizing density matrices averaged over several electronic states of the atoms [103] including, in some cases, states of positive and negative

ions [104, 105]. The other type are the ‘correlation-consistent’ polarized valence basis sets of Dunning and co-workers [106] denoted cc-pV $_x$ Z ( $x = D, T, Q, 5, 6$  for double-, triple-, quadruple-, quintuple- and hexuple-zeta, respectively) and aug-cc-pV $_x$ Z (for basis sets augmented with diffuse functions). The cc basis sets are particularly useful for studying systematic trends with basis set enlargement, and facilitate extrapolation to the limit of a complete basis [107, 108].

It should be understood that basis sets designed for the treatment of valence-shell electron correlation cannot, in general, provide useful descriptions of core-core and core-valence correlation effects. Calculations attempting to correlate all electrons using such valence-type basis sets are not justified, and may even be harmful, since the fraction of core correlation contributions they recover is rather small and not meaningful [57]. Enlarged cc basis sets that include functions useful for the description of core-valence correlation, denoted cc-pCV $_x$ Z, have been added recently [109].

The ANO and cc basis sets provide very satisfactory solutions to the basis set problem, at least in situations in which large enough versions of these sets can be used. With the addition of the extrapolation capabilities it is now possible, in many cases, to distinguish errors due to basis set incompleteness from errors due to limitations of the correlation treatment.

### 3.5. Orbital choices

The configuration state functions in CI expansions are constructed from orbitals which are linear combinations of the basis functions. Most commonly in single-reference CI expansions these are the canonical SCF (Hartree–Fock) orbitals, both occupied and virtual, of the molecule in the electronic state being studied. In open-shell cases, restricted SCF orbitals typically are used, or sometimes orbitals of a closely related closed-shell state. (The use of different orbitals for  $\alpha$  and  $\beta$  spins is rarely advisable in CI calculations.) A common choice in multireference CI expansions are orbitals obtained in corresponding MCSCF calculations.

In general, the results of a CI calculation are invariant to any linear transformation of a set of orbitals which are treated equivalently in the construction of the expansion. For example, in single-reference calculations which include all excitations of a given set of levels (e.g., all single and double excitations, CISD), separate linear transformations of the SCF-occupied and virtual orbitals do not affect the final wavefunction and energy. The same is true of frozen-core calculations with respect to separate linear transformations of the core, occupied valence, and virtual orbitals. The same is true also of multireference CI calculations using a complete-

active-space (CAS) reference space with respect to separate transformations of the inactive-occupied, active, and inactive-virtual orbitals. However, if some of the orbitals are to be discarded or frozen, or if individual CSFs are to be selected for inclusion in the CI expansion, then the choice of the orbital transformation can make a substantial difference [53, 110].

Most attempts to improve upon the SCF orbitals for use in CI calculations focus upon the virtual orbitals. The virtual canonical SCF orbitals are obtained as eigenfunctions of a Fock operator representing an  $N$ -electron potential, rather than the effective  $(N - 1)$ -electron potential acting on the electrons in occupied orbitals. As a result, the lower-energy virtual orbitals tend to be relatively diffuse and not very effective for correlating the electrons in occupied orbitals [53]. In fact, most of the exact virtual Hartree–Fock orbitals (as would be obtained in numerical calculations) are continuum orbitals, representing a free electron in the field of the neutral molecule. Modified virtual orbitals obtained in an  $(N - 1)$ -electron potential have been used by Kelly [111] and by Hunt and Goddard [112], and correspond more closely to SCF orbitals occupied in excited states. Other modifications to the virtual orbitals have been developed by Bender and Davidson [113], Huzinaga and Arnau [114], Whitten [115], Luken [116], Cooper and Pounder [117], Bauschlicher [118], Adamowicz and Bartlett [119] and others. Some approaches modified both the occupied and the virtual orbitals, as in Davidson’s ‘internally consistent’ SCF orbitals [120].

An important class of orbital useful in CI calculations is natural orbitals (NOs) [121], usually obtained in a preliminary approximate calculation [122–124] or determined iteratively in a sequence of CI calculations [67]. An expansion in terms of NOs tends to be more compact, in the sense that fewer terms are needed for a given accuracy [110], but unless this property is exploited by orbital set truncation or CSF selection, little is gained. A particularly powerful application of natural orbitals ideas is the ‘pair natural orbitals’ (PNO) approach [125–129], applied most effectively in the ‘self-consistent electron pair’ (SCEP) method [127, 130].

Expansions in terms of localized orbitals [131–133] can lead also to compact wavefunctions [134, 135], particularly for larger molecules, though usually they entail giving up the use of spatial symmetry.

### 3.6. Integral transformation

An important step in a CI calculation (and in most correlated calculations) is the transformation of the one-electron and two-electron basis set integrals to corresponding integrals over the orbitals. While this step

can be avoided or partially avoided in some correlated treatments [126–130, 136, 137] generally it is simplest to formulate the Hamiltonian matrix element calculation in terms of fully transformed orbital integrals.

In the early work of Boys [19], Nesbet [138], and others, when basis sets were very small and computer storage was extremely limited, it was found most convenient to perform the transformation of the two-electron integrals in a two-stage process in which the computational effort was proportional to the sixth power of the basis set size. In later work the more efficient four-stage  $n^5$  process was adopted [36, 139–141], and optimized procedures for its implementation were developed [142–145]. The assembly of the integral matrices prior to the transformation and their reordering between transformation steps were facilitated greatly by the bin sorting method of Yoshimine [146] (see also Bunge and Cisneros [147]).

An interesting variation of the treatment of the integral transformation step is due to Beebe and Linderberg [148] (see also Wilson [149]). Their approach, which is a form of singular-value decomposition, is based on Cholesky decomposition of the two-electron integrals matrix followed by truncation, and was designed to deal with problems of near linear dependence of the basis set and the limited precision of the computer arithmetic.

### 3.7. Matrix eigenvalue problem

Most Hamiltonian matrices that occur in CI calculations are sparse and diagonally dominant. As a result, iterative methods employing simple element-by-element updates based on perturbation theory [19, 150] usually are quite effective, at least for the lowest root. Important advantages of such methods are that they scale as the square of the matrix dimension (instead of the third power for direct methods), that the matrix is not modified, and that space in the computer central memory is required for only one or two vectors at a time. A generalization for several low roots, based on an improved ‘optimal relaxation’ algorithm involving minimization of the Rayleigh quotient [151] was introduced by Shavitt *et al.* [152]. A constraint of these methods is that they require the Hamiltonian matrix to be read in from external storage one row at a time, in sequence. This constraint creates no difficulties in conventional CI treatments, in which the Hamiltonian matrix elements are computed once, in the desired order, and stored on magnetic tape or disk.

An important new approach was introduced by Davidson [153] in 1975. In the spirit of the Lanczos method [154] the Davidson approach is based on an expansion of the desired eigenvector in an accumulating series of trial vectors but, unlike the Lanczos method, it exploits the diagonal dominance of the matrix by

generating the trial vectors by perturbation-based corrections. This method has two important advantages: it allows the calculation of higher roots without requiring the prior calculation of all lower roots, and it does not require that the matrix elements be provided in any particular order. This latter property, which is due to the fact that the principal computational step of the algorithm is simply the multiplication of the matrix into the current estimate of the eigenvector, is particularly important in facilitating direct CI calculations, in which the matrix elements are available in an order dictated by the processing order of the integrals or by related considerations. As a result, the Davidson method now is the standard method for the solution of the matrix eigenvalue problem in CI calculations.

The method of optimal relaxation (MOR) and the Davidson method have been reformulated also for the simultaneous calculation of several roots, resulting in the ‘block MOR’ [155, 156] and ‘block Davidson’ [157] methods. Other modifications of the Davidson method have been proposed [44, 158–165] (see also Davidson [166] and references therein).

#### 4. The new age of big CI: direct CI

An extremely important development, which opened the way for very large CI calculations, was the introduction of direct CI by Roos and Siegbahn [167, 168]. The basic idea of direct CI is the avoidance of the formal, sequential calculation and storage of the Hamiltonian matrix, concentrating instead on the direct calculation of the product of the matrix into the current trial vector in the iterative procedure for the solution of the matrix eigenvalue problem. This product is calculated directly from the one- and two-electron integrals, using ‘coupling coefficients’ which specify the nonzero contributions of each integral to the matrix elements. At first glance this approach may appear to be counter-productive, since the matrix element contributions have to be recomputed in each iteration. However, most nonzero matrix elements have nonzero contributions from only one or two integrals, and the procedure lends itself to very efficient and streamlined operation, with few logical manipulations, resulting in a substantial net gain in speed over conventional CI. Furthermore, this method is extremely easy to adapt to vector computing. The avoidance of Hamiltonian matrix storage removes a significant barrier for very large CI calculations, and the efficiency of the direct CI approach has made such large calculations quite practical.

The original direct CI procedure was developed in a spin-adapted form for single-reference closed-shell CISD calculations, for which the determination of the coupling coefficients was quite easy [167]. Later [168] it was extended to SR-CISD expansions in a deter-

minantal basis for any state and to full CI for three electrons. Subsequent extensions to full CI in a determinantal basis made possible the proliferation of benchmark full CI calculations [37–49], some of them employing several billion determinants [44, 46, 47]. Spin-adapted extensions for single-reference triplet states [169] and for multireference closed-shell cases limited to closed-shell reference CSFs [170] were reported also. The SCEP method [130] also can be considered a form of direct CI.

Generalization of direct CI in a spin-adapted CSF basis to any open-shell state and to multireference CI expansions became possible with the introduction of the unitary group approach [86] (UGA), particularly in its graphical form [87] (GUGA). Several computer programs applying the graphical unitary group approach [171–175] and variations based on the symmetric group [88] and other graphical schemes [176] or related ideas [137, 177] were developed, and together with the introduction of powerful supercomputers, these programs made possible MR-CISD calculations using millions of CSFs (e.g., Kedziora and Shavitt [178]). In recent years, the introduction of parallel computers and the adaptation of several computer programs to take full advantage of their capabilities have facilitated even larger CI calculations. For example, a parallel version of the Columbus program [179] has been used recently to carry out MR-CISD calculations with over two hundred million CSFs [180]. Parallel versions of full CI programs have been used in full CI calculations with over a billion determinants [47].

In comparing determinantal based CI calculations and spin-adapted expansions it is useful to note that in a full CI expansion for  $N$  electrons using  $n$  orbitals, ignoring spatial symmetry, the number of determinants exceeds the number of spin-adapted CSFs by a factor of

$$\frac{n_{\text{det}}}{n_{\text{CSF}}} = \frac{m + S + 1}{2S + 1} \left( 1 - \frac{m - S}{n + 1} \right)$$

where  $m = N/2$  and  $S$  is the total spin quantum number. This ratio is between four and five for most of the full CI calculations reported. For example, the FCI calculation on the Mg atom [44, 46], containing about 2.5 billion determinants in  $D_{2h}$  symmetry, corresponds to about half a billion spin-adapted CSFs.

Another important development in CI methodology is the introduction of ‘contracted’ CI methods, which gain increases in the scope of achievable MRCI calculations at the cost of reduced flexibility in the variational expansion and, therefore, some sacrifice in the energy compared with fully unconstrained expansions. Two different contraction approaches have been introduced, both aimed at reducing the number of independently varied coefficients and thus greatly reducing the size of

the matrix eigenvalue problem. The first, ‘externally contracted’ CI [181] is no longer in use today. It employs a perturbation procedure to fix the relative values of the coefficients in sets of CSFs that share the same internal (active-space) part.

In the more common ‘internally contracted’ CI [129, 182, 183] the multiconfigurational reference function, optimized in an MCSCF calculation, is treated as a single contracted reference configuration, and excited configurations are generated by the application of excitation operators to this contracted function. Each excited configuration is then a linear combination of many ordinary CSFs, with the linear coefficients fixed by the reference wavefunction. As a result, the number of independently varied coefficients is similar to the number of terms in a single-reference calculation. For given numbers of orbitals and electrons, the length of an uncontracted MR-CISD expansion is approximately proportional to the number of reference configurations. Therefore internal contraction can provide a drastic reduction in the length of the CI vector and allow the use of substantially larger reference spaces than would be practical in uncontracted calculations, making the use of complete valence active spaces more affordable. At the same time it should be noted that the reduction in the computational effort is not as drastic as in the length of the CI vector, since the Hamiltonian matrix in contracted CI is not nearly as sparse as for uncontracted expansions.

Usually energy loss due to internal contraction, compared with uncontracted MRCI, is very small [184] and energy differences, such as dissociation energies, are reproduced well [108] but there are some exceptions [108], particularly in the vicinity of avoided crossings in potential energy curves and surfaces, for which the location of the avoided crossing may differ substantially between the reference MCSCF wavefunction and the corresponding MRCI wavefunction. A generalization which overcomes this problem by using more than one multiconfigurational reference function has been reported [185]. The power of the internally contracted CI method is demonstrated, for example, by a recent application to the calculation of a water molecule potential energy surface [186].

### 5. Strengths and weaknesses

The conceptual simplicity of the configuration interaction method is very appealing, and its variational nature is an important advantage, but its principal strength lies in its flexibility and generality. It can be applied straightforwardly to any electronic state, and can be spin- and symmetry-adapted relatively easily. Its multireference formulation is straightforward, and applicable readily to any type of reference space,

complete or otherwise. Apart from the increased size, and therefore increased computational requirements, multireference CI is not notably more difficult than the single-reference form, and the ability to use incomplete active spaces can be employed to limit the computational requirements substantially. As a result, MRCI is usually the method of choice for dealing with non-dynamic electron correlation [187] (reflecting near degeneracies and related effects), including the treatment of bond breaking and potential energy surfaces [188]. In particular, the reference space can be chosen to minimize bias in the description of different regions of a potential energy surface.

The multireference capabilities of CI contrast with the situation in many-body perturbation theory (MBPT) and coupled cluster (CC) theory, for which multireference generalizations are substantially more difficult than their single-reference counterparts and for which the use of incomplete reference spaces introduces additional difficulties. Also, unlike multireference many-body methods, no problems of intruder states arise in MRCI.

The principal weakness of truncated configuration interaction is its lack of proper scaling with the size of the system. The proper scaling of a computational model, referred to as ‘extensivity’ or ‘size extensivity’ [189] is the main facet of the ‘separability condition’ [190, 191]. It can be related to its many-body diagrammatic representation, and is dependent on the absence of ‘unlinked diagram’ contributions in its energy expression (see, e.g., Paldus and Čížek [192], Bartlett and co-workers [189, 193], and Harris *et al.* [194]). In an extensive model such as MBPT or CC, in which the energy is expressed entirely in terms of linked diagrams, the energy of an assembly of non-interacting identical subsystems is proportional to the number of subsystems, and the energy of a uniform system, such as an electron gas, is proportional to its extent. It is obvious, for example, that the CISD energy of a collection of non-interacting helium atoms does not satisfy this requirement, since it provides the full CI energy for a single atom but not for more than one atom. In fact, the CISD energy of such a collection scales as the square root of the number of atoms as this number becomes large [191, 195, 196]. The lack of extensivity also affects the accuracy of computed ionization potentials and electron affinities, unless appropriate corrections are applied.

The energy contribution associated with an unlinked diagram consisting of  $k$  separate parts is proportional to the  $k$ th power of the size of the system, and therefore such contributions must cancel if extensivity is to be maintained. These unlinked diagram contributions do cancel for the exact (full CI) energy, as well as in each order of Rayleigh–Schrödinger perturbation theory and

at each excitation level of a coupled-cluster treatment. However, the unlinked diagram contributions at a given excitation level of CI are cancelled by contributions from other excitation levels, so that unlinked terms remain in a truncated CI energy, resulting in lack of extensivity.

Unlike the energy, which should be additively separable, the wavefunction should be multiplicatively separable [190] and its diagrammatic expansion contains disconnected (but not unlinked) diagrams.† Such diagrams represent disconnected clusters which describe simultaneous independent interactions in smaller clusters of electrons as products of lower-level connected clusters [191]. The most important of these terms are products of double excitations. It is the lack in CISD (but not in its coupled clusters counterpart, CCSD) of the disconnected quadruple excitation contributions deriving from products of double excitations which is its most serious defect, and is responsible for most of its deviation from extensivity. It is this disconnected quadruples contribution for which the various correction formulas for CISD try to compensate.

Another facet of the separability condition is ‘size consistency’ [136, 197]. A computational model is size consistent if, when applied to a molecule dissociated into two or more parts, the energy of the dissociated molecule, treated as one system, equals the sum of the energies of the subsystems computed by the same model. Again, truncated CI fails this test, and as a result, when it is applied naïvely, fails to provide satisfactory dissociation energies and some other energy differences. This deficiency can be reduced by the application of various corrections, as discussed in the next section. Satisfactory dissociation energies also can be obtained by treating the dissociated limit as a ‘supermolecule’, using the same type of CI expansion as for the bound system [198]. In fact, in multireference treatments, this supermolecule approach is the only consistent method for the calculation of dissociation energies and for the asymptotic regions of potential energy surfaces [178].

Extensivity and size consistency, although closely related, are not equivalent [189]. For example, a single-reference many-body correlation treatment built upon a closed-shell restricted Hartree–Fock reference function for a molecule is not size consistent with respect

to dissociation into open-shell fragments, yet usually it satisfies the extensivity criterion because of its linked-diagram energy expression. On the other hand, multi-configurational wavefunctions often can be constructed to be size consistent without being extensive.

Although the use of higher than doubly-excited CSFs in CI expansions is easy in principle, the exponential increase in the size of a CI expansion with the level of excitation usually makes such calculations impractical. Also, the extension of direct CI programs to handle higher excitation CSFs is complicated by the increased complexity of the coupling coefficients determination. As a result of this latter factor, most attempts to include higher excitations [52] or to implement full CI calculations [37–49] use a determinantal formulation.

The difficulty of extending the CI expansion to higher excitations is a serious shortcoming because of its very slow convergence. Unlike the situation in the many-body methods, the connected and disconnected cluster contributions to each excited CSF are inextricably combined in the CI formalism. Thus it is not possible to separate the disconnected cluster wavefunction contributions from the connected cluster contributions at the same overall excitation level. From the quadruple excitations level and up, the disconnected cluster contributions are much more important than the connected terms. Because these contributions are represented by different diagrams, they are separated in the many-body formalism, where the disconnected contributions are much easier to compute than the connected terms, and appear in lower orders of perturbation theory and lower CC excitation levels. As a result, quadruple and higher excitation terms are much more important in CI than in CC. For example, the major CI quadruple excitation contributions that are particularly important for extensivity are obtained in factorizable form at fourth order in MBPT, at relatively low cost, and are included as disconnected cluster terms (as products of double excitations) in the double excitation CC wavefunction [191, 199–204].

The use of a multireference CISD expansion can account for some of the most important contributions arising from higher excitations in single-reference models, but is not sufficient to offset the intrinsic limitation of the truncated CI approach. Furthermore, as previously noted, the length of a multireference CISD expansion is approximately proportional to the number of reference configurations, making the use of a theoretically desirable CAS reference space prohibitively expensive in many cases. While this difficulty can be reduced by the use of incomplete active spaces of various kinds [42, 62, 63, 178] such tactics are not entirely satisfactory, particularly in the treatment of potential energy surfaces.

† Some of the earlier literature does not distinguish properly between the terms ‘unlinked’ and ‘disconnected’. An unlinked diagram contains separate *closed* parts. A disconnected, but linked diagram contains separate *open* parts, but no closed parts. Unlinked diagrams cancel in both the exact energy expression and the exact wavefunction; disconnected diagrams are proper constituents of the exact wavefunction (though they cancel in the coupled cluster *equations*).

## 6. Corrections and modifications

As discussed in the previous section, the principal defect of the configuration interaction method is the lack of extensivity and size consistency of truncated CI expansions. The various approaches that have been used to compensate for this deficiency fall into two classes; the first class applies *post hoc* corrections to CISD results, while the second modifies the CISD algorithm itself.

The *post hoc* corrections often are called ‘quadruples corrections’, because they attempt to account for the disconnected quadruple excitation contributions that are needed to cancel the unlinked diagram components in the CISD energy [203, 205]. They modify the CISD energy, but do not produce a corrected wavefunction or modify derived properties. The best known and most widely used of these are the Davidson correction [206] and its variations [196, 207]. The original Davidson formula tends to overestimate the magnitude of the missing disconnected quadruples contributions to the total energy [208], primarily because it ignores the problem of ‘exclusion-principle-violating’ (EPV) terms [203]. The modified corrections exacerbate the problem because they increase the magnitude of the correction. In fact, while the Davidson correction tends to overestimate the disconnected quadruples contribution, there is nothing in its formulation to account for other missing terms, such as connected triple excitation contributions, and therefore the corrected CISD energy usually lies above the full CI limit. However, such fortuitous and unsystematic cancellation of errors cannot be counted on reliably in the determination of binding energies and other energy differences.

A scale factor that sometimes has been applied to the Davidson corrections is  $(N - 2)/N$  [136, 209], where  $N$  is the number of electrons being correlated. It is designed to eliminate the correction entirely for a two-electron system (for which CISD is equivalent to full CI). A more recently proposed scale factor is  $(N - 2)(N - 3)/[N(N - 1)]$  [210], which eliminates the correction for both two-electron and three-electron systems.

While the Davidson correction was developed originally for single-reference CISD calculations, a straightforward generalization [209] without formal justification, has been applied widely to multireference expansions. Generally it has been successful (e.g., [39–41, 186, 209, 211]), but the name ‘full CI correction’ that sometimes has been applied to it [209] is not appropriate, since it is designed only to deal with one of the various types of contribution missing in an MR-CISD expansion. A more systematic multireference generalization of the Davidson correction was proposed by Jankowski *et al.* [212].

Another popular extensivity correction for SR-CISD is the Pople correction [136]. It was designed to produce exact energies for assemblies of non-interacting two-electron systems, and vanishes automatically for the two-electron case. The performance of two versions of the Davidson correction, with and without scaling, and of the Pople correction has been compared in calculations of binding energies of several complexes by Del Bene and co-workers [198]. Other interesting comparisons of several correction formulas were reported, for example, by Martin *et al.* [213].

The second type of approach for dealing with the extensivity defect of truncated CI involves modifications of the CI procedure itself. The modifications are based on electron-pair concepts [129, 130, 191, 199, 200, 214–216] deriving from coupled cluster ideas. Early attempts to treat pair correlations independently, in the form of the independent electron-pair approximation (IEPA) [191, 199, 200] were not very successful [126–128, 191, 217], and gave way to several versions of the coupled electron-pair approximation (CEPA) [127, 128, 191, 201, 218]. These versions range from CEPA(0) to CEPA(5) [219], depending mainly on the way they try to account for EPV diagram effects. The simplest version, CEPA(0), ignores the EPV problem entirely, and is known also as linearized coupled pair many-electron theory (LCPMET) [201] or the linearized coupled cluster method (LCCM), because it can be obtained by linearization of the coupled cluster doubles (CCD) or singles and doubles (CCSD) equations. The other versions are more complicated, and include in their formulas pair correlation energies obtained by summing sets of double excitation coefficients in the wavefunction expansion.

One limitation of the CEPA method and related approximations is that their energy expression is not obtained by a stationarity condition for an energy functional. While this feature is of no consequence for energy calculations, it is a disadvantage in the analytical calculation of energy derivatives. The alternative ‘coupled pair functional’ (CPF) [220] and ‘modified CPF’ (MCPF) [221] approximations obtain the energy by minimizing a modified energy functional, and have been tested in a number of molecular calculations [39–41].

The CEPA and CPF approximations were derived for single-reference treatments. A multireference generalization of LCCM was derived by Laidig *et al.* [222]. Multi-reference generalizations for several CEPA models were proposed by Fulde and Stoll [223]. A simplified form of CPF applicable to multireference treatments is the ‘averaged coupled pair functional’ (ACPF) of Gdanitz and Ahlrichs [224]. This approach uses a flexible functional form which can be varied to obtain a range

of approximations, including a multireference LCCM. One such variant of the functional, based on the Meissner scale factor idea [210], has been introduced recently under the name ‘averaged quadratic coupled cluster’ (AQCC) approximation [225]. A number of other variants have been proposed by Füsti-Molnár and Szalay [226], who provide interesting comparisons of several models. All these methods are at least approximately extensive in most applications. They maintain the functional stationarity feature of CPF, and thus are convenient in applications in which energy derivatives are to be calculated. The principal algorithmic effect of these various approximations is that they convert the matrix eigenvalue problem to a system of linear equations (for LCCM) or a system intermediate between an eigenvalue problem and a simultaneous equations problem. Comparisons of ACPF and LCCM results with other models in calculations of binding energies of several complexes have been reported [198].

Numerous other analyses and proposed correction formulas and modifications for dealing with the extensivity problem of CI have been published, and only a subset of them can be mentioned here [205, 227–241].

Finally, we mention the  $B_k$  approximation [242] (see Shavitt [243] and references therein), in which the CSFs are divided into a relatively small primary set and a much larger secondary set, and all off-diagonal matrix elements between pairs of secondary CSFs are neglected. It is not strictly an extensivity correction, but it has been used in some cases to estimate triple and quadruple excitation contributions on top of CISD [243].

## 7. Summary

Configuration interaction is a very versatile and powerful *ab initio* method. Aided by the remarkable advances in computers in the last few decades, it has developed and matured to a sophisticated level applicable to many problems and capable of providing useful answers to questions of physical and chemical interest. Although it suffers from some important limitations, notably lack of extensivity and slow convergence, and although it has been supplanted to a considerable extent by modern many-body methods, particularly coupled cluster theory, CI still has an important role to play in molecular electronic structure theory. This situation is likely to prevail at least until multireference coupled cluster methods become more standardized and accessible to the chemistry research community.

Modified CI approaches and configuration-based multireference perturbation theory can also be very useful in the arsenal of computational quantum chemistry methods.

## References

- [1] RITZ, W., 1909, *J. reine angew. Math.*, **135**, 1.
- [2] KELLNER, G. W., 1927, *Z. Phys.*, **44**, 91, 110.
- [3] HYLLERAAS, E. A., 1928, *Z. Phys.*, **48**, 469.
- [4] HYLLERAAS, E. A., 1929, *Z. Phys.*, **54**, 347; Hylleraas, E. A., and UNDHEIM, B., 1930, *Z. Phys.*, **65**, 759.
- [5] JAMES, H. M., and COOLIDGE, A. S., 1933, *J. chem. Phys.*, **1**, 825.
- [6] WEINBAUM, S., 1933, *J. chem. Phys.*, **1**, 593.
- [7] HIRSCHFELDER, J., EYRING, H., and ROSEN, N., 1936, *J. chem. Phys.*, **4**, 121.
- [8] SLATER, J. C., 1929, *Phys. Rev.*, **34**, 1293.
- [9] CONDON, E. U., 1930, *Phys. Rev.*, **36**, 1121.
- [10] BACHER, R. F., 1933, *Phys. Rev.*, **43**, 264.
- [11] UFFORD, C. W., 1933, *Phys. Rev.*, **44**, 732.
- [12] NAGAMIYA, T., 1936, *Proc. phys.-math. Soc. Jap.*, **18**, 497.
- [13] HARTREE, D. R., HARTREE, W., and SWIRLES, B., 1939, *Phil. Trans. R. Soc. Lond. A*, **238**, 229.
- [14] PARR, R. G., and CRAWFORD, B. L., JR., 1948, *J. chem. Phys.*, **16**, 526.
- [15] CRAIG, D. P., 1950, *Proc. R. Soc. Lond. A*, **200**, 474.
- [16] SKLAR, A. L., 1939, *J. chem. Phys.*, **7**, 984.
- [17] PARR, R. G., CRAIG, D. P., and ROSS, I. G., 1950, *J. chem. Phys.*, **18**, 1561.
- [18] BOYS, S. F., 1950, *Proc. R. Soc. Lond. A*, **200**, 542.
- [19] BOYS, S. F., 1950, *Proc. R. Soc. Lond. A*, **201**, 125.
- [20] BERNAL, M. J. M., and BOYS, S. F., 1952, *Phil. Trans. R. Soc. Lond. A*, **245**, 139.
- [21] BOYS, S. F., 1953, *Proc. R. Soc. Lond. A*, **217**, 136.
- [22] BOYS, S. F., 1953, *Proc. R. Soc. Lond. A*, **217**, 235.
- [23] TAYLOR, G. R., and PARR, R. G., 1952, *Proc. Natn. Acad. Sci. USA*, **38**, 154.
- [24] SHULL, H., and LÖWDIN, P.-O., 1955, *J. chem. Phys.*, **23**, 1565.
- [25] WALSH, J. M., and MATSEN, F. A., 1951, *J. chem. Phys.*, **19**, 526.
- [26] KASTLER, D., 1953, *J. Chim. phys.*, **50**, 556.
- [27] MECKLER, A., 1953, *J. chem. Phys.*, **21**, 1750.
- [28] BOYS, S. F., and PRICE, V. E., 1954, *Phil. Trans. R. Soc. Lond. A*, **246**, 451.
- [29] ELLISON, F. O., and SHULL, H., 1955, *J. chem. Phys.*, **23**, 2348.
- [30] BOYS, S. F., COOK, G. B., REEVES, C. M., and SHAVITT, I., 1956, *Nature*, **178**, 1207.
- [31] KAPLAN, H., 1957, *J. chem. Phys.*, **26**, 1704.
- [32] KOTANI, M., MIZUNO, Y., KAYAMA, K., and ISHIGURO, E., 1957, *J. phys. Soc. Jap.*, **12**, 707.
- [33] OHNO, K., 1957, *J. phys. Soc. Jap.*, **12**, 938.
- [34] KRAUSS, M., and WEHNER, J. F., 1958, *J. chem. Phys.*, **29**, 1287.
- [35] FOSTER, J. M., and BOYS, S. F., 1960, *Rev. mod. Phys.*, **32**, 305.
- [36] SHAVITT, I., 1977, *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (New York: Plenum), p. 189.
- [37] HANDY, N. C., 1980, *Chem. Phys. Lett.*, **74**, 280; SAXE, P., SCHAEFER, H. F., III, and HANDY, N. C., 1981, *Chem. Phys. Lett.*, **79**, 202; HARRISON, R. J., and HANDY, N. C., 1983, *Chem. Phys. Lett.*, **95**, 386; **98**, 97.
- [38] KNOWLES, P. J., and HANDY, N. C., 1984, *Chem. Phys. Lett.*, **111**, 315; 1989, *J. chem. Phys.*, **91**, 2396; 1989, *Comput. Phys. Commun.*, **54**, 75; KNOWLES, P. J., 1989, *Chem. Phys. Lett.*, **155**, 513.

- [39] BAUSCHLICHER, C. W., JR., LANGHOFF, S. R., TAYLOR, P. R., and PARTRIDGE, H., 1986, *Chem. Phys. Lett.*, **126**, 436; BAUSCHLICHER, C. W., JR., LANGHOFF, S. R., TAYLOR, P. R., HANDY, N. C., and KNOWLES, P. J., 1986, *J. chem. Phys.*, **85**, 1469; BAUSCHLICHER, C. W., JR., LANGHOFF, S. R., PARTRIDGE, H., and TAYLOR, P. R., 1986, *J. chem. Phys.*, **85**, 3407.
- [40] BAUSCHLICHER, C. W., JR., and TAYLOR, P. R., 1986, *J. chem. Phys.*, **85**, 2779, 6510; 1987, *J. chem. Phys.*, **86**, 858, 1420, 5600; 1987, *Theor. Chim. Acta*, **71**, 263.
- [41] BAUSCHLICHER, C. W., JR., and LANGHOFF, S. R., 1987, *J. chem. Phys.*, **86**, 5595; **87**, 2919, 4665; 1988, *J. chem. Phys.*, **89**, 2116, 4246; BAUSCHLICHER, C. W., JR., LANGHOFF, S. R., and TAYLOR, P. R., *Adv. chem. Phys.*, **77**, 103.
- [42] OLSEN, J., ROOS, B. O., JØRGENSEN, P., and JENSEN, H. J. A., 1988, *J. chem. Phys.*, **89**, 2185.
- [43] ZARRABIAN, S., SARMA, C. R., and PALDUS, J., 1989, *Chem. Phys. Lett.*, **155**, 183; HARRISON, R. J., and ZARRABIAN, S., 1989, *Chem. Phys. Lett.*, **158**, 393.
- [44] OLSEN, J., JØRGENSEN, P., and SIMONS, J., 1990, *Chem. Phys. Lett.*, **169**, 463.
- [45] BENDAZZOLI, G. L., and EVANGELISTI, S., 1993, *J. chem. Phys.*, **98**, 3141; 1993, *Int. J. Quantum Chem. Symp.*, **27**, 287; EVANGELISTI, S., BENDAZZOLI, G. L., and GAGLIARDI, L., 1994, *Chem. Phys.*, **185**, 47; EVANGELISTI, S., and BENDAZZOLI, G. L., 1995, *Nuovo Cimento D*, **17**, 289.
- [46] MITRUSHENKOV, A. O., 1994, *Chem. Phys. Lett.*, **217**, 559.
- [47] EVANGELISTI, S., BENDAZZOLI, G. L., ANSALONI, R., and ROSSI, E., 1995, *Chem. Phys. Lett.*, **233**, 353; EVANGELISTI, S., BENDAZZOLI, G. L., ANSALONI, R., DURÌ, F., and ROSSI, E., 1996, *Chem. Phys. Lett.*, **252**, 437.
- [48] CHRISTIANSEN, O., KOCH, H., JØRGENSEN, P., and OLSEN, J., 1996, *Chem. Phys. Lett.*, **256**, 185.
- [49] OLSEN, J., JØRGENSEN, P., KOCH, H., BALKOVA, A., and BARTLETT, R. J., 1996, *J. chem. Phys.*, **104**, 8007.
- [50] NESBET, R. K., 1958, *Phys. Rev.*, **109**, 1632.
- [51] PIPANO, A., and SHAVITT, I., 1968, *Int. J. Quantum Chem.*, **2**, 741.
- [52] SHERRILL, C. D., and SCHAEFER, H. F., III, 1996, *J. phys. Chem.*, **100**, 6069.
- [53] WHITTEN, J. L., and HACKMEYER, M., 1969, *J. chem. Phys.*, **51**, 5584; HACKMEYER, M., and WHITTEN, J. L., 1971, *J. chem. Phys.*, **54**, 3739; WHITTEN, J. L., 1972, *J. chem. Phys.*, **56**, 5458.
- [54] PEYERIMHOFF, S. D., and BUENKER, R. J., 1972, *Chem. Phys. Lett.*, **16**, 235; BUENKER, R. J., and PEYERIMHOFF, S. D., 1974, *Theor. Chim. Acta*, **35**, 33.
- [55] McLEAN, A. D., and LIU, B., 1973, *J. chem. Phys.*, **58**, 1066; BAGUS, P. S., LIU, B., McLEAN, A. D., and YOSHIMINE, M., 1973, *Computational Methods for Large Molecules and Localized States in Solids*, edited by F. Herman, A. D. McLean, and R. K. Nesbet (New York: Plenum), p. 87.
- [56] KAHN, L. R., HAY, P. J., and SHAVITT, I., 1974, *J. chem. Phys.*, **61**, 3530.
- [57] BAUSCHLICHER, C. W., JR., LANGHOFF, S. R., and TAYLOR, P. R., 1988, *J. chem. Phys.*, **88**, 2540; ALMLÖF, J., DELEEUW, B. J., TAYLOR, P. R., BAUSCHLICHER, C. W., JR., and SIEGBAHN, P., 1989, *Int. J. Quantum Chem. Symp.*, **23**, 345; TAYLOR, P. R., 1992, *Lecture Notes in Quantum Chemistry, Lecture Notes in Chemistry*, Vol. 58, edited by B. O. Roos (Berlin: Springer), p. 325.
- [58] NESBET, R. K., 1955, *Proc. R. Soc. Lond. A*, **230**, 312.
- [59] SHAVITT, I., 1984, *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, edited by C. E. Dykstra (Dordrecht: Reidel), p. 185.
- [60] ROOS, B. O., TAYLOR, P. R., and SIEGBAHN, P. E. M., 1980, *Chem. Phys.*, **48**, 157; ROOS, B. O., 1980, *Int. J. Quantum Chem. Symp.*, **14**, 175.
- [61] RUEDENBERG, K., SCHMIDT, M. W., GILBERT, M. M., and ELBERT, S. T., 1982, *Chem. Phys.*, **71**, 41, 65.
- [62] MALMQVIST, P.-Å., RENDELL, A., and ROOS, B. O., 1990, *J. phys. Chem.*, **94**, 5477.
- [63] HARDING, L. B., and GODDARD, W. A., III, 1975, *J. Am. chem. Soc.*, **97**, 6293; DUNNING, T. H., JR., CARTWRIGHT, D. C., HUNT, W. J., HAY, P. J., and BOBROWICZ, F. W., 1976, *J. chem. Phys.*, **64**, 4755.
- [64] DUNNING, T. H., JR., 1984, *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, edited by C. E. Dykstra (Dordrecht: Reidel), p. 67.
- [65] BUNGE, A., 1970, *J. chem. Phys.*, **53**, 20.
- [66] SCHAEFER, H. F., III, KLEMM, R. A., and HARRIS, F. E., 1969, *Phys. Rev.*, **181**, 137; 1969, *J. chem. Phys.*, **51**, 4643.
- [67] BENDER, C. F., and DAVIDSON, E. R., 1966, *J. phys. Chem.*, **70**, 2675; 1969, *Phys. Rev.*, **183**, 23.
- [68] RAFFENETTI, R. C., HSU, K., and SHAVIT, I., 1977, *Theor. Chim. Acta*, **45**, 33.
- [69] WIGNER, E., 1927, *Z. Phys.*, **40**, 492, 883; 1931, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Braunschweig: Vieweg) English translation: 1959, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (New York: Academic Press)
- [70] WEYL, H., 1928, *Gruppentheorie und Quantenmechanik* (Leipzig: Hirzel) English translation: 1931, *The Theory of Groups and Quantum Mechanics* (London: Methuen)
- [71] DIRAC, P. A. M., 1929, *Proc. R. Soc. Lond. A*, **123**, 714.
- [72] WALLER, I., and HARTREE, D. R., 1929, *Proc. R. Soc. Lond. A*, **124**, 119.
- [73] SERBER, R., 1934, *J. chem. Phys.*, **2**, 697; 1934, *Phys. Rev.*, **45**, 461.
- [74] YAMANOUCHI, T., 1935, *Proc. phys.-math. Soc. Jap.*, **17**, 274; 1937, *Proc. phys.-math. Soc. Jap.*, **19**, 436.
- [75] KOTANI, M., OHNO, K., and KAYAMA, K., 1961, *Encyclopedia of Physics*, edited by S. Flügge (Berlin: Springer), Vol. 37/2, p. 1.
- [76] MATSEN, F. A., 1964, *Adv. Quantum Chem.*, **1**, 59.
- [77] RUEDENBERG, K., 1971, *Phys. Rev. Lett.*, **27**, 1105; SALMON, W. I., and RUEDENBERG, K., 1972, *J. chem. Phys.*, **57**, 2776.
- [78] LÖWDIN, P.-O., 1955, *Phys. Rev.*, **97**, 1509; 1956, *Adv. Phys.*, **5**, 1.
- [79] PAUNCZ, R., 1967, *Alternant Molecular Orbital Method* (Philadelphia: Saunders); 1979, *Spin Eigenfunctions* (New York: Plenum).
- [80] MANNE, R., 1966, *Theor. Chim. Acta*, **6**, 116.
- [81] SMITH, V. H., and HARRIS, F. E., 1969, *J. math. Phys.*, **10**, 771.
- [82] HEITLER, W., and RUMER, G., 1931, *Z. Phys.*, **68**, 12.
- [83] REEVES, C. M., 1957, Ph.D. Thesis, Cambridge University; 1966, *Commun. ACM*, **9**, 276.
- [84] SUTCLIFFE, B. T., 1966, *J. chem. Phys.*, **45**, 235.

- [85] COOPER, I. L., and McWEENY, R., 1966, *J. chem. Phys.*, **45**, 226, 3484.
- [86] PALDUS, J., 1974, *J. chem. Phys.*, **61**, 5321; 1976, *Theoretical Chemistry: Advances and Perspectives*, edited by H. Eyring and D. Henderson (New York: Academic Press), Vol. 2, p. 131.
- [87] SHAVITT, I., 1977, *Int. J. Quantum Chem. Symp.*, **11**, 131; 1978, *Int. J. Quantum Chem. Symp.*, **12**, 5; 1981, *The Unitary Group, Lecture Notes in Chemistry* 22, edited by J. Hinze (Berlin: Springer), p. 51; 1988, *Mathematical Frontiers in Computational Chemical Physics*, edited by D. G. Truhlar (New York: Springer), p. 300.
- [88] DUCH, W., and KARWOWSKI, J., 1979, *Theor. Chim. Acta*, **51**, 175; DUCH, W., 1980, *Theor. Chim. Acta*, **57**, 299.
- [89] WIGNER, E., 1927, *Z. Phys.*, **43**, 624; **45**, 601.
- [90] BOYS, S. F., 1951, *Proc. R Soc. Lond. A*, **207**, 181, 197; 1952, *Phil. Trans. R Soc. Lond. A*, **245**, 95; BERNAL, M. J. M., and BOYS, S. F., 1952, *Phil. Trans. R Soc. Lond. A*, **245**, 116; BOYS, S. F., and SAHNI, R. C., 1954, *Phil. Trans. R Soc. Lond. A*, **246**, 463.
- [91] NESBET, R. K., 1961, *J. math. Phys.*, **2**, 701.
- [92] SALMON, W. I., and RUEDENBERG, K., 1972, *J. chem. Phys.*, **57**, 2776.
- [93] BUNGE, C. F., and BUNGE, A., 1973, *Int. J. Quantum Chem.*, **7**, 927.
- [94] SASAKI, F., 1974, *Int. J. Quantum Chem.*, **8**, 605.
- [95] MUNCH, D., and DAVIDSON, E. R., 1975, *J. chem. Phys.*, **63**, 980.
- [96] GERSHGORN, Z., and SHAVITT, I., 1967, *Int. J. Quantum Chem. Symp.*, **1**, 403.
- [97] PIPANO, A., and SHAVITT, I., 1968, unpublished work; PIPANO, A., GILMAN, R. R., BENDER, C. F., and SHAVITT, I., 1970, *Chem. Phys. Lett.*, **4**, 583; HAY, P. J., and SHAVITT, I., 1974, *J. chem. Phys.*, **60**, 2865.
- [98] NESBET, R. K., 1958, *Ann. Phys. (N.Y.)*, **3**, 397.
- [99] SIMONS, J., and HARRIMAN, J. E., 1969, *J. chem. Phys.*, **51**, 296.
- [100] SHAVITT, I., 1993, *Israel J. Chem.*, **33**, 357.
- [101] RAFFENETTI, R. C., 1973, *J. chem. Phys.*, **58**, 4452.
- [102] ALMLÖF, J., and TAYLOR, P. R., 1987, *J. chem. Phys.*, **86**, 4070; 1990, *J. chem. Phys.*, **92**, 551; 1991, *Adv. Quantum Chem.*, **22**, 301.
- [103] BAUSCHLICHER, C. W., JR., 1987, *Chem. Phys. Lett.*, **142**, 71; BAUSCHLICHER, C. W., JR., and TAYLOR, P. R., 1993, *Theor. Chim. Acta*, **86**, 13.
- [104] LANGHOFF, S. R., BAUSCHLICHER, C. W., JR., and TAYLOR, P. R., 1988, *J. chem. Phys.*, **88**, 5715; **89**, 7650.
- [105] WIDMARK, P.-O., MALMQVIST, P.-Å., and ROOS, B. O., 1990, *Theor. Chim. Acta*, **77**, 291; WIDMARK, P.-O., PERSSON, B.-J., and ROOS, B. O., 1991, *Theor. Chim. Acta*, **79**, 419.
- [106] DUNNING, T. H., JR., 1989, *J. chem. Phys.*, **90**, 1007; KENDALL, R. A., DUNNING, T. H., JR., and HARRISON, R. J., 1992, *J. chem. Phys.*, **96**, 6796; WOON, D. E., and DUNNING, T. H., JR., 1993, *J. chem. Phys.*, **98**, 1358; **99**, 3730; 1994, *J. chem. Phys.*, **100**, 2975.
- [107] FELLER, D., 1992, *J. chem. Phys.*, **96**, 6104; 1993, *J. chem. Phys.*, **98**, 7059; WOON, D. E., and DUNNING, T. H., JR., 1993, *J. chem. Phys.*, **99**, 1914.
- [108] PETERSON, K. A., KENDALL, R. A., and DUNNING, T. H., JR., 1983, *J. chem. Phys.*, **99**, 1930, 9790.
- [109] WOON, D. E., and DUNNING, T. H., JR., 1995, *J. chem. Phys.*, **103**, 4572.
- [110] SHAVITT, I., ROSENBERG, B. J., and PALALIKIT, S., 1976, *Int. J. Quantum Chem. Symp.*, **10**, 33; 1977, *Int. J. Quantum Chem. Symp.*, **11**, 651.
- [111] KELLY, H. P., 1964, *Phys. Rev.*, **136**, B896.
- [112] HUNT, W. J., and GODDARD, W. A., III, 1969, *Chem. Phys. Lett.*, **3**, 414.
- [113] BENDER, C. F., and DAVIDSON, E. R., 1967, *J. chem. Phys.*, **47**, 4972.
- [114] HUZINAGA, S., and ARNAU, C., 1970, *Phys. Rev. A*, **1**, 1285; 1971, *J. chem. Phys.*, **54**, 1948.
- [115] WHITTEN, J. L., 1972, *J. chem. Phys.*, **56**, 5458.
- [116] LUKEN, W. L., 1979, *Chem. Phys.*, **40**, 301.
- [117] COOPER, I. L., and POUNDER, N. M., 1979, *J. chem. Phys.*, **71**, 957.
- [118] BAUSCHLICHER, C. W., JR., 1980, *J. chem. Phys.*, **72**, 880.
- [119] ADAMOWICZ, L., and BARTLETT, R. J., 1987, *J. chem. Phys.*, **86**, 6314.
- [120] DAVIDSON, E. R., 1972, *J. chem. Phys.*, **57**, 1999.
- [121] LÖWDIN, P.-O., 1955, *Phys. Rev.*, **97**, 1474; LÖWDIN, P.-O., and SHULL, H., 1956, *Phys. Rev.*, **101**, 1730.
- [122] HAY, P. J., 1973, *J. chem. Phys.*, **59**, 2468.
- [123] SIU, A. K. Q., and HAYES, E. F., 1974, *J. chem. Phys.*, **61**, 37.
- [124] JAFRI, J. A., and WHITTEN, J. L., 1977, *Theor. Chim. Acta*, **44**, 305.
- [125] EDMISTON, C., and KRAUSS, M., 1966, *J. chem. Phys.*, **45**, 1833.
- [126] MEYER, W., 1971, *Int. J. Quantum Chem. Symp.*, **5**, 341; 1973, *J. chem. Phys.*, **58**, 1017.
- [127] MEYER, W., 1974, *Theor. Chim. Acta*, **35**, 277.
- [128] AHLRICHS, R., LISCHKA, H., STAEMMLER, V., and KUTZELNIGG, W., 1975, *J. chem. Phys.*, **62**, 1225; AHLRICHS, R., DRIESSLER, F., LISCHKA, H., STAEMMLER, V., and KUTZELNIGG, W., 1975, *J. chem. Phys.*, **62**, 1235.
- [129] MEYER, W., 1977, *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (New York: Plenum), p. 413.
- [130] AHLRICHS, R., and DRIESSLER, F., 1975, *Theor. Chim. Acta*, **36**, 275; MEYER, W., 1976, *J. chem. Phys.*, **64**, 2901; DYKSTRA, C. E., SCHAEFER, H. F., III, and MEYER, W., 1976, *J. chem. Phys.*, **65**, 2740.
- [131] LENNARD-JONES, J., and POPE, J. A., 1950, *Proc. R Soc. Lond. A*, **202**, 166.
- [132] FOSTER, J. M., and BOYS, S. F., 1960, *Rev. mod. Phys.*, **32**, 300; BOYS, S. F., 1966, *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P.-O. Löwdin (New York: Academic Press), p. 253.
- [133] EDMISTON, C., and RUEDENBERG, K., 1963, *Rev. mod. Phys.*, **35**, 457.
- [134] WILHITE, D. L., and WHITTEN, J. L., 1973, *J. chem. Phys.*, **58**, 948.
- [135] PULAY, P., 1983, *Chem. Phys. Lett.*, **100**, 151; SÆBØ, S., and PULAY, P., 1985, *Chem. Phys. Lett.*, **113**, 13.
- [136] POPE, J. A., SEEGER, R., and KRISHNAN, R., 1977, *Int. J. Quantum Chem. Symp.*, **11**, 149.
- [137] SAUNDERS, V. R., and VAN LENTHE, J. H., 1983, *Molec. Phys.*, **48**, 923.
- [138] NESBET, R. K., 1963, *Rev. mod. Phys.*, **35**, 552.
- [139] TANG, K. C., and EDMISTON, C., 1970, *J. chem. Phys.*, **52**, 997.

- [140] McLEAN, A. D., 1971, *Proceedings of the Conference on Potential Energy Surfaces in Chemistry*, edited by W. A. Lester Jr., Report RA-18, IBM Research Laboratory, San Jose, California, p. 87.
- [141] BENDER, C. F., 1972, *J. comput. Phys.*, **9**, 547.
- [142] ELBERT, S. T., 1973, Ph.D. Thesis, University of Washington.
- [143] DIERCKSEN, G. H. F., 1974, *Theor. Chim. Acta*, **33**, 1.
- [144] PENDERGAST, P., and FINK, W. H., 1974, *J. comput. Phys.*, **14**, 286.
- [145] LE RUOZO, H., RASEEV, G., and SILVI, B., 1978, *Comput. Chem.*, **2**, 15.
- [146] YOSHIMINE, M., 1973, *J. comput. Phys.*, **11**, 449.
- [147] BUNGE, C. F., and CISNEROS, G., 1986, *Comput. Chem.*, **10**, 101, 109; CISNEROS, G., POULAIN, E., and BUNGE, C. F., 1986, *Comput. Chem.*, **10**, 135.
- [148] BEEBE, N. H. F., and LINDERBERG, J., 1977, *Int. J. Quantum Chem.*, **12**, 683.
- [149] WILSON, S., 1990, *Comput. Phys. Commun.*, **58**, 71.
- [150] COOPER, J. L. B., 1948, *Quart. appl. Math.*, **6**, 179; NESBET, R. K., 1965, *J. chem. Phys.*, **43**, 311; SHAVITT, I., 1970, *J. comput. Phys.*, **6**, 124.
- [151] FADEEV, D. K., and FADEEVA, V. N., 1963, *Computational Methods of Linear Algebra* (San Francisco: Freeman).
- [152] SHAVITT, I., BENDER, C. F., PIPANO, A., and HOSTENY, R. P., 1973, *J. comput. Phys.*, **11**, 90.
- [153] DAVIDSON, E. R., 1975, *J. comput. Phys.*, **17**, 87.
- [154] LANCZOS, C., 1950, *J. Res. Natl. Bur. Stand.*, **45**, 255.
- [155] SHAVITT, I., 1977, *Reduction of I/O Costs and Improvement of Convergence in the Evaluation of Eigenvalues and Eigenvectors of Large Matrices in Configuration Interaction Calculations of Molecular Structure* (Report to the National Aeronautics and Space Administration), Battelle Columbus Laboratories, Columbus, Ohio.
- [156] RAFFENETTI, R. C., 1979, *J. comput. Phys.*, **32**, 403.
- [157] LIU, B., 1978, *Numerical Algorithms in Chemistry: Algebraic Methods*, edited by C. Moler and I. Shavitt, Report LBL-8158, Lawrence Berkeley Laboratory, Berkeley, California, p. 49.
- [158] WOOD, D. M., and ZUNGER, A., 1985, *J. Phys. A: Math. Gen.*, **18**, 1343.
- [159] MORGAN, R. B., and SCOTT, D. S., 1986, *SIAM J. sci. stat. Comput.*, **7**, 817.
- [160] BENDAZZOLI, G. L., EVANGELISTI, S., and PALMERI, P., 1987, *Int. J. Quantum Chem.*, **31**, 663.
- [161] VAN LENTHE, J. H., and PULAY, P., 1990, *J. comput. Chem.*, **11**, 1164.
- [162] MURRAY, C. W., RACINE, S. C., and DAVIDSON, E. R., 1992, *J. comput. Phys.*, **103**, 382.
- [163] BOFILL, J. M., and ANGLADA, J. M., 1994, *Chem. Phys.*, **183**, 19.
- [164] GADEA, F. X., 1994, *Chem. Phys. Lett.*, **227**, 201.
- [165] VAN DAM, H. J. J., VAN LENTHE, J. H., SLEIJPEN, G. L. G., and VAN DER VORST, H. A., 1996, *J. comput. Chem.*, **17**, 267.
- [166] DAVIDSON, E. R., 1989, *Comput. Phys. Commun.*, **53**, 49.
- [167] ROOS, B., 1972, *Chem. Phys. Lett.*, **15**, 153.
- [168] ROOS, B. O., and SIEGBAHN, P. E. M., 1977, *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (New York: Plenum) p. 277.
- [169] LUCCHESI, R. R., and SCHAEFER, H. F., III, 1978, *J. chem. Phys.*, **68**, 769.
- [170] ROOS, B. O., and SIEGBAHN, P. E. M., 1980, *Int. J. Quantum Chem.*, **17**, 485.
- [171] WETMORE, R. W., and SEGAL, G. A., 1975, *Chem. Phys. Lett.*, **36**, 478; SEGAL, G. A., WETMORE, R. W., and WOLF, K., 1978, *Chem. Phys.*, **30**, 269.
- [172] BROOKS, B. R., and SCHAEFER, H. F., III, 1979, *J. chem. Phys.*, **70**, 5092; BROOKS, B. R., LAIDIG, W. D., SAXE, P., HANDY, N. C., and SCHAEFER, H. F., III, 1980, *Phys. Scripta*, **21**, 312; SAXE, P., FOX, D. J., SCHAEFER, H. F., III, and HANDY, N. C., 1982, *J. chem. Phys.*, **77**, 5584.
- [173] SIEGBAHN, P. E., 1979, *J. chem. Phys.*, **70**, 5391; 1980, *J. chem. Phys.*, **72**, 1647.
- [174] LISCHKA, H., SHEPARD, R., BROWN, F. B., and SHAVITT, I., 1981, *Int. J. Quantum Chem. Symp.*, **15**, 91; AHLRICHS, R., BÖHM, H.-J., EHRHARDT, C., SCHARF, P., SCHIFFER, H., LISCHKA, H., and SCHINDLER, M., 1985, *J. comput. Chem.*, **6**, 200; SHEPARD, R., SHAVITT, I., PITZER, R. M., COMEAU, D. C., PEPPER, M., LISCHKA, H., SZALAY, P. G., AHLRICHS, R., BROWN, F. B., and ZHAO, J.-G., 1988, *Int. J. Quantum Chem. Symp.*, **22**, 149.
- [175] GULDBERG, A., RETTRUP, S., BENDAZZOLI, G. L., and PALMERI, P., 1987, *Int. J. Quantum Chem. Symp.*, **21**, 513.
- [176] DUCH, W., 1986, *GRMS or Graphical Representation of Model Spaces* (Berlin: Springer).
- [177] SIEGBAHN, P. E. M., 1984, *Chem. Phys. Lett.*, **109**, 417.
- [178] KEDZIORA, G. S., and SHAVITT, I., 1997, *J. chem. Phys.*, **106**, 8733.
- [179] SCHÜLER, M., KOVAR, T., LISCHKA, H., SHEPARD, R., and HARRISON, R. J., 1993, *Theor. Chim. Acta*, **84**, 489; DACHSEL, H., LISCHKA, H., SHEPARD, R., NIEPLOCHA, J., and HARRISON, R. J., 1997, *J. comput. Chem.*, **18**, 430.
- [180] LISCHKA, H., 1997, private communication.
- [181] SIEGBAHN, P. E. M., 1977, *Chem. Phys.*, **25**, 197; 1983, *Int. J. Quantum Chem.*, **23**, 1869.
- [182] SIEGBAHN, P. E. M., 1980, *Int. J. Quantum Chem.*, **18**, 1229.
- [183] WERNER, H.-J., and REINSCH, E.-A., 1982, *J. chem. Phys.*, **76**, 3144; WERNER, H.-J., and KNOWLES, P. J., 1988, *J. chem. Phys.*, **89**, 5803.
- [184] WERNER, H.-J., 1987, *Adv. chem. Phys.*, **69**, 1.
- [185] KNOWLES, P. J., and WERNER, H.-J., 1992, *Theor. Chim. Acta*, **84**, 95.
- [186] PARTRIDGE, H., and SCHWENKE, D. W., 1997, *J. chem. Phys.*, **106**, 4618.
- [187] MOK, D. K. W., NEUMANN, R., and HANDY, N. C., 1996, *J. phys. Chem.*, **100**, 6225.
- [188] BROWN, F. B., SHAVITT, I., and SHEPARD, R., 1984, *Chem. Phys. Lett.*, **105**, 363.
- [189] BARTLETT, R. J., and PURVIS, G. D., 1978, *Int. J. Quantum Chem.*, **14**, 561.
- [190] PRIMAS, H., 1965, *Modern Quantum Chemistry*, edited by O. Sinanoğlu (New York: Academic Press), Part II, p. 45.
- [191] KUTZELNIGG, W., 1977, *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (New York: Plenum), p. 129.
- [192] PALDUS, J., and ČÍŽEK, J., 1975, *Adv. Quantum Chem.*, **9**, 105.

- [193] BARTLETT, R. J., 1981, *Ann. Rev. Phys. Chem.*, **32**, 359; KUCHARSKI, S. A., and BARTLETT, R. J., 1986, *Adv. Quantum Chem.*, **18**, 281.
- [194] HARRIS, F. E., MONKHORST, H. J., and FREEMAN, D. L., 1992, *Algebraic and Diagrammatic Methods in Many-Fermion Theory* (New York: Oxford University Press).
- [195] SASAKI, F., 1977, *Int. J. Quantum Chem. Symp.*, **11**, 125.
- [196] DAVIDSON, E. R., and SILVER, D. W., 1977, *Chem. Phys. Lett.*, **52**, 403.
- [197] POPLE, J. A., BINKLEY, J. S., and SEEGER, R., 1976, *Int. J. Quantum Chem. Symp.*, **10**, 1.
- [198] DEL BENE, J. E., and SHAVITT, I., 1989, *Int. J. Quantum Chem. Symp.*, **23**, 445.; DEL BENE, J. E., STAHLBERG, E. A., and SHAVITT, I., 1990, *Int. J. Quantum Chem. Symp.*, **24**, 455.
- [199] SINANOĞLU, O., 1961, *Proc. R. Soc. Lond. A*, **260**, 379; 1962, *J. chem. Phys.*, **36**, 706, 3198.
- [200] NESBET, R. K., 1965, *Adv. chem. Phys.*, **9**, 321.
- [201] ČÍŽEK, J., 1966, *J. chem. Phys.*, **45**, 4256; 1969, *Adv. chem. Phys.*, **14**, 35.
- [202] HURLEY, A. C., 1976, *Electron Correlation in Small Molecules* (London: Academic Press).
- [203] BARTLETT, R. J., and SHAVITT, I., 1977, *Int. J. Quantum Chem. Symp.*, **11**, 165; 1978, *Int. J. Quantum Chem. Symp.*, **12**, 543.
- [204] BARTLETT, R. J., DYKSTRA, C. E., and PALDUS, J., 1984, *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, edited by C. E. Dykstra (Dordrecht: Reidel), p. 127.
- [205] MEUNIER, A., LEVY, B., and BERTHIER, G., 1976, *Int. J. Quantum Chem.*, **10**, 1061.
- [206] DAVIDSON, E. R., 1974, *The World of Quantum Chemistry*, edited by R. Daudel and B. Pullman (Dordrecht: Reidel), p. 17; LANGHOFF, S. R., and DAVIDSON, E. R., 1974, *Int. J. Quantum Chem.*, **8**, 61.
- [207] SIEGBAHN, P. E. M., 1978, *Chem. Phys. Lett.*, **55**, 386.
- [208] PALDUS, J., 1983, *New Horizons of Quantum Chemistry*, edited by P.-O. Löwdin and B. Pullman (Dordrecht: Reidel), p. 31.
- [209] BURTON, P. G., BUENKER, R. J., BRUNA, P. J., and PEYERIMHOFF, S. D., 1983, *Chem. Phys. Lett.*, **95**, 379; PHILLIPS, R. A., BUENKER, R. J., BRUNA, P. J., and PEYERIMHOFF, S. D., 1984, *Chem. Phys.*, **84**, 11.
- [210] MEISSNER, L., 1988, *Chem. Phys. Lett.*, **146**, 204.
- [211] BUENKER, R. J., and PEYERIMHOFF, S. D., 1983, *New Horizons of Quantum Chemistry*, edited by P.-O. Löwdin and B. Pullman (Dordrecht: Reidel), p. 183.
- [212] JANKOWSKI, K., MEISSNER, L., and WASILEWSKI, J., 1985, *Int. J. Quantum Chem.*, **28**, 931.
- [213] MARTIN, J. M. L., FRANÇOIS, J. P., and GIJBELS, R., 1990, *Chem. Phys. Lett.*, **172**, 346, 354.
- [214] HURLEY, A. C., LENNARD-JONES, J., and POPLE, J. A., 1953, *Proc. R. Soc. Lond. A*, **220**, 446.
- [215] PARKS, J. M., and PARR, R. G., 1958, *J. chem. Phys.*, **28**, 335.
- [216] SZÁSZ, L., 1960, *Z. Naturforsch.*, **15a**, 909; 1962, *Phys. Rev.*, **126**, 169; 1963, *Phys. Rev.*, **132**, 936; 1968, *J. chem. Phys.*, **49**, 679.
- [217] NESBET, R. K., BARR, T. L., and DAVIDSON, E. R., 1969, *Chem. Phys. Lett.*, **4**, 203; BARR, T. L., and DAVIDSON, E. R., 1970, *Phys. Rev. A*, **1**, 644.
- [218] KELLY, H. P., 1964, *Phys. Rev.*, **134**, A1450.
- [219] KOCH, S., and KUTZELNIGG, W., 1981, *Theor. Chim. Acta*, **59**, 387.
- [220] AHLRICHS, R., SCHARF, P., and EHRHARDT, C., 1985, *J. chem. Phys.*, **82**, 890; AHLRICHS, R., SCHARF, P., and JANKOWSKI, K., 1985, *Chem. Phys.*, **98**, 381.
- [221] CHONG, D. P., and LANGHOFF, S. R., 1986, *J. chem. Phys.*, **84**, 5606.
- [222] LAIDIG, W. D., and BARTLETT, R. J., 1984, *Chem. Phys. Lett.*, **104**, 424; LAIDIG, W. D., SAXE, P., and BARTLETT, R. J., 1987, *J. chem. Phys.*, **86**, 887.
- [223] FULDE, P., and STOLL, H., 1992, *J. chem. Phys.*, **97**, 4185.
- [224] GDANITZ, R. J., and AHLRICHS, R., 1988, *Chem. Phys. Lett.*, **143**, 413.
- [225] SZALAY, P. G., and BARTLETT, R. J., 1995, *J. chem. Phys.*, **103**, 3600.
- [226] FÜSTI-MOLNÁR, L., and SZALAY, P. G., 1996, *J. phys. Chem.*, **100**, 6288.
- [227] STAMPER, J. G., 1968, *Theor. Chim. Acta*, **11**, 459.
- [228] PRIME, S., and ROBB, M. A., 1975, *Chem. Phys. Lett.*, **35**, 86; PRIME, S., REES, C., and ROBB, M. A., 1981, *Molec. Phys.*, **44**, 173.
- [229] KARLSTRÖM, G., 1977, *Theor. Chim. Acta*, **44**, 165.
- [230] LUKEN, W. L., 1978, *Chem. Phys. Lett.*, **58**, 421.
- [231] MEUNIER, A., and LEVY, B., 1979, *Int. J. Quantum Chem.*, **16**, 955.
- [232] RUTTINK, P. J. A., 1981, *Chem. Phys. Lett.*, **79**, 253; RUTTINK, P. J. A., VAN LENTHE, J. H., ZWAANS, R., and GROENBOOM, G. C., 1991, *J. chem. Phys.*, **94**, 7212.
- [233] BANERJEE, A., and SIMONS, J., 1981, *Int. J. Quantum Chem.*, **19**, 207; 1982, *J. chem. Phys.*, **76**, 4548.
- [234] WENZEL, K. B., 1982, *J. Phys. B: atom. molec. Phys.*, **15**, 835.
- [235] BRĀNDAS, E. J., COMBS, L. L., and CORREIA, N. S., 1982, *Int. J. Quantum Chem.*, **21**, 259; BRĀNDAS, E. J., BENDAZZOLI, G. L., and ORTOLANI, F., 1983, *Int. J. Quantum Chem. Symp.*, **17**, 321.
- [236] PULAY, P., 1983, *Int. J. Quantum Chem. Symp.*, **17**, 257.
- [237] TANAKA, K., and TERASHIMA, H., 1984, *Chem. Phys. Lett.*, **106**, 558; TANAKA, K., SAKAI, T., and TERASHIMA, H., 1989, *Theor. Chim. Acta*, **76**, 213; SAKAI, T., and TANAKA, K., 1993, *Theor. Chim. Acta*, **85**, 451.
- [238] CAVE, R. J., and DAVIDSON, E. R., 1988, *J. chem. Phys.*, **88**, 5770; **89**, 6798; MURRAY, C., RACINE, S. C., and DAVIDSON, E. R., 1992, *Int. J. Quantum Chem.*, **42**, 273.
- [239] HOFFMANN, M. R., and SIMONS, J., 1989, *J. chem. Phys.*, **90**, 3671.
- [240] HEULLY, J.-L., and MALRIEU, J.-P., 1992, *Chem. Phys. Lett.*, **199**, 545; DAUDEY, J.-P., HEULLY, J.-L., and MALRIEU, J.-P., 1993, *J. Chem. Phys.*, **99**, 1240; MALRIEU, J.-P., DAUDEY, J.-P., and CABALLOL, R., 1994, *J. Chem. Phys.*, **101**, 8908.
- [241] FINK, R., and STAEMMLER, V., 1993, *Theor. Chim. Acta*, **87**, 129.
- [242] GERSHGORN, Z., and SHAVITT, I., 1968, *Int. J. Quantum Chem.*, **2**, 751.
- [243] SHAVITT, I., 1992, *Chem. Phys. Lett.*, **192**, 135.