

Selected configuration interaction with truncation energy error and application to the Ne atom

Carlos F. Bunge^{a)}

Instituto de Química Computacional, Universitat de Girona, Campus de Montilivi, 17071 Girona, Spain and Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, México 01000, México

(Received 8 November 2005; accepted 1 May 2006; published online 6 July 2006)

Selected configuration interaction (SCI) for atomic and molecular electronic structure calculations is reformulated in a general framework encompassing all CI methods. The linked cluster expansion is used as an intermediate device to approximate CI coefficients B_K of disconnected configurations (those that can be expressed as products of combinations of singly and doubly excited ones) in terms of CI coefficients of lower-excited configurations where each K is a linear combination of configuration-state-functions (CSFs) over all degenerate elements of K . Disconnected configurations up to sextuply excited ones are selected by Brown's energy formula, $\Delta E_K = (E - H_{KK})B_K^2 / (1 - B_K^2)$, with B_K determined from coefficients of singly and doubly excited configurations. The truncation energy error from disconnected configurations, ΔE^{dis} , is approximated by the sum of ΔE_{KS} of all discarded K s. The remaining (connected) configurations are selected by thresholds based on natural orbital concepts. Given a model CI space M , a usual upper bound E_S is computed by CI in a selected space S , and $E_M = E_S + \Delta E^{\text{dis}} + \delta E$, where δE is a residual error which can be calculated by well-defined sensitivity analyses. An SCI calculation on Ne ground state featuring 1077 orbitals is presented. Convergence to within near spectroscopic accuracy (0.5 cm^{-1}) is achieved in a model space M of 1.4×10^9 CSFs (1.1×10^{12} determinants) containing up to quadruply excited CSFs. Accurate energy contributions of quintuples and sextuples in a model space of 6.5×10^{12} CSFs are obtained. The impact of SCI on various orbital methods is discussed. Since ΔE^{dis} can readily be calculated for very large basis sets without the need of a CI calculation, it can be used to estimate the orbital basis incompleteness error. A method for precise and efficient evaluation of E_S is taken up in a companion paper. © 2006 American Institute of Physics. [DOI: 10.1063/1.2207620]

I. INTRODUCTION

For atoms and small molecules, Schrödinger's equation can be approximated by a matrix-eigenvalue equation,

$$\mathbf{H}\mathbf{C}_\mu = E_\mu^{\text{FCI}}\mathbf{C}_\mu, \quad (1)$$

where \mathbf{H} is the representation of H in terms of the Slater determinants or N -electron symmetry-eigenfunctions constructed from a given orbital basis. Equation (1), which can be applied to the complete range of quantum mechanical problems associated to the given system, defines the full configuration interaction (CI) method¹ and E_μ^{FCI} is the full CI (FCI) energy. In terms of FCI quantities, the exact eigenvalues E_μ of Schrödinger's equation may be expressed as

$$E_\mu = E_\mu^{\text{FCI}} + \Delta E_\mu^{\text{OBI}}, \quad (2)$$

where $\Delta E_\mu^{\text{OBI}}$ is the error due to orbital basis incompleteness.²⁻⁵ Henceforth the subscript μ will be dropped in the understanding that the following also applies to excited states. ΔE^{OBI} shall be further discussed in Sec. VII B.

Full CI, on the other hand, is the central referent of all orbital methods based on Hamiltonians obtained from the first principles:^{6,7} highly correlated CI (HCCI),⁸

symmetry-adapted-cluster⁹ (SAC) and SAC—CI,¹⁰⁻¹² size-consistent CI,¹³ coupled cluster (CC) methods,^{14,15} many-body perturbation theory (MBPT),^{16,17} electron propagator theory,^{18,19} and, more recently, density matrix variational theory,^{20,21} the density matrix renormalization group method,²² iterative CI (Refs. 23 and 24) and extended CC,²⁵ and *ab initio* density functional theory.²⁶ (Quantum Monte Carlo methods²⁷ are becoming increasingly competitive but use an entirely different methodology.)

Traditional FCI is an impossible task, except to test *ab initio* electronic structure methods²⁸ with (necessarily) too small orbital bases lacking predictive value. The new FCI methods^{22,23,29,30} considerably extend the scope of traditional FCI but will continue to be limited by the size of the orbital bases. This paper addresses HCCI methods in general.⁸ Let us convene calling HCCI any CI method which, despite a formal lack of size extensivity,³¹⁻³⁵ competes on a par with the better founded coupled cluster methods such as CCSD,³⁴ CCSD(T),^{36,37} CCSDT,^{38,39} CCSDT(Q),⁴⁰ CCSDTQ,^{41,42} or even CCSDTQqn,⁴³ for a given problem at hand. (S, D, T, Q, Qn, Sx, etc., refer to singles, doubles, triples, quadruples, quintuples, sextuples, etc.)

Comprehensive studies on the water molecule^{44,45} in which the HOH angle is fixed at 110.6° and the OH distance

^{a)}Electronic mail: bunge@fisica.unam.mx

is varied between R_e and $3R_e$ with $R_e \approx 1.843\ 45$ a.u. show that in order to compete with CCSDT, a CISDTQ treatment is adequate

$$\text{CISDTQ} \approx \text{CCSDT}.$$

The previous assertion applies, in general, to similar situations, atoms and small molecules. The reason for the obstinate endurance of CISDTQ vis-à-vis CCSDT is its variational character, not shared by standard CC methods. This is consistent with recent results^{46,47} in *variational* CC calculations⁴⁸ achieving close to FCI quality. Accordingly, whereas nonvariational CC methods for N -electron systems include up to N -excited determinants that are normally absent in HCCI, the latter provides the best expansion coefficients up to the level of excitations actually incorporated, and that is enough—at least energy wise—to compensate for lack of size consistency. The problem with straight CISDTQ, nevertheless, has been the excessive computer resources required for current and even future computational power.

Continuing with the water molecule, a recent application of the ultimate of CC tools, namely, CCSDTQQn,⁴³ suggests that CISDTQQnSx is a clear match,

$$\text{CISDTQQnSx} \approx \text{CCSDTQQn}.$$

This paper presents a complete and efficient approach to approximate CISDTQQnSx for atoms and small molecules to within reliable and acceptable errors by means of selected CI (SCI) and its corresponding truncation and residual energy errors relative to the full CISDTQQnSx treatment. (The residual energy error accounts for inaccuracies in the truncation energy error itself and for other errors requiring sensitivity analyses.)

SCI calls for three methodological requirements:

- (i) *a priori* selection of configurations,^{8,49–51}
- (ii) *a priori* estimate of truncation energy errors, and
- (iii) *a posteriori* assessment of all other errors not calculated in (ii).

The present SCI method differs from its predecessors in two important aspects: (i) truncation energy errors are quantitatively assessed all along making use of Brown's energy formula,⁵² and (ii) the selection scheme targets configurations rather than configuration-state functions (CSFs) or determinants, both advances, in combination, leading to orders of magnitude improvements in accuracy and precision. CI notation and the Brown formula are given in Sec. II. In Sec. III, the linked cluster expansion is compared with the determinantal cluster expansion to obtain n -excited determinantal CI coefficients in terms of those of lower-excited determinants, as already known^{7,53} but unexploited. The expressions for determinantal coefficients are then generalized to approximate configurational coefficients in a quick and reliable way, therefore opening the way for large-scale *a priori* applications of Brown's formula.

Selection of configurations involves additional conceptualizations discussed in Sec. IV. Truncation and residual energy errors are taken up in Sec. V, and an application on the Ne atom is presented in Sec. VI. Present achievements, their impact on other *ab initio* methods and conclusions are given

in Sec. VII. Various details are given elsewhere.⁵⁴ Efficiency requirements in connection with the matrix-eigenvalue problem demand the development of yet another variational method presented in a companion paper.⁵⁵

II. CI NOTATION AND BROWN'S FORMULA

A general HCCI model wave function can be written as⁵⁶

$$\Psi = \sum_{K=1}^{K_x} \sum_{g=1}^{g_K} F_{gK} C_{gK}. \quad (3)$$

K and g label configurations and degenerate elements, respectively, and C_{gK} denotes a CI coefficient. Triply and higher-excited configurations can be classified into disconnected and connected ones. Disconnected configurations are those that can be expressed as products of combinations of singly and doubly excited ones, whereas connected configurations are all others. F_{gK} is an N -electron symmetry eigenfunction or CSF expressed as a linear combination of n_K Slater determinants D_{iK} ,

$$F_{gK} = O(\Gamma, \gamma) \sum_{i=1}^g D_{iK} b_i^g = \sum_{i=1}^{n_K} D_{iK} c_i^g, \quad g = 1, \dots, g_K, \quad (4)$$

where $O(\Gamma, \gamma)$ is a symmetric projection operator⁵⁷ for all pertinent symmetry operators Γ and a given (N -electron) irreducible representation γ .^{58–61}

Let $\Psi(-F_{gK})$ denote $\mathcal{N}(\Psi - F_{gK} C_{gK})$ where \mathcal{N} is a normalization factor, viz., let us assume that after deletion of F_{gK} , the new wave function $\Psi(-F_{gK})$ has the same remaining expansion coefficients except for renormalization. The energy contribution ΔE_{gK} of F_{gK} can be approximated by

$$\Delta E_{gK} = \langle \Psi | H | \Psi \rangle - \langle \Psi(-F_{gK}) | H | \Psi(-F_{gK}) \rangle, \quad (5)$$

which readily yields Brown's formula,⁵²

$$\Delta E_{gK} = (E - H_{gK, gK}) C_{gK}^2 / (1 - C_{gK}^2). \quad (6)$$

In Eq. (6), $E = \langle \Psi | H | \Psi \rangle$. Approximation (6) is particularly good for small values of ΔE_{gK} , viz., for expansion terms F_{gK} eventually to be discarded, like triply and up to sextuply excited configurations. As pointed out in Ref. 62 similar equations of perturbational lineage have been used by other authors.

Equation (6) requires previous knowledge of C_{gK} coefficients which so far could only be obtained *after* making a calculation.⁶³ Quick prediction of C_{gK} s for each g of a given K is probably hopeless. Fortunately, as shown in Sec. III E, it is possible to predict configurational B_K coefficients defined below.

First, Eq. (3) is rewritten as

$$\Psi = \sum_{K=1}^{K_x} G_K B_K, \quad (7)$$

in terms of normalized symmetry configurations G_K ,

$$G_K = N_K \sum_{g=1}^{g_K} F_{gK} C_{gK}, \quad (8)$$

therefore,

C. Predictor of determinantal coefficients

By replacing the rhs of (18) in (19) one gets

$$\frac{1}{c_0} c_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{c_0^2} (c_i^a c_j^b - c_i^b c_j^a). \quad (21)$$

When (18) and (21) are replaced into the rhs of (20) it follows:

$$\begin{aligned} \frac{1}{c_0} c_{ijk}^{abc} = & t_{ijk}^{abc} + \frac{1}{c_0^2} (c_i^a c_j^b c_k^c - c_i^b c_j^a c_k^c + c_i^c c_j^a c_k^b - c_i^a c_j^c c_k^b - c_i^b c_j^c c_k^a + c_i^c c_j^b c_k^a) \\ & - \frac{2}{c_0^3} (c_i^a c_j^b c_k^c - c_i^a c_j^c c_k^b - c_i^b c_j^a c_k^c + c_i^b c_j^c c_k^a \\ & + c_i^c c_j^a c_k^b - c_i^c c_j^b c_k^a). \end{aligned} \quad (22)$$

Equation (22) shows that c_{ijk}^{abc} coefficients are given exactly in terms of coefficients of lower excited detors plus the irreducible amplitude t_{ijk}^{abc} . Apart from the occurrence of c_0 , these and similar equations for the coefficients associated to higher-excited determinants are particular cases of Eq. (A4') of Ref. 53. The exciting promise of the above equations stems from the reasonable hypothesis that distinct from $c_{ijkl\dots}^{abc\dots}$ coefficients, the $t_{ijk\dots}^{abc\dots}$ amplitudes diminish quickly with the order of excitation (in analogy with the virial expansion in imperfect gas theory⁶⁵), and can be neglected.

In general one has

$$\frac{1}{c_0} c_{ijk\dots}^{abc\dots} = t_{ijk\dots}^{abc\dots} + F(c_{ijk\dots}^{ab\dots}). \quad (23)$$

Equation (23) is a shorthand for a predictor of CI coefficients of the n -excited determinants in terms of coefficients of lower excited detors if triply and higher-excited irreducible $t_{ijk\dots}^{abc\dots}$ amplitudes on the rhs can be neglected. If $t_{ijk\dots}^{abc\dots} \approx 0$, as first envisioned by Sinanoğlu, Eq. (22) and similar ones can be used to estimate $c_{ijk\dots}^{abc\dots}$ coefficients for evaluation of approximate truncation energy errors of disconnected determinants through an equation similar to (6) or (10). This is different from Sinanoğlu's original proposal⁶⁵ to use Eq. (22) and similar ones as part of a scheme to calculate the total energy itself. Also, the need for large-scale CI is here anticipated as unavoidable. Moreover, as it is well known,⁷² $t_{ijk}^{abc} \approx 0$ and even $t_{ijkl}^{abcd} \approx 0$ is not always justified, causing the need of additional considerations to be discussed in Sec. IV.

D. From determinants to configurations

Simplifications that are essential for large-scale application of Brown's formula will now be considered for the first time. In molecules there is no much of an incentive to contract determinantal expansions into CSFs.⁸ But the situation changes, even in molecules, when the final purpose becomes to contract sums of determinants into symmetry configurations G_K , Eq. (8), embracing *all degenerate* elements into a single term. Here the effective contraction factor becomes $1/n_K$, viz., it is equal to the reciprocal of the number of determinants for a given configuration K , which is around 0.05 for CISDTQ with the Abelian point-symmetry groups, falling under 0.0001 in atomic CISDTQ with orbitals of high angular momentum, continuing to decrease for higher exci-

tations. Therefore, the configurational counterpart of equations such as (22) is considered next.

The configurational cluster expansion is given by

$$\begin{aligned} \Psi = & \Phi_0 B_0 + \sum_i \sum_a \Phi_i^a B_i^a + \sum_{i \leq j} \sum_{a \leq b} \Phi_{ij}^{ab} B_{ij}^{ab} \\ & + \sum_{i \leq j \leq k} \sum_{a \leq b \leq c} \Phi_{ijk}^{abc} B_{ijk}^{abc} + \dots, \end{aligned} \quad (24)$$

where \leq has now taken the place of $<$ in Eq. (12), symmetry-orbitals replace spin-orbitals, and the summation over the degeneracy index g has already taken place thus hiding the linear variational coefficients C_{gK} through Eqs. (8) and (9). Formally, other than for calculation purposes, (24) is entirely equivalent to (12) as well as to (7) and (3), thus any $\Phi_{ijk\dots}^{abc\dots}$ is identical with some G_K of (7).

E. Predictor of configurational coefficients

A priori prediction of the C_{gK} coefficients of Eq. (3) was discussed by Pipano and Shavitt⁷³ but the lengthy calculations of their proposal were never implemented. Rather than deriving equations similar to (23), approximate equations to predict the configurational coefficients $B_{ijk\dots}^{abc\dots}$ of Eq. (24) shall be guessed. The correctness of the guessed equations will be tested by means of actual calculations.

When there are no equal signs among the participating orbitals and all concerned degeneracies are equal to one, the predictor equations for the configurational coefficients B_K of (9) or $B_{ijk\dots}^{abc\dots}$ of (24) should be identical to those for the $c_{ijk\dots}^{abc\dots}$ coefficients of determinantal expansions, Eq. (22), and similar ones. The question to be answered then is how Eq. (22), for example, is to be modified when there are equal orbital indices. Let us consider the extreme case when all occupied orbitals i are equal among themselves, as well as the excited orbitals a . Since the expansion in Eq. (24) does not contain repeated coefficients, the recipe must be to drop all terms with repeated coefficients. Consequently, for configurational coefficients, Eq. (22) changes into

$$\frac{1}{B_0} B_{iii}^{aaa} = \hat{B}_{iii}^{aaa} + \frac{1}{B_0^2} B_i^a B_{ii}^{aa} - \frac{2}{B_0^3} B_i^a B_i^a B_i^a. \quad (25)$$

\hat{B}_{iii}^{aaa} in the rhs of (25) is a linked or irreducible coefficient (in Sinanoğlu's nomenclature) which will be neglected in the

evaluation of the left-hand side (lhs) of (25). In this way, of the 15 terms of Eq. (22) only two survive. The codes expressing the 1440 formulas for up to sextuply excited coefficients [2(2q-2) formulas for coefficients of q-excited configurations] were produced by FORTRAN programs and are further discussed elsewhere.⁵⁴ Moreover, the irreducible components $\hat{B}_{ijk\dots}^{abc\dots}$ are significant in many triple excitations, and also in those instances where the remaining terms in the rhs of (25) are zero, as discussed in Sec. IV.

IV. SELECTION OF CONFIGURATIONS

A. Disconnected and connected configurations

The selection process described so far may be summarized as follows: given a model space M , all disconnected configurations K with energy contributions ΔE_K greater than an energy threshold T^{egy}

$$|\Delta E_K| > T^{\text{egy}}, \quad (26)$$

are included in a selected space S that will subsequently be subjected to a variational treatment. However, other configurations also require systematic incorporation since there are two instances when the above criterion is inadequate:

- (i) It is not operative if, for a given set of indices $_{ijk\dots}^{abc\dots}$, only $t_{ijk\dots}^{abc\dots}$ in the rhs of (23) is different from zero. Such configurations shall be called connected configurations,⁷⁴ while all others are called disconnected ones. Examples of connected configurations are *pdf* in Li 2S and *pdfg* in Be 1S .⁷⁵
- (ii) it is not sufficient for triply excited *disconnected* configurations: here, the largest part of the energy contributions comes from nonnegligible irreducible t_{ijk}^{abc} s and corresponding \hat{B}_{ijk}^{abc} coefficients,⁷⁶ independently of the magnitude of the disconnected terms in (22).

Connected configurations do not exist when using orbital bases lacking spatial symmetry. They necessarily occur when at least one irrep does not appear as a fully occupied orbital in the reference configuration Φ_0 , namely, in all atomic and linear-molecule states, and in few-electron molecules with spatial symmetry. Our aim shall just be to guarantee that all deleted connected configurations, together with disconnected triples that were discarded by Brown's energy criterion, contribute less than a given amount of energy.

B. Additional selection criterion

The occurrence of connected configurations makes it necessary to introduce a new requisite: the correlation orbitals a, b, c, \dots must be approximate natural orbitals,⁷⁷ viz., eigenfunctions of the reduced first-order density matrix or, better yet, average natural orbitals⁷⁸ so that orbital symmetry is preserved.

Let $\gamma(1, 1')$ be the average reduced first-order density matrix with eigenfunctions χ_a and eigenvalues (occupation numbers) n_a ,

$$\gamma(1, 1') = \sum n_a \chi_a^*(1) \chi_a(1'). \quad (27)$$

In studies on atomic electron correlation⁷⁹ it was found that configurations can be chosen by the following criterion: for each q -excited configuration K the product $P(q, K)$ of corresponding occupation numbers is calculated

$$P(q, K) = \prod_{i=1}^q n_{K_i}, \quad (28)$$

where K_i represents a correlation natural orbital. If g is the symmetry degeneracy of natural orbital a , $n_{Ka} = gn_a$. The whole configuration (all corresponding degenerate elements) is incorporated if $P(q, K)$ is greater than some occupation number threshold T^{on} ,

$$P(q, K) > T^{\text{on}}. \quad (29)$$

A functional form for T^{on} can be expressed in terms of the excitation level q and of a parameter m as

$$T^{\text{on}}(m) = 10^{-mq}, \quad (30)$$

where m is shown explicitly on the lhs of (30) for later purposes. Thus, 10^{-m} may be interpreted as an average occupation number below which configurations involving a given natural orbital are deleted from an original model space M . In practice, starting from a sufficiently small energy threshold T^{egy} , the value of m is increased until successive energy lowerings start to converge to within a prescribed residual energy error. Since the actual value of m in (30) guaranteeing a given contribution to the residual energy error depends on the holes i, j, k, \dots of the configuration involved, there is ample room for enriching Eq. (30).⁵⁴

C. Strategy for configuration selection

The following strategy for configuration selection is adopted

- (i) All triples with $P(3, K) \geq 10^{-3m}$ are selected. This criterion is applied to all triply excited configurations alike, disconnected and connected ones. The value of m must be sufficiently high to guarantee that the energy contribution of all deleted connected configurations is negligible. This is all that is to be done to select connected triples.
- (ii) As to the disconnected triples that were not selected in (i), all those with $|\Delta E_K| \geq T^{\text{egy}}$ are selected while the energy contributions of the discarded ones are accumulated into the total truncation energy error ΔE^{dis} , Sec. V A.
- (iii) All connected quadruples with $P(4, K) \geq 10^{-4m}$ are selected. This is the mechanism used to incorporate t_{ijkl}^{abcd} s associated to connected configurations.
- (iv) All disconnected quadruples with $|\Delta E_K| \geq T^{\text{egy}}$ are selected while the energy contributions of the discarded ones are accumulated into $\Delta E_{\text{af}}^{\text{dis}}$. This implies to neglect all t_{ijkl}^{abcd} associated to disconnected configurations deleted by the T^{egy} test, no matter how significant they might be.

- (v) Quintuple- and sextuply excited configurations are selected according to (iii) and (iv).

V. ENERGY EXPRESSION

The discussions in Secs. II and IV allow to develop an appropriate notation and a general equation for the CI energy in terms of the usual energy upper bound, a computable (rather than formal) truncation energy error, and a residual energy error. The latter two contain a part corresponding to disconnected configurations, which can be estimated *a priori*, and another one due to connected configurations, which can be evaluated after studying energy convergence as a function of the parameter m of Eq. (30).

A. Effect of truncating disconnected terms

The *a priori* computable truncation energy error ΔE^{dis} comes from truncations of disconnected configurations,

$$\Delta E^{\text{dis}} = \sum_{\text{deleted } K} \Delta E_K, \quad (31)$$

with ΔE_K given by Eqs. (10) and (11) and predictor equations for CI coefficients such as Eq. (25) and similar ones.⁵⁴ ΔE^{dis} decreases monotonically with the threshold T^{egy} introduced in (26).

ΔE^{dis} is an approximation to an exact, usually unknown truncation energy error $\Delta E_{\text{exact}}^{\text{dis}}$,

$$\Delta E_{\text{exact}}^{\text{dis}} = \Delta E^{\text{dis}} + \delta E^{\text{dis}}. \quad (32)$$

For large values of ΔE^{dis} , the unknown quantity δE^{dis} is comparatively small. As T^{egy} is made smaller, ΔE^{dis} becomes tiny and δE^{dis} , which may end up being *larger* than ΔE^{dis} , can be interpreted as a residual error which may be obtained through sensitivity analyses.

In atoms, ΔE^{dis} has two sources: $\Delta E_{\text{bf}}^{\text{dis}}$ from truncations before CSF evaluation and $\Delta E_{\text{af}}^{\text{dis}}$ from truncations afterwards

$$\Delta E^{\text{dis}} = \Delta E_{\text{bf}}^{\text{dis}} + \Delta E_{\text{af}}^{\text{dis}}. \quad (33)$$

B. Effect of truncating connected terms

The existence of connected configurations, and the need to truncate most of them, brings in a new kind of error, to be denoted δE^{con} . Distinct from ΔE^{dis} and analogously as δE^{dis} , δE^{con} cannot be computed *a priori*; it can only be estimated after studying suitable patterns of energy convergence, see Ref. 54. For sufficiently small thresholds, δE^{con} can also be understood as a residual error. The sign of δE^{con} is always negative, since the latter is made up of bonafide variational energy contributions which have not been incorporated into the final calculation.

C. Energy in a model space M

The energy E_M in a model space M is written as

$$E_M = E_S + \Delta E^{\text{dis}} + \delta E^{\text{dis}} + \delta E^{\text{con}}, \quad (34)$$

where δE values are conditioned by various thresholds \mathcal{T} .⁵⁴ Since E_M is well defined, its value can in principle be obtained by a limiting process, letting all thresholds in \mathcal{T} to become sufficiently small, thus

$$\lim_{\mathcal{T} \rightarrow 0} E_M = E_S. \quad (35)$$

In very precise calculations, however, one must always settle for threshold values in \mathcal{T} that are still too large to qualify as sufficiently small, and therefore the use of residual errors δE^{dis} and δE^{con} is inevitable

$$E_M = E_S + \Delta E^{\text{dis}} + \delta E^{\text{dis}} + \delta E^{\text{con}} = E_S + \Delta E^{\text{dis}} + \delta E. \quad (36)$$

Before δE becomes known, convergence studies necessarily center upon gross values E'_M ,

$$E'_M = E_S + \Delta E^{\text{dis}}, \quad (37)$$

eventually converging to the net value E_M . Equation (37) can easily be applied and may well be all that is needed if precision requirements on E_M are not too tight. Otherwise, one must fall back into the more detailed Eq. (36).

VI. RESULTS

A. Choice of system

As a numerical test, the Ne ground state is chosen because it is the simplest well known example^{66,79–83} exhibiting many of the complexities of a highly correlated CI. The basis set consists of 103 energy-optimized radial orbitals⁷⁹ up to $\ell=13:12s12p11d10f10g9h8i7k6l5m4n3o3q3r$, amounting to 1077 orbitals.

Use was made of two programs: AUTOCL (106 000 lines of code and comments), for the calculation of pruned lists of CSFs together with the corresponding truncation energy error $\Delta E_{\text{bf}}^{\text{dis}}$, and ATMOL (159 000 lines of code and comments), for atomic and molecular SCI. The relatively large sizes of the above codes comes from the formulas used to predict energy contributions from quintuply and sextuply excited configurations. Both programs can be downloaded from a website.⁵⁴

Full CI with the chosen basis calls for 2.4×10^{25} CSFs (Ref. 84) and 1.4×10^{26} determinants disregarding spatial symmetry. CISDTQnSx up to $\ell=7$ demands 6.5×10^{12} CSFs (4.2×10^{15} distinct determinants) CISDTQ only requires 1.4×10^9 CSFs containing 1.1×10^{12} determinants. Thus the size of the calculation to be presented exceeds by orders of magnitude the size of any calculations previously attempted.

Despite neglect of relativistic effects, cm^{-1} precision within the CISDTQnSx model is sought in order to exhibit various challenges and opportunities.

TABLE I. Convergence of the CISDTQQnSx ground state energy of Ne with a $12s12p11d10f10g9h8i7k6l5m4n3o3q3r$ basis, as a function of $T^{\text{egy}} = 10^{-n}$ a.u., using fourfold iterated CI coefficients

n	N_{sd}	N_{csf}	N_{hme}	$-E_S$	$-\Delta E_{\text{bf}}^{\text{dis}}$	$-\Delta E_{\text{bf}}^{\text{dis}}(\text{QnSx})$	$-\Delta E_{\text{af}}^{\text{dis}}$	$-E'_M$	$\delta E_{\text{af}}^{\text{dis}}$
8	28.05	55.95	4.58	128.936 460 61	6.07	373.16	105.71	128.936 945 55	33.15
9	28.24	57.04	4.69	128.936 513 93	6.07	373.16	23.80	128.936 919 96	4.57
10	28.72	59.68	4.99	158.936 528 72	6.07	373.16	4.55	128.936 912 50	0.11
11	29.78	65.12	5.68	128.936 532 41	6.07	373.16	0.75	128.936 912 39	0.00
12	31.75	74.64	7.11	128.936 533 09	6.07	373.16	0.10	128.936 912 42	-0.03
13	34.76	88.35	9.59	128.936 533 15	6.07	373.16	0.01	128.936 912 39	0.00
11	41.07	86.00	8.21	128.936 532 75	6.07	373.16	0.75	128.936 912 75 ^a	0.00

^a $T^{\text{on}} = 10^{-8q}$, three times smaller than in the calculations above.

B. Beginning of calculation

A complete calculation starts as follows:

- (i) A CISD is run to obtain approximate natural orbitals.
- (ii) Using these approximate natural orbitals, a CISDT is carried out and its energy as well as the CI coefficients of single, double, and leading triple excitations are saved on a file for later use in the prediction of configurational B_K coefficients needed for the *a priori* evaluation of estimates of energy contributions of disconnected configurations.
- (iii) With data from (ii), a pruned list of CSFs for CISDTQQnSx is calculated using suitable pruning parameters.⁵⁴
- (iv) Using the list of CSFs obtained in (iii), an approximate CISDTQ wave function is obtained for the purpose of improving over the coefficients of single, double, and triple excitations first calculated in (ii).
- (v) These are used to run (iii) once more, yielding a very similar list of CSFs. The new CI coefficients of singles, doubles and triples yield more accurate truncation energy errors $\Delta E_{\text{bf}}^{\text{dis}}$ and $\Delta E_{\text{af}}^{\text{dis}}$. In all, the said CI coefficients were iterated fourfold.

The eigenproblem is determined variationally by a method whose accuracy can be controlled,⁵⁵ presently to within less than one microhartree in the largest reported calculations.

C. General strategy

Convergence of connected configurations was first studied in detail⁵⁴ as a function of m until reaching very small values of $T^{\text{on}}(m)$ using triples and quadruples truncated after $\ell=7$ for the purpose of gaining an idea about convergence behavior and expected values of m for $\ell=13$.

The final parameters for pruning the configuration list before CSF evaluation were obtained from various studies⁵⁴ aiming at both a sufficiently small truncation energy error ΔE_{bf} and a negligible residual error δE_{bf} . In particular, the maximum value of degenerate elements g_K per configuration was set at $g_K=261$, whereas a maximum value of $n_K=70\,000$ was chosen for reasons explained in Ref. 54.

D. CISDTQQnSx results for Ne ground state

After the several studies outlined in the previous subsection CISDTQQnSx calculations are presented as a function of T^{egy} in Table I. The occupation number thresholds are set at $T^{\text{on,dis}} = T^{\text{on,con}} = 3 \times 10^{-8q}$

The second and third columns show the number of determinants, N_{sd} (in 10^9), and of CSFs, N_{csf} (in millions), respectively. These large numbers in many routine calculations are comparable to those in state-of-the-art full CI prowess,²⁸ except that in the present case the orbital bases are considerably larger while the sparseness of the CI matrices is greatly reduced due to the selection process. The fourth column holds the number of nonzero Hamiltonian matrix elements, N_{hme} (in 10^{12}). In the penultimate row, this number amounts to 9.59×10^{12} , entailing 153 terabytes of disk storage in a traditional application of Davidson's eigensolver⁸⁵ in which the matrix elements are expensive to evaluate thus precluding their recalculation at each iteration. Fortunately, this demand is obviated by the use of a select-divide-and-conquer method⁵⁵ to solve the eigenproblem.

Neglecting residual errors δE coming from quintuples and sextuples, the following conclusions are obtained.

- (i) For $T^{\text{egy}} = 10^{-8}$, $\Delta E_{\text{af}}^{\text{dis}}$ is larger than the actual energy lowering, yielding a too low gross energy. However, as T^{egy} becomes 10^{-10} a.u. and smaller, $\Delta E_{\text{af}}^{\text{dis}}$ values achieve remarkable accuracy, allowing to produce a reliable converged energy as far as disconnected configurations are concerned; it is estimated that $|\delta E_{\text{af}}^{\text{dis}}| \leq 0.05 \mu\text{hartree}$.
- (ii) In order to estimate $\delta E_{\text{af}}^{\text{con}}$, a final calculation with $T^{\text{egy}} = 10^{-11}$ a.u., and $T^{\text{on,dis}} = T^{\text{on,con}} = 10^{-8q}$ was carried out and reported in the last row of Table I. Considering patterns of energy convergence of connected configurations from previous studies⁵⁴ it may be estimated $-\delta E_{\text{af}}^{\text{con}} \leq 0.55 \pm 0.15 \mu\text{hartree}$.
- (iii) Studies of $\Delta E_{\text{bf}}^{\text{dis}}$ values in various circumstances⁵⁴ indicate that $\delta E_{\text{bf}}^{\text{dis}}$ is negligible, around $\pm 0.15 \mu\text{hartree}$.
- (iv) From pilot calculations it was estimated $-\delta E_{\text{bf}}^{\text{con}} \leq 0.5 \mu\text{hartree}$. The significance of connected configurations for still higher values of g_K and n_K not yet considered is deemed to be equally negligible. Adding both contributions, $-\delta E_{\text{bf}}^{\text{con}} \leq 1 \mu\text{hartree}$.

As to the truncation error $\Delta E_{\text{bf}}^{\text{dis}}(\text{QnSx})$ from quintuples and sextuples, it amounts to 373 $\mu\text{hartree}$ subdivided as fol-

TABLE II. Comparison with best previous calculation using the same orbital basis; energies in a.u.(Ne).

Description	Energy
E_S , Ref. 79	128.935 802
E_S , Table I	128.936 533
E_M , CISDTQ, Eq. (36), Sec. VI D.	128.936 541(2)
E_M , CISDTQQnSx, Eq. (36), Table I	128.936 914(2)
ΔE^{OBI} , Ref. 79	0.000 643(20)
$E(\text{CISDTQQnSx})$	128.937 557
E^{exact} , Ref. 86	128.937 570

lows: 22 $\mu\text{hartree}$ from quintuples (16 from singles times doubles times doubles, and 6 from connected triples times doubles), and 351 $\mu\text{hartree}$ from sextuples (doubles times doubles times doubles).

By taking together all previous considerations, it is estimated $\delta E^{\text{con}} = -1.5 \pm 2.0 \mu\text{hartree}$, thus $E_S = -128.936\,541(2)$ and the total energy in the model space M , Eq. (36), becomes $E_M = -128.936\,914(2)$ a.u.(Ne), neglecting δE from quintuples and sextuples.

E. Comparison with previous Ne results

The best previous variational calculation⁷⁹ used the same orbital set and consisted of a multireference CISD (MRCI-SD) supplemented with connected configurations selected according to Eqs. (33) and (35) including 0.35×10^6 CSFs and 34×10^6 determinants. Unknown and unsuspected to the authors at the time,⁷⁹ its CI energy error amounted to 739 $\mu\text{hartree}$, as it may be deduced from Table I after subtracting the energy contribution from quintuples and sextuples.

From the previous subsection, $E_S = -128.936\,541$ a.u.(Ne), and $E_M = -128.936\,914(2)$ a.u.(Ne) (Table II). The energy error ΔE^{OBI} due to orbital basis incompleteness was computed previously as $-643 \pm 20 \mu\text{hartree}$ (this value may be deduced from Table VI of Ref. 79) through studies of successive saturation with radial functions for a given ℓ value at the CISD level of approximation, together with patterns of convergence of angular energy limits.^{2,66}

Adding E_M to ΔE^{OBI} , an upper bound $E_u = -128.937\,557$ a.u.(Ne) is obtained, 13 $\mu\text{hartree}$ above the “exact” value estimated by Chakravorty *et al.*,⁸⁶ and probably fortuitously close to it since septuples and higher excitations are deemed to contribute slightly more than the observed 13 $\mu\text{hartree}$. More accurate estimates of ΔE^{OBI} and of energy contributions beyond quadruples are needed to test the reliability of this exact energy prediction.⁸⁶

VII. DISCUSSION

A. Achievements

A priori SCI together with truncation and residual energy errors, Eq. (36), has been generally formulated, and a practical approach to approximate CISDTQQnSx has been given. SCI rests upon

- (i) Brown’s formula⁵² (Sec. II),

- (ii) the use of predictors for configurational CI coefficients to select and assess disconnected configurations via Brown’s formula,
- (iii) the use of natural orbital concepts to select connected configurations and disconnected triples, and
- (iv) sensitivity analyses to determine residual errors.

Predictors for configurational rather than determinantal coefficients are essential to reduce computational requirements by several orders of magnitude. Gross energies converge from below, however, as T^{eg} becomes sufficiently small, $\Delta E_{\text{af}}^{\text{dis}}$ values become remarkably accurate, well under 1 $\mu\text{hartree}$ (see Table I).

As implemented here, the method can be applied quite in general to an important range of electronic systems including all atoms, for CISDTQQnSx calculations in model CI spaces exceeding 10^{12} CSFs and quadrillions of determinants.

SCI has been tested on the Ne ground state using a single computer processor. A rapidly convergent sequence of energies and wave functions (Table I) together with calculated truncation and residual energy errors is used to achieve an precision of 2 $\mu\text{hartree}$ within a CISDTQ model. A less precise result within a CISDTQQnSx model is also given. The final energy result still needs to be complemented by similar analyses with septuply and higher-excited configurations, and also by more accurate estimates of $\Delta E_{\mu}^{\text{OBI}}$ due to orbital basis incompleteness,^{3,4} as discussed earlier in the Introduction in connection with Eq. (2).

The largest previous CI calculation²⁸ involved ten electrons, 34 orbitals, 9.68×10^9 determinants, 128 processors, and attained absolute convergence to within 5 $\mu\text{hartree}$. For comparison, the largest calculation in this paper (penultimate row of Table I) also involves ten electrons, 1077 energy-optimized orbitals, 88×10^9 CSFs expanded in 35×10^9 determinants in the selected space S with all corresponding CI coefficients being calculated variationally at least once, while energy convergence in S attains a fraction of 1 $\mu\text{hartree}$. (The last entry of Table I features 41×10^9 determinants.) A recent FCI calculation⁸⁷ on the eight valence electrons of the C_2 molecule uses 68 orbitals, 65×10^9 determinants, and 432 processors, achieving convergence with a residual norm of 10^{-5} .

B. Estimate of the orbital basis incompleteness error ΔE^{OBI}

Whatever *ab initio* method is being used, Eqs. (31)–(33) can be applied to quickly estimate the orbital basis incompleteness error ΔE^{OBI} without ever carrying out a major calculation, if connected configurations can be neglected or do not occur altogether: ΔE^{OBI} can be approximated by the difference between $\Delta E_{\text{af}}^{\text{dis}}$ values for one *very* large basis set and for the original basis. To do so one only needs

- (i) CI coefficients of singly, doubly, and triply excited configurations, from CISDT, CCSD(T) or HCCI wave functions,
- (ii) one diagonal matrix element between the Slater determinants for each configuration involved together with corresponding one- and two-electron integrals, and

- (iii) the configurational coefficients calculated from the predictor equations, Eq. (25) and similar ones.

A sequence of calculations with increasing basis set size can be used to yield increasingly small ΔE^{OBI} values (in magnitude) which may be extrapolated.

C. Impact on other methods and outlook

In order to formulate a theoretical model⁸⁸ one must settle for

- accuracy with respect to the Breit-Dirac-Schrödinger theory or experiment,
- precision with respect to the model itself (truncation and residual errors for energies, and sensitivity tests for all properties, in general), and
- the method to be used, for example, CISDTQnSx, or any of the suggestions below.

Selected CI is too general to constitute a theoretical model on its own, however, it can be used to formulate new theoretical models or to improve upon existing ones.

Brown's formula, Eq. (10), used in conjunction with the predictor equations for CI coefficients of higher than double excitations, can smoothly replace perturbation theory in all so called PT2 methods^{89,90} since it is more accurate and about as efficient, thanks to Eq. (11). In principle, it can also be applied beyond PT2. The same may be said about the selection process in CI methods based on the symmetry-adapted-cluster expansion, generically called SAC/SAC-CI methods.^{9-11,91}

Multireference CI (Refs. 92-96) continues to be actively developed.⁹⁷ In carrying the transition to SCI, MRCI can first be supplemented with the truncation energy error $\Delta E_{\text{af}}^{\text{dis}}$, Eq. (33), and with connected configurations,⁷⁹ given the case. Next, the configuration generator in MRCI can be extended from MRCI-SD to MRCI-SDTQ. If Qn and Sx excitations are considered only at the level of evaluation of truncation energy errors, the corresponding effort (which increases linearly with the number of configurations) is a small fraction of the one required for a selected CISDTQ calculation. In any case, introduction of leading selected quintuples and sextuples into the wave function is straightforward.

General incorporation of higher than sextuply excited SCI is not a good idea, in general, although septuples and octuples are feasible in atoms.⁵⁴ In molecules, variational expansion coefficients $c_{ijk\dots}^{abc\dots}$ can be used to obtain accurate $t_{ijk\dots}^{abc\dots}$ amplitudes, which in turn can be fed into a CC ansatz,⁷ hopefully improving the energy and the efficiency of CC methods in a single step without need of CC iterations. Perhaps more interesting, accurate CI wave functions may be used to tailor CCSD.⁹⁸

The density matrix renormalization group method,²⁹ and the growing family of iterative CI methods^{23-25,99,100} can be used with the largest possible bases to estimate the energy errors due to truncations beyond quadruples, thus enhancing SCI capabilities.

By advancing reliable CISDTQnSx, the present SCI method considerably extends the scope of accurate atomic

and molecular *ab initio* electronic structure applications. If the orbital bases are well chosen^{101,102} or well developed (for example, through energy optimization^{79,103}), one may envision unprecedented accuracy for problems tractable by CIS-DTQnSx or by the SCI-improved methods mentioned above.

Needless to emphasize, SCI applies *mutatis mutandis* to the Dirac-Schrödinger equation,¹⁰⁴ and also to the Breit-Dirac-Schrödinger equation,¹⁰⁵ provided only positive-energy orbitals are used, viz., within the *no-pair* Hamiltonian approximation.¹⁰⁶ In fact, the computer program ATMOL⁵⁴ has precisely that capability for general atomic states.

After what has been said, there remains the input/output bottleneck¹⁰⁷ inherent to large-scale applications of Davidson's eigensolver⁸⁵ when applied to CI matrices expressed in terms of CSFs. In the following paper,⁵⁵ this bottleneck is overcome by a select-divide-and-conquer variational procedure based on the present configuration selection scheme.

ACKNOWLEDGMENTS

I am indebted to Professor Ramon Carbó-Dorca for stimulating conversations and lasting friendship during my sabbatical year at the Institute of Computational Chemistry of University of Girona (Catalonia, Spain) in 2001-2002. Discussions with various colleagues stirred further motivations, particularly with Professors Ignacio Garzón (Mexico, D.F.), Ingvar Lindgren (Goteborg, Sweden), and Alejandro Ramírez-Solís (Cuernavaca, Mexico), and Dr. Oliverio Jitrik. The sharp and kind criticism of Professor Isahia Shavitt (Urbana, Illinois) is deeply appreciated. The Dirección General de Servicios de Cómputo Académico (DGSCA) of Universidad Nacional Autónoma de México, and the Computing Center at my own institute are thanked for their excellent and free services. Support from CONACYT through Grant Nos. E-26726 and 44363-F is gratefully acknowledged.

¹P.-O. Löwdin, Adv. Chem. Phys. **2**, 207 (1959).

²C. F. Bunge, Theor. Chim. Acta **16**, 126 (1970).

³T. H. Dunning Jr., K. A. Peterson, and D. E. Woon, in *Encyclopedia of Computational Chemistry*, edited by P. von R. Schleyer (Wiley, New York, 1998).

⁴W. Klopper, K. L. Bak, P. Jorgensen, J. Olsen, and T. Helgaker, J. Phys. B **32**, R103 (1999).

⁵G. A. Petersson, D. K. Malick, M. J. Frisch, and M. Braunstein, J. Chem. Phys. **123**, 074111 (2005).

⁶I. Lindgren and J. Morrison, *Atomic Many-Body Theory* (Springer-Verlag, Berlin, 1986).

⁷F. E. Harris, H. J. Monkhorst, and D. L. Freeman, *Algebraic and Diagrammatic Methods in Many-Fermion Theory* (Oxford University Press, New York, 1992).

⁸C. D. Sherrill and H. F. Schaefer III, Adv. Quantum Chem. **34**, 143 (1999).

⁹H. Nakatsuji and K. Hirao, J. Chem. Phys. **68**, 2053 (1978).

¹⁰H. Nakatsuji, Chem. Phys. Lett. **67**, 329 (1979).

¹¹H. Nakatsuji, Chem. Phys. Lett. **67**, 334 (1979).

¹²M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Gaussian, Inc., Pittsburgh, PA, 2003.

¹³J. A. Pople, M. Head-Gordon, and R. Raghavachari, J. Chem. Phys. **87**, 5968 (1987).

¹⁴J. Čížek, J. Chem. Phys. **45**, 4256 (1966).

¹⁵R. J. Bartlett, Mol. Phys. **94**, 1 (1998).

¹⁶H. P. Kelly, Adv. Chem. Phys. **14**, 129 (1969).

¹⁷J. Q. Sun and R. J. Bartlett, Phys. Rev. Lett. **80**, 349 (1998).

- ¹⁸J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic, New York, 1973).
- ¹⁹J. V. Ortiz, in *Computational Chemistry: Reviews of Current Trends* (World Scientific, Singapore, 1997), Vol. 2, pp. 1–61.
- ²⁰C. Garrod and J. K. Percus, *J. Math. Phys.* **5**, 1756 (1964).
- ²¹D. A. Mazziotti, *J. Chem. Phys.* **121**, 10957 (2004).
- ²²S. R. White and R. L. Martin, *J. Chem. Phys.* **110**, 4127 (1999).
- ²³H. Nakatsuji, *J. Chem. Phys.* **113**, 2949 (2000).
- ²⁴H. Nakatsuji and E. R. Davidson, *J. Chem. Phys.* **115**, 2000 (2001).
- ²⁵H. Nakatsuji, *J. Chem. Phys.* **115**, 2465 (2001).
- ²⁶R. J. Bartlett, V. F. Lotrich, and V. Schweigert, *J. Chem. Phys.* **123**, 062205 (2005).
- ²⁷A. Aspuru-Guzik, O. El Akramine, and W. A. Lester Jr., *J. Chem. Phys.* **120**, 3049 (2004).
- ²⁸E. Rossi, G. L. Bendazzoli, S. Evangelisti, and D. Maynau, *Chem. Phys. Lett.* **310**, 530 (1999).
- ²⁹G. K.-L. Chan and M. Head-Gordon, *J. Chem. Phys.* **118**, 8551 (2003).
- ³⁰H. Nakatsuji and M. Ehara, *J. Chem. Phys.* **122**, 194108 (2005).
- ³¹H. Primas, in *Modern Quantum Chemistry*, edited by O. Sinanoğlu (Academic, New York, 1965), Part II, p. 45, and references therein.
- ³²J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem., Symp.* **10**, 1 (1976).
- ³³W. Kutzelnigg, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 3, p. 129.
- ³⁴R. J. Bartlett and G. D. Purvis, *Int. J. Quantum Chem.* **14**, 561 (1978).
- ³⁵J. M. Herbert and J. E. Harriman, *J. Chem. Phys.* **117**, 7464 (2002).
- ³⁶K. Raghavachari, G. W. Trucks, M. Head-Gordon, and J. A. Pople, *Chem. Phys. Lett.* **157**, 479 (1989).
- ³⁷R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990).
- ³⁸J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987).
- ³⁹G. E. Scuseria and H. F. Schaefer III, *Chem. Phys. Lett.* **152**, 388 (1988).
- ⁴⁰Y. J. Bomble, J. F. Stanton, M. Kállay, and J. Gauss, *J. Chem. Phys.* **123**, 054101 (2005).
- ⁴¹S. A. Kucharski and R. J. Bartlett, *Theor. Chim. Acta* **80**, 387 (1991).
- ⁴²N. Oliphant and L. Adamowicz, *J. Chem. Phys.* **95**, 6645 (1991).
- ⁴³M. Musial, S. A. Kucharski, and R. J. Bartlett, *J. Chem. Phys.* **116**, 4382 (2002).
- ⁴⁴J. Olsen, P. Jorgensen, H. Koch, A. Balkova, and R. J. Bartlett, *J. Chem. Phys.* **104**, 8007 (1996).
- ⁴⁵S. Hirata and R. J. Bartlett, *Chem. Phys. Lett.* **321**, 216 (2000).
- ⁴⁶T. Van Voorhis and M. Head-Gordon, *J. Chem. Phys.* **115**, 5033 (2001).
- ⁴⁷P. Piecuch, K. Kowalski, P.-D. Fan, and K. Jedziniak, *Phys. Rev. Lett.* **90**, 113001 (2003).
- ⁴⁸R. J. Bartlett and J. Noga, *Chem. Phys. Lett.* **150**, 29 (1988).
- ⁴⁹B. Huron, J.-P. Malrieu, and P. Rancurel, *J. Chem. Phys.* **58**, 5745 (1973).
- ⁵⁰B. O. Roos, *Adv. Chem. Phys.* **69**, 399 (1987).
- ⁵¹J. Olsen, B. O. Roos, P. Jorgensen, and H. J. A. Jensen, *J. Chem. Phys.* **89**, 2185 (1988).
- ⁵²R. E. Brown, Ph.D. thesis, Department of Chemistry, Indiana University, 1967.
- ⁵³T. P. Živković and H. J. Monkhorst, *J. Math. Phys.* **19**, 1007 (1978).
- ⁵⁴<http://www.fisica.unam.mx/teorica/bunge>
- ⁵⁵C. F. Bunge and R. Carbó-Dorca, *J. Chem. Phys.* **124**, 014108 (2006), following paper.
- ⁵⁶C. F. Bunge, *Phys. Rev.* **168**, 92 (1968).
- ⁵⁷E. P. Wigner, *Group Theory* (Academic, New York, 1959).
- ⁵⁸A. V. Bunge, C. F. Bunge, R. Jáuregui, and G. Cisneros, *Comput. Chem. (Oxford)* **13**, 201 (1989).
- ⁵⁹R. Jáuregui, C. F. Bunge, A. V. Bunge, and G. Cisneros, *Comput. Chem. (Oxford)* **13**, 223 (1989).
- ⁶⁰A. V. Bunge, C. F. Bunge, R. Jáuregui, and G. Cisneros, *Comput. Chem. (Oxford)* **13**, 239 (1989).
- ⁶¹G. Cisneros, R. Jáuregui, C. F. Bunge, and A. V. Bunge, *Comput. Chem. (Oxford)* **13**, 255 (1989).
- ⁶²I. Shavitt, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 3, p. 189.
- ⁶³C. F. Bender and E. R. Davidson, *J. Phys. Chem.* **70**, 2675 (1966).
- ⁶⁴R. K. Nesbet, *Phys. Rev.* **109**, 1632 (1958).
- ⁶⁵O. Sinanoğlu, *J. Chem. Phys.* **36**, 706 (1962).
- ⁶⁶F. Sasaki and M. Yoshimine, *Phys. Rev. A* **9**, 17 (1974).
- ⁶⁷K. A. Brueckner, *Phys. Rev.* **100**, 36 (1955).
- ⁶⁸J. Goldstone, *Proc. R. Soc. London, Ser. A* **239**, 267 (1957).
- ⁶⁹J. Hubbard, *Proc. R. Soc. London, Ser. A* **240**, 539 (1957).
- ⁷⁰F. Coester, *Nucl. Phys.* **7**, 421 (1958).
- ⁷¹F. Coester and H. Kümmel, *Nucl. Phys.* **17**, 477 (1960).
- ⁷²T. van Mourik and T. H. Dunning Jr., *J. Chem. Phys.* **111**, 9248 (1999).
- ⁷³A. Pipano and I. Shavitt, *Int. J. Quantum Chem.* **2**, 741 (1968).
- ⁷⁴The author is indebted to Professor Ingvar Lindgren for suggesting this terminology.
- ⁷⁵Connected triply excited configurations are related only to t_{ijk}^{abc} amplitudes. Connected quadruply excited configurations may come from t_{ijk}^{abc} or just from t_{ijkl}^{abcd} amplitudes, whereas disconnected configurations have contributions from all cluster amplitudes up to the corresponding excitation level.
- ⁷⁶J. Paldus, J. Čížek, and I. Shavitt, *Phys. Rev. A* **5**, 50 (1972).
- ⁷⁷P.-O. Löwdin, *Phys. Rev.* **97**, 1474 (1955).
- ⁷⁸E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic, New York, 1976).
- ⁷⁹O. Jitrik and C. F. Bunge, *Phys. Rev. A* **56**, 2614 (1997).
- ⁸⁰C. F. Bunge and E. M. A. Peixoto, *Phys. Rev. A* **1**, 1277 (1970).
- ⁸¹J. Olsen, P. Jorgensen, and J. Simons, *Chem. Phys. Lett.* **169**, 463 (1990).
- ⁸²A. Rizzo, E. Clementi, and M. Sekiya, *Chem. Phys. Lett.* **177**, 477 (1991).
- ⁸³T. Noro, K. Ohtsuki, and F. Sasaki, *Int. J. Quantum Chem.* **51**, 225 (1994).
- ⁸⁴J. Paldus, *J. Chem. Phys.* **61**, 5321 (1974).
- ⁸⁵E. R. Davidson, *J. Comput. Phys.* **15**, 87 (1975).
- ⁸⁶S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and Ch. Froese Fischer, *Phys. Rev. A* **47**, 3649 (1993).
- ⁸⁷Z. Gan and R. J. Harrison, presented at Supercomputing 2005, November 2005 (unpublished); <http://sc05.supercomputing.org>
- ⁸⁸J. A. Pople, *Rev. Mod. Phys.* **71**, 1267 (1999).
- ⁸⁹K. Andersson, P. Malmqvist, and B. O. Roos, *J. Chem. Phys.* **96**, 1218 (1992).
- ⁹⁰B. O. Roos, K. Andersson, M. P. Fülscher, P.-A. Malmqvist, L. Serrano-Andrés, K. Pierloot, and M. Merchán, *Adv. Chem. Phys.* **93**, 219 (1996).
- ⁹¹M. Ehara, Y. Ohtsuka, H. Nakatsuji, M. Takahashi, and Y. Udagawa, *J. Chem. Phys.* **122**, 234319 (2005).
- ⁹²J. L. Whitten and M. Hackmeyer, *J. Chem. Phys.* **51**, 5584 (1969).
- ⁹³M. Hackmeyer and J. L. Whitten, *J. Chem. Phys.* **54**, 3739 (1971).
- ⁹⁴L. R. Kahn, P. J. Hay, and I. Shavitt, *J. Chem. Phys.* **61**, 3530 (1974).
- ⁹⁵R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta* **35**, 33 (1974).
- ⁹⁶M. W. Schmidt and M. S. Gordon, *Annu. Rev. Phys. Chem.* **49**, 233 (1998).
- ⁹⁷P. Stampfuß and W. Wenzel, *J. Chem. Phys.* **122**, 024110 (2005).
- ⁹⁸T. Kinoshita, O. Hino, and R. J. Bartlett, *J. Chem. Phys.* **123**, 074106 (2005).
- ⁹⁹H. Nakatsuji, *Phys. Rev. Lett.* **93**, 030403 (2004).
- ¹⁰⁰H. Nakatsuji and H. Nakashima, *Phys. Rev. Lett.* **95**, 050407 (2005).
- ¹⁰¹H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules* (Addison Wesley, Reading, MA, 1972).
- ¹⁰²T. H. Dunning Jr., *J. Phys. Chem. A* **104**, 9062 (2000).
- ¹⁰³Z. Xiong, M. I. Velgakis, and N. C. Bacalis, *Int. J. Quantum Chem.* **104**, 418 (2005).
- ¹⁰⁴R. Jáuregui, C. F. Bunge, and E. Ley-Koo, *Phys. Rev. A* **55**, 1781 (1997).
- ¹⁰⁵C. F. Bunge, E. Ley-Koo, and R. Jáuregui, *Int. J. Quantum Chem.* **80**, 461 (2000).
- ¹⁰⁶J. Sucher, *Phys. Rev. A* **22**, 348 (1980).
- ¹⁰⁷R. Shepard, I. Shavitt, and H. Lischka, *J. Comput. Phys.* **23**, 1121 (2002).