Select-divide-and-conquer method for large-scale configuration interaction

Carlos F. Bunge[a)]
Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, México 01000, México

Ramon Carbó-Dorca[b)]
Instituto de Química Computacional, Universitat de Girona, Campus de Montilivi, 17071 Girona, Spain

A select-divide-and-conquer variational method to approximate configuration interaction (CI) is presented. Given an orthonormal set made up of occupied orbitals (Hartree-Fock or similar) and suitable correlation orbitals (natural or localized orbitals), a large N-electron target space S is split into subspaces $S_0, S_1, S_2, \ldots, S_R$. S_0, of dimension d_0, contains all configurations K with attributes (energy contributions, etc.) above thresholds $\mathcal{T}_0 \equiv \{T_0^{\text{egy}}, T_0^{\text{etc.}}\}$; the CI coefficients in S_0 remain always free to vary. S_1 accommodates Ks with attributes above $\mathcal{T}_1 \leq \mathcal{T}_0$. An eigenproblem of dimension $d_0 + d_1$ for $S_0 + S_1$ is solved first, after which the last d_1 rows and columns are contracted into a single row and column, thus freezing the last d_1 CI coefficients hereinafter. The process is repeated with successive $S_j (j \geq 2)$ chosen so that corresponding CI matrices fit random access memory (RAM). Davidson's eigensolver is used R times. The final energy eigenvalue (lowest or excited one) is always above the corresponding exact eigenvalue in S. Threshold values $\{\mathcal{T}_j; j=0,1,2,\ldots,R\}$ regulate accuracy; for large-dimensional S, high accuracy requires $S_0 + S_1$ to be solved outside RAM. From there on, however, usually a few Davidson iterations in RAM are needed for each step, so that Hamiltonian matrix-element evaluation becomes rate determining. One μhartree accuracy is achieved for an eigenproblem of order 24×10^6, involving 1.2×10^{12} nonzero matrix elements, and 8.4×10^9 Slater determinants. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2207621]

I. INTRODUCTION

Quantum chemistry largely revolves around the development and application of methods to approximate Schrödinger's equation for stationary states,

$$H\Psi_\mu = E_\mu \Psi_\mu. \tag{1}$$

Orbital basis set methods provide the most general approach[1] when the number of *active* electrons is not too large.[2] After selection of a suitable orbital set, which is essential to obtain meaningful chemical or physical results,[3] the main question is what to do with a computationally intractable representation **H** of the Hamiltonian in the given orbital set,

$$\mathbf{H}\mathbf{C}_\mu = E_\mu \mathbf{C}_\mu. \tag{2}$$

Naturally, this complete or full configuration interaction (CI) needs to be drastically simplified, resulting in several approximate methods.[1,4–10] Within the CI approaches, highly correlated configuration interaction[11] (HCCI) methods, viz., CI going well beyond the singles and doubles treatment, constitutes a practical alternative to using a full Hamiltonian representation, particularly after the developments in the companion paper[12] to be referred to as I.

One possibility is to select a *priori* a subspace S having invariant properties with respect to separate unitary transformations of the occupied orbitals and of distinct sets of cor-

relation orbitals grouped in a well-defined manner,[11] giving rise to multireference CI (MRCI),[13–18] complete active space (CAS) CI,[19] restricted active space (RAS) CI,[20] and so on.[21] The corresponding CI-matrix eigenvalue problem is

$$\mathbf{H}^S \mathbf{C} = E_S \mathbf{C}, \tag{3}$$

where the subindex μ was dropped in the understanding that the following also applies to excited states. Equation (3) is often solved by Davidson's method.[22,23] Typically, an accuracy of 10^{-8} a.u. for a ground state requires 40–60 iterations dominated by the evaluation of a vector σ,

$$\sigma = \mathbf{H}\mathbf{v}, \tag{4}$$

in terms of an approximate eigenvector **v**. In a basis of N-electron symmetry eigenfunctions or configuration-state-functions (CSFs) the corresponding $H_{\mu\nu}$s are given by lengthy formulas whose application may require hundreds of computer processor cycles, justifying to store them in disk memory after being evaluated only once. Thus in a CSF framework, the upper-limit size for evaluation of Eq. (4) is determined by the capacity of the disks employed and by the willingness to spend comparatively large amounts of time to retrieve **H** while the computer processors remain idle or are used by competing programs. Alternatively, for determinantal CI spaces, each nonzero $H_{\mu\nu}$ can be evaluated in a few cycles of computer time[11] so that the entire Hamiltonian matrix can be recalculated on-the-fly as needed for each iteration of Eq. (4) therefore overcoming the necessity to store

---

a)Electronic mail: bunge@fisica.unam.mx
b)Electronic mail: quantumqsar@hotmail.com

125, 014108-1

$H_{\mu\nu}$s in disk. This was, in fact, the reason behind the move from CSFs to determinants about two decades ago.[20,24]

Concurrently, and departing from invariant spaces, another possibility was advanced in the previous paper[12] where it was shown that a model space M can be split *a priori* into a selected space S harboring the energetically most important configurations, and a remainder whose energy effect ΔE can be predicted with fair accuracy through variational-like estimates *before* embarking on an HCCI calculation. The corresponding energy E_M is given by

$$E_M = E_S + \Delta E + \delta E, \tag{5}$$

where δE is a residual error that can be estimated after some work.[12] Whatever HCCI method is invoked, the energy of a stationary state can be approximated by the rhs of Eq. (5) which in turn demands the solution of (3). In order to obtain small and reliable ΔE and δE values, however, it is still necessary to deal with S spaces which are too large to handle by modern HCCI.[11]

If the input-output bottleneck of the eigenproblem[25] is overcome, a return to CSFs has the following advantages: (i) the number of nonzero $H_{\mu\nu}$s is significantly reduced, resulting in a corresponding reduction of the number of arithmetic operations to evaluate Eq. (4), (ii) by diminishing the size of vectors σ and $\mathbf{v}$ by several orders of magnitude, data localization is improved thus speeding up data transit between memory hierarchies, and (iii) excited states are readily and unequivocally identified. While retaining Davidson's or similar algorithms,[26] this paper presents a select-divide-and-conquer variational method (SDC-CI) for the specific solution of the atomic or molecular CI-matrix eigenvalue problem with little or no resort to external storage devices. After introducing CI notation and a general strategy to select configurations in Sec. II, SDC-CI is formulated in Sec. III. An example and a general discussion are given in Sec. IV.

II. MOTIVATION, CI NOTATION AND SELECTED CI

A. Motivation

Let S be a target space calling for a CI treatment. It is convenient that S be made up of CSFs. These are built up from a suitable orthonormal set of occupied orbitals. As before, $\mathbf{H}^S$ is the representation of the Hamiltonian in S;

$$\mathbf{H}^S \mathbf{C} = E_S \mathbf{C}. \tag{6}$$

Here we have rewritten Eq. (3) just to emphasize a new and necessary requirement [not present in Eq. (3)]. The use of natural orbitals[27,28] or localized orbitals[29] as correlation orbitals, in order to facilitate an *a priori* and quantitative selection and deletion of CSFs.[12] Distinct from general eigenproblems, Eq. (6) is a very special eigenvalue problem in which various eigenvector components are related among themselves in a way which can be anticipated[12] before knowing its solution. This circumstance allows the subdivision of S into subspaces $S_0, S_1, S_2, \ldots, S_R$ each characterized by configurations with decreasing importance in their energy contributions. Other criteria to select S_i subspaces will also be discussed.

B. CI notation and Brown's formula

A general HCCI wave function can be written as[30]

$$\Psi = \sum_{K=1}^{K_x} \sum_{g=1}^{g_K} F_{gK} C_{gK}. \tag{7}$$

In Eq. (7), K and g label configurations and degenerate elements, respectively, and C_{gK} denotes a CI coefficient. F_{gK} is a CSF expressed as a linear combination of Slater determinants D_{iK},

$$F_{gK} = O(\Gamma, \gamma) \sum_{i=1}^{g} D_{iK} b_i^g = \sum_{i=1}^{n_K} D_{iK} c_i^g, \tag{8}$$

where $O(\Gamma, \gamma)$ is a symmetric projection operator[31] for all appropriate symmetry operators Γ and a given irreducible representation γ.[32] The calculations in this paper will use the full range of g_K degenerate elements, although this is not necessary, in general.[30,33]

Given a CI wave function Ψ, the energy contribution ΔE_{gK} of F_{gK} is defined as

$$\Delta E_{gK} = \langle \Psi | H | \Psi \rangle - \langle \Psi(-F_{gK}) | H | \Psi(-F_{gK}) \rangle, \tag{9}$$

where $\Psi(-F_{gK})$ denotes $\mathcal{N}(\Psi - F_{gK} C_{gK})$ and $\mathcal{N}$ is a normalization factor, such that the wave function $\Psi(-F_{gK})$ has the same remaining expansion coefficients as Ψ except for renormalization. ΔE_{gK} can be approximated by Brown's formula,[34]

$$\Delta E_{gK} = (E - H_{gK,gK}) C_{gK}^2 / (1 - C_{gK}^2), \tag{10}$$

where $E = \langle \Psi | H | \Psi \rangle$. Equation (7) is now rewritten as

$$\Psi = \sum_{K=1}^{K_x} G_K B_K, \tag{11}$$

in terms of normalized symmetry configurations G_K,

$$G_K = \text{Sign} \cdot N_K \sum_{g=1}^{g_K} F_{gK} C_{gK}, \tag{12}$$

$$B_K = \frac{1}{N_K}, \quad N_K = \text{Sign} \sqrt{1 \Big/ \sum_{g=1}^{g_K} C_{gK}^2}, \tag{13}$$

in an obvious notation. In Eq. (12) and (13), Sign is the minus sign if the contribution of negative C_{gK} coefficients to the sum of squares is larger than the one provided by the positive coefficients, and vice versa. Unsigned B_K coefficients are also of interest.[12] Similarly as ΔE_{gK} in Eq. (10), ΔE_K for expansion (11) is given by

$$\Delta E_K = (E - H_{KK}) B_K^2 / (1 - B_K^2), \tag{14}$$

which is used just for estimating the truncation energy error. A thorough discussion of Eq. (14) together with predictive formulas for B_K coefficients up to sextuply excited configurations is found in Paper I.

C. Energy threshold T^{egy}

Brown's formula provides a useful criterion to select configurations K based on energy thresholds T^{egy}, provided the coefficients B_K can be predicted. This happens when K can be formed as a product of combinations of singly and doubly excited configurations, such as any triply or quadruply excited configuration in a MRCI singles and doubles out of a single reference configuration. Such configurations are called disconnected configurations.[12] A subdivision of S into subspaces S_j, $(j=0,1,2,\ldots,R)$ can be partially characterized by

$$|\Delta E_K| > T_j^{\text{egy}}, \tag{15}$$

$$T_0^{\text{egy}} \geqslant T_1^{\text{egy}} \geqslant T_2^{\text{egy}} \geqslant \ldots \geqslant T_R^{\text{egy}}. \tag{16}$$

D. Occupation number threshold T^{on}

The rest of the configurations are called connected configurations. They are selected according to occupation number thresholds T^{on} based on density matrix concepts. As already mentioned, the SDC-CI method may require the correlation orbitals a,b,c to be approximate natural orbitals,[27,28] viz., eigenfunctions χ_a of the reduced first-order density matrix $\gamma(1,1')$,

$$\gamma(1,1') = \sum n_a \chi_a^*(1)\chi_a(1'), \tag{17}$$

where the n_as are the eigenvalues or occupation numbers. Alternatively, in extended molecules, if localized orbitals[29] are used, the occupation numbers n_a have to be replaced by effective occupation numbers n_a^{eff},

$$n_a^{\text{eff}} = \sqrt{\sum_j |\gamma_{aj}|^2}. \tag{18}$$

For each q-excited configuration K the product $P(q,K)$ of corresponding occupation numbers is given by

$$P(q,K) = \prod_{i=1}^{q} n_{K_i}, \tag{19}$$

where K_i represents either a correlation natural orbital or a localized orbital. The characterization of the subspaces S_j, $(j=0,1,2,\ldots,R)$ is enriched by enforcing

$$P(q,K) > T_j^{\text{on}}. \tag{20}$$

$$T_0^{\text{on}} \geqslant T_1^{\text{on}} \geqslant T_2^{\text{on}} \geqslant \cdots \geqslant T_R^{\text{on}}. \tag{21}$$

In (20) and (21), T_j^{on} may be a number or, more generally, a suitable function of some parameters,

$$T^{\text{on}}(m) = F_{\text{dh}} F_{\text{con}} 10^{-mg}, \tag{22}$$

where $F_{\text{dh}} \geqslant 1$ is a deep-hole factor[12] associated to holes involving inner electrons, and $F_{\text{con}} \geqslant 1$ is a factor for connected configurations.[12] The introduction of F_{dh} and F_{con} is to recognize the well characterized families of configurations that are comparatively less important for a given value of $P(q,K)$.[12] The parameter m is shown explicitly on the left-hand side (lhs) of (22) for later purposes. $10^{-m}(F_{\text{dh}}F_{\text{con}})^{1/4}$ may be interpreted as an average occupation number below

which configurations involving that natural orbital are deleted from an original model space M.

E. Harmonic truncation threshold T^{har}

A final subdivision of S into subspaces S_j, $(j=0,1,2,\ldots,R)$ is specified by a harmonic truncation threshold T_j^{har} indicating that subspace S_j is truncated in the orbital basis after a given harmonic ℓ_j,

$$T_j^{\text{har}} = \frac{1}{\ell_j}. \tag{23}$$

Resort to a fraction is dictated by the rule that first occurring subspaces have larger thresholds than subspaces further down the sequence

$$T_0^{\text{har}} \geqslant T_1^{\text{har}} \geqslant T_2^{\text{har}} \geqslant \cdots \geqslant T_R^{\text{har}}. \tag{24}$$

F. Selection strategy

A subspace S_j consists of the following configurations:

(i)   All (connected and disconnected) triples with $T_{j-1}^{\text{on}} \geqslant P(3,K) \geqslant T_j^{\text{on}}$. Here, the occurrence of disconnected triples is due to their carrying connected contributions in the many-body perturbation theory sense.[12]

(ii) Of the remaining (disconnected) triples, those with $T_{j-1}^{\text{egy}} \geqslant |\Delta E_K| > T_j^{\text{egy}}$.

(iii) Connected quadruples with $T_{j-1}^{\text{on}} \geqslant P(4,K) > T_j^{\text{on}}$.

(iv) Disconnected quadruples with $T_{j-1}^{\text{egy}} \geqslant |\Delta E_K| > T_j^{\text{egy}}$. Here it is assumed that disconnected quadruples have negligible connected contributions; otherwise, they must also enter in (iii).

(v)   Quintuple- and higher-excited configurations can be selected according to (iii) and (iv).

(vi) Finally, for atoms, S_j contains configurations with harmonics up to $1/T_j^{\text{har}}$. A similar threshold for molecules may be provided if warranted.

III. SELECT-DIVIDE-AND-CONQUER CI

In synthesis, the target space S is split into subspaces $S_0,S_1,S_2,\ldots,S_R$ each characterized by configurations $\{\Phi_{ij}; i=1,2,\ldots,d_j; \; j=0,1,\ldots,R\}$ above thresholds $\{\mathcal{T}_j \equiv T_j^{\text{egy}}, T_j^{\text{on}}, T_j^{\text{har}}; j=0,1,\ldots,R\}$:

$$S_0 \equiv \{\Phi_{i0}; i=1,2,\ldots,d_0\}, \quad T_0^{\text{egy}}, T_0^{\text{on}}, T_0^{\text{har}}, \tag{25a}$$

$$S_1 \equiv \{\Phi_{i1}; i=1,2,\ldots,d_1\}, \quad T_1^{\text{egy}}, T_1^{\text{on}}, T_1^{\text{har}}, \tag{25b}$$

$$S_j \equiv \{\Phi_{ij}; i=1,2,\ldots,d_j\}, \quad T_j^{\text{egy}}, T_j^{\text{on}}, T_j^{\text{har}}, \tag{25c}$$

with

$$T_0^{\text{egy}} \geqslant T_1^{\text{egy}} \geqslant T_j^{\text{egy}}, \tag{26a}$$

$$T_0^{\text{on}} \geqslant T_1^{\text{on}} \geqslant T_j^{\text{on}}, \tag{26b}$$

$$T_0^{\text{har}} \geqslant T_1^{\text{har}} \geqslant T_j^{\text{har}}. \tag{26c}$$

Successive $S_j(j \geqslant 2)$ are chosen so that corresponding CI matrices fit random access memory (RAM). We start by solving an eigenproblem of dimension $d_0 + d_1$ in $S_0 + S_1$,

$$\mathbf{H}^{S_0+S_1}\mathbf{C}^{(0+1)} = E^{(0+1)}\mathbf{C}^{(0+1)}, \tag{27}$$

after which the last d_1 rows and columns are contracted into a single row and column,

$$\mathbf{H}_{i,d_0+1} = \sum_{j=1}^{d_1} \langle \Phi_{i0}|H|\Phi_{j1}\rangle C_{i0}C_{j1}, \tag{28}$$

$$\mathbf{H}_{d_0+1,d_0+1} = \sum_{j=1}^{d_1}\sum_{j'=1}^{d_1} \langle \Phi_{j1}|H|\Phi_{j'1}\rangle C_{j1}C_{j'1}, \tag{29}$$

giving

$$\mathbf{H}^{S_0+c_1}\mathbf{C}^{(0+c_1)} = E^{(0+c_1)}\mathbf{C}^{(0+c_1)}, \tag{30}$$

where subspace S_1 was contracted into a single dimensional space c_1; of course, $E^{(0+1)}$ in (27) is equal to $E^{(0+c_1)}$ in (30) except for roundoff errors. This amounts to freeze the last d_1 CI coefficients hereinafter. Upon completion of this first step, the resulting matrix of dimension d_0+1 is enlarged by adding d_2 rows and columns associated to S_2,

$$\mathbf{H}^{S_0+c_1+S_2}\mathbf{C}^{(0+c_1+2)} = E^{(0+c_1+2)}\mathbf{C}^{(0+c_1+2)}, \tag{31}$$

and the process is repeated,

$$\mathbf{H}^{S_0+s_r+S_r}\mathbf{C}^{(0+s_r+r)} = E^{(0+s_r+r)}\mathbf{C}^{(0+s_r+r)}, \tag{32a}$$

$$s_r = \sum_{q=1}^{r-1} c_q, \tag{32b}$$

until incorporation of subspace S_R exhausts the target space S. Each step yields increasingly accurate eigenvalues $E^{(0+s_r+r)}$ converging from above, and wave functions $\Psi^{(r)}$,

$$\Psi^{(r)} = \sum_{i=1}^{d_0} \Phi_{i0}C_{i0}^{(r)} + \sum_{q=1}^{r-1} \Phi^{(q)}C_q^{(r)} + \sum_{j=1}^{d_r} \Phi_{jr}C_{jr}, \tag{33a}$$

$$(r = 1,2,\ldots,R),$$

$$\Phi^{(q)} = N_q \sum_{i=1}^{d_q} \Phi_{iq}C_{iq}, \quad (q=1,2,\ldots,R). \tag{33b}$$

In practice, the value of R may attain several thousands. In the present computer code, $d_0+r-1+d_r$ is required not to exceed 65 536, so that each index μ and ν in $H_{\mu\nu}$ can be stored in only two bytes (16 bits), a demand that can be lifted for large RAM memories. (We actually use suitable offsets to extend the range of μ and ν values to a large extent past 65 536 while still using two bytes per index.)

Since $H_{\mu\nu}$s with $\mu \leqslant d_0$, $\nu \leqslant d_0$, are present in all CI matrices, the CI coefficients $C_{i0}^{(r)}$ in S_0 always remain free to vary. Clearly, the final energy eigenvalue $E^{(0+s_R+R)}$ (lowest or an excited one) is at or above its exact partner in S,

TABLE I. Convergence of the Ne ground state energy with T_1^{on} and T_1^{har}; $T_1^{\text{egy}} = 10^{-11}$ a.u. is kept fixed.

m, Eq. (21)	ℓ	$d_0 + d_1$	$-E^{(0+1)}$	$-E^{(0+s_R+R)}$
4	3	265 189	128.935 234 56	128.936 512 67
4.5	4	440 159	128.936 008 60	128.936 516 01
5	4	559 235	128.936 015 35	128.936 616 65
5.5	4	779 431	128.936 017 46	128.936 516 85
6	4	108 055 2	128.936 017 94	128.936 516 99
4.5	5	550 097	128.936 240 19	128.936 515 33
5	5	818 263	128.936 250 66	128.936 516 31
4.5	6	622 138	128.936 323 65	128.936 514 92
5	6	105 553 8	128.936 336 41	128.936 516 15

$$E_S = E^{(0+s_R+R)} - \delta\epsilon, \tag{34}$$

where $\delta\epsilon$ is another residual error (with positive sign) that needs to be assessed. The first two terms of the sequence $\{\mathcal{T}_j\}$, $\mathcal{T}_0$, and $\mathcal{T}_1$, are the main threshold values regulating $\delta\epsilon$, as illustrated in the next section.

IV. APPLICATION AND DISCUSSION

A. Application and accuracy

SDC-CI interferes with the rigorous solution of the eigenproblem (6) by freezing most of the linear variational coefficients after a first variational estimate on a relatively small subspace of CSFs. Only the linear variational coefficients of CSFs in S_0 are free to vary all the time. Both the energy and the wave function are affected by these variational constraints; we shall only consider energy effects, exhibited by $\delta\epsilon$ in Eq. (34).

As an example, we choose the CI matrix of the Ne ground state for one of the largest calculations of Paper I. The model space M is a full CISDTQ (CI singles, doubles, triples, and quadruples) in a $12s12p11d10f10g9h8i7k6l5m4n3o3q3r$ orbital basis spanning a CSF space of dimension 1.4×10^9, and involving 1.1×10^{12} distinct Slater determinants.[12] This model space M is pruned before evaluation of symmetry eigenfunctions, as discussed in Paper I; the pruned subspace P is about one sixth the size of M, and carries a truncation energy error about 13 μhartree (Ref. 12) with respect to M, which is mentioned just to clarify the general context.

The target subspace S is obtained by truncating the pruned subspace P with the following thresholds: $T_R^{\text{egy}} = 10^{-11}$ a.u., and T_R^{on} given by Eq. (22) with $m = 6.5$ ($T^{\text{on}} = F_{\text{dh}}F_{\text{con}} \cdot 3 \times 10^{-7}$). Thus, S is here obtained by the selected CI (SCI) method.[12] As it turns out, subspace S harbours 859 903 configurations, 24.06×10^6 CSFs, 8.36×10^9 detors, and gives rise to 1.18×10^{12} nonzero Hamiltonian matrix elements. The truncation energy error accumulated in going from the pruned space P into the selected space S is of no concern here but is carefully discussed in Paper I.

We now focus on assessing the uncertainty $\delta\epsilon$ in Eq. (34). In Table I the SDC-CI energy $E^{(0+s_R+R)}$ (fifth column) is shown as a function of T_1^{on} values (first column), and also as a function of the highest ℓ value in the orbitals spanning the S_0 and S_1 subspaces (second column). The remaining perti-

nent thresholds are fixed $T_0^{\text{egy}} = 10^{-5}$ a.u., $T_1^{\text{egy}} = 10^{-8}$ a.u., and $T_j^{\text{egy}} = 10^{-11}$ a.u. $(j = 2, 3, \ldots, R)$; the T_j^{on}s are given by Eq. (21) with $m = 2.7$ $(j = 0)$, and $m = 6.5$ $(j = 2, 3, \ldots, R)$, respectively. The third and fourth columns show the order $d_0 + d_1$ of the matrix to be treated outside RAM, and the corresponding energy eigenvalue, respectively. It is seen that achieving a low energy eigenvalue E^{0+1} in $S_0 + S_1$ is not a requisite for an accurate energy $E^{(0+s_R+R)}$.

As thresholds are tightened, the evolution of the energy $E^{(0+s_R+R)}$ towards the exact result E_S (usually unknown and unattainable with contemporary workstations), is from above, of course. Monotonic behavior is generally obtained for fixed values of T_0^{har} and T_1^{har}. The most favorable results, viz., those with lowest and most rapidly convergent energies, occur for $T^{\text{har}} = 1/\ell = 1/4$, and are used to push down T^{on} hoping to reach adequate convergence, as shown in lines 2–5 of Table I. These results suggest an accuracy better than 1 μhartree ($\delta\epsilon = 1$ μhartree), which is also supported by smooth energy convergence patterns in Paper I, at the one-tenth of 1 μhartree level. This is more precise than the few μhartree typically used to assess convergence in full CI benchmarks.[35]

The occurence of energy oscillations with decreasing values of T^{har} shows that significant interactions are being frozen at various steps, thus imposing constraints which impair the full extent of the variational procedure to the degree shown in the last column of Table I. The problem is finding an appropriate way to select *a priori* those sets of configurations that must be taken together in order to achieve a desired accuracy. Our approach here has been circumscribed to vary T_1^{on} and T_1^{har} thresholds after reaching convergence with the less sensitive thresholds T_1^{egy} and $\mathcal{T}_0$. Another obvious criterion (not considered) is to limit natural orbitals in S_1 to those with occupation numbers above some threshold. At any rate, there is still much to be learnt about accuracy control in SCI-CI.

The studies of Table I were repeated by changing the occupied orbitals from Hartree-Fock to Brueckner ones,[36,37] viz., orbitals for which the coefficients of singly excited configurations are zero. Brueckner orbitals were approximated in the framework of a CISD using a general method,[38] valid for the ground state, and also for excited states. Unfortunately, the results were similar to those shown in Table I, the energy converging 24 μhartree above the one obtained with the Hartree-Fock orbitals, indicating a higher energy limit for CISDTQ of Ne ground state when calculated in terms of Brueckner orbitals instead of the Hartree-Fock orbitals.

B. Further thoughts

Since Davidson's eigensolver is used R times, the usual threshold for energy convergence in Davidson's algorithm must be divided by R, viz., for an accuracy of 10^{-8} a.u. and $R = 1000$, each Davidson application must be required to converge to within 10^{-11} a.u.

High accuracy may require a large value of $d_0 + d_1$ demanding the eigenproblem in $S_0 + S_1$ to be solved outside RAM. That, however, only affects the first iteration. From there on, all work proceeds in RAM. Also, in general, just a

few Davidson iterations are needed for each step, even with such tight energy convergence threshold as 10^{-11} a.u. for each Davidson application, since the most important energy contributions and eigenvector components are already in S_0 and S_1. Moreover, because of the relatively small dimension of the vectors σ and $\mathbf{v}$ in (4), the data set is considerably more localized. Profiles of program execution running 13 h entirely in RAM (Ref. 12) show that about 8% of the time is spent on Eq. (4) (3% on code in RAM and 5% on code using disk), the rest being used mainly in the evaluation of $H_{\mu\nu}$s.

C. Comparison with previous work and outlook

The idea to freeze CI coefficients is not a new one. Back in 1969, one of the authors (Bunge) was asked[39] whether it would be sensible to use the configurational expansion Eq. (7) in small chuncks, then lock C_{gK} coefficients $(g = 1, 2, \ldots, g_K)$ by Eq. (12), and finally use the corresponding configurations in the less general Eq. (11). Formally, after some generalization, the idea can be embodied in Eqs. (27)–(33). In retrospective, had Schaefer's suggestion been seriously pursued, the ingredients of SCI to achieve acceptable accuracy might have appeared shortly afterwards, probably following Kutzlenigg's review on electron-pair theories[40] and Shavitt's review on CI (Ref. 41) in consecutive chapters of Schaefer's volume 3 of *Modern Theoretical Chemistry*. More recently, the other author (Carbó-Dorca) played with the idea of avoiding the eigenproblem altogether;[42] that idea was also short of providing the necessary accuracy. These two ideas, however, met with SCI needs and SCI possibilities, giving way to SDC-CI.

In an effort to lower the size of MRCI expansions, internally contracted MRCI was proposed.[43] Meyer's and similar approaches[11] using perturbation theory estimates of various CI coefficients are the nearest relatives of SDC-CI. The latter is more accurate at the expense of having to evaluate *all* pertinent matrix elements. We encourage young workers to apply perturbation theory[44,45] to SDC-CI in an effort to search for a middle ground between our's and Meyer's ideas, where not all matrix elements would be necessary.

Other investigations are also warranted: (i) to reduce $\delta\epsilon$ in Eq. (34), (ii) to lessen the computational time to evaluate $H_{\mu\nu}$s, and (iii) to run simultaneously on many processors. With regard to (i), more flexible selections of subspaces have to be examined. Wholesale evaluation of $H_{\mu\nu}$s, on the other hand, is open to several theoretical alternatives: for atoms,[33,46] and for molecules,[11,33] and a wealth of computer implementations yet to be explored.

D. Conclusions

Typical $\mathbf{H}^S$ matrices encountered in SCI need tens or hundreds of terabytes of disk to store expensive-to-evaluate $H_{\mu\nu}$s, and considerable disk retrieval performance for each Davidson iteration.[47,48] A general eigensolver has to face the full implications of such disk-read bottleneck,[25,48] and pressing demands through memory hierarchies to access widely scattered elements of the vectors σ and $\mathbf{v}$ in the evaluation of (4). The computationally tractable SDC-CI method, on the other hand, overcomes the input-output bottleneck and part

of the scattered data problem, and can be applied to a target space S provided the orbital set is made up of Hartree-Fock (or Brueckner) occupied orbitals, plus approximate natural orbitals (or localized orbitals). The price paid by SDC-CI is a small loss of accuracy relative to general algorithms[22,23] when both methods can be used. This small loss of accuracy, however, is more than compensated by the SDC-CI capability to deal with CI matrices having trillions of expensive-to-evaluate nonzero matrix elements between CSFs,[12] much larger than ever attempted by other methods on a single processor, and comparable with a recent calculation on 432 processors.[48]

SCI (Ref. [12]) and SDC-CI are intimately intertwined: without SDC-CI the accuracy of SCI would fall short by several orders of magnitude, and without SCI, SDC-CI cannot even be formulated. For this reason, we believe that all HCCI methods eventually making use of SDC-CI will ultimately be assimilated into an SCI framework. The reverse, however, is not true, selection of configurations finds application in many other methods that do not require a variational solution.[12]

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

[2] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).

[3] H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules* (Addison Wesley, Reading, MA, 1972).

[4] J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic, New York, 1973).

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

[6] M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, J. Chem. Phys. **114**, 8282 (2001).

[7] S. R. White and R. L. Martin, J. Chem. Phys. **110**, 4127 (1999).

[8] H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000).

[9] H. Nakatsuji and E. R. Davidson, J. Chem. Phys. **115**, 2000 (2001).

[10] D. A. Mazziotti, J. Chem. Phys. **121**, 10957 (2004).

[11] C. D. Sherrill and H. F. Schaefer III, in *Advances in Quantum Chemistry*, edited by P.-O. Löwdin (Academic, New York, 1999), Vol. 34, p. 143.

[12] C. F. Bunge, J. Chem. Phys. **124**, 014107 (2006), preceding paper.

[13] J. L. Whitten and M. Hackmeyer, J. Chem. Phys. **51**, 5584 (1969).

[14] M. Hackmeyer and J. L. Whitten, J. Chem. Phys. **54**, 3739 (1971).

[15] L. R. Kahn, P. J. Hay, and I. Shavitt, J. Chem. Phys. **61**, 3530 (1974).

[16] R. J. Buenker and S. D. Peyerimhoff, Theor. Chim. Acta **35**, 33 (1974).

[17] H.-J. Werner, in *Advances in Chemical Physics*, edited by K. P. Lawley (Wiley, New York, 1987), Vol. 69, pp. 1–62.

[18] R. Shepard, in *Advances in Chemical Physics*, edited by K. P. Lawley (Wiley, New York, 1987), Vol. 69, pp. 63–200.

[19] B. O. Roos, in *Advances in Chemical Physics*, edited by K. P. Lawley (Wiley, New York, 1987), pp. 399–445.

[20] J. Olsen, B. O. Roos, P. Jorgensen, and H. J. A. Jensen, J. Chem. Phys. **89**, 2185 (1988).

[21] M. W. Schmidt and M. S. Gordon, Annu. Rev. Phys. Chem. **49**, 233 (1998).

[22] E. R. Davidson, J. Comput. Phys. **15**, 87 (1975).

[23] E. R. Davidson, Comput. Phys. **7**, 519 (1994).

[24] P. J. Knowles and N. C. Handy, Chem. Phys. Lett. **111**, 315 (1984).

[25] R. Shepard, I. Shavitt, and H. Lischka, J. Comput. Chem. **23**, 1121 (2002).

[26] J. Bofill, J. Comput. Chem. **13**, 101 (1999).

[27] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).

[28] P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).

[29] C. Angeli, C. J. Calzada, R. Cimiraglia, S. Evangelisti, V. Gvihery, T. Leininger, J.-P. Malriev, D. Maynau, J. V. Pitarch Ruiz, and M. Sparta, Mol. Phys. **101**, 1389 (2003).

[30] A. Bunge, J. Chem. Phys. **53**, 20 (1970).

[31] E. P. Wigner, *Group Theory* (Academic, New York, 1959).

[32] A. V. Bunge, C. F. Bunge, R. Jáuregui, and G. Cisneros, Comput. Chem. (Oxford) **13**, 201 (1989).

[33] O. Jitrik and C. F. Bunge, Phys. Rev. A **56**, 2614 (1997).

[34] R. E. Brown, Ph.D. thesis, Department of Chemistry, Indiana University, 1967.

[35] E. Rossi, G. L. Bendazzoli, S. Evangelisti, and D. Maynau, Chem. Phys. Lett. **310**, 530 (1999).

[36] R. K. Nesbet, Phys. Rev. **109**, 632 (1958).

[37] P.-O. Löwdin, J. Math. Phys. **3**, 1171 (1962).

[38] C. F. Bunge, R. Jáuregui, and E. Ley-Koo, Can. J. Phys. **76**, 421 (1998).

[39] H. F. Schaefer III (personal communication).

[40] W. Kutzelnigg, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 3, p. 129.

[41] I. Shavitt, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 3, p. 189.

[42] E. Besalú and R. Carbó-Dorca, J. Math. Chem. **10**, 100 (1998).

[43] W. Meyer, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 3, pp. 413–446.

[44] P. Claverie, S. Diner, and J.-P. Malrieu, Int. J. Quantum Chem. **1**, 751 (1967).

[45] Z. Gershgorn and I. Shavitt, Int. J. Quantum Chem. **2**, 751 (1968).

[46] Z. Rudzikas, *Theoretical Atomic Spectroscopy* (Cambridge University Press, Cambridge, 1997).

[47] P. Stampfuß and W. Wenzel, J. Chem. Phys. **122**, 024110 (2005).

[48] Z. Gan and R. J. Harrison, presented at Supercomputing 2005, November 2005 (unpublished); http://sc05.supercomputing.org