

Atomic configuration interaction and studies of He, Li, Be, and Ne ground states

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The atomic configuration interaction (CI) is reconsidered. We compare the algebraic and geometric approaches to the construction of the CI matrix and point out advantages of the latter. One-electron basis sets of quality comparable to numerical multiconfigurational Hartree-Fock are readily obtained. The generation of large CI lists of symmetry eigenfunctions is monitored by a prescription establishing an *a priori* identification of relevant contributions to the wave function. Systematic and well-defined truncations to multireference CI's are examined. A formula for energy contributions of six-excited unlinked clusters is derived and shown to give reasonable estimates. Ensuing nonrelativistic CI calculations on He, Li, Be, and Ne ground states yield the lowest upper bounds in the literature, capturing 99.978, 99.923, 99.919, and 99.59% of the accepted correlation energies, respectively. [S1050-2947(97)04909-3]

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I. INTRODUCTION

The problem of calculating reliable estimates of atomic correlation energies still persists in spite of improved *ab initio* methods and computer technology, and constitutes a major barrier to theoretical predictions of spectroscopic accuracy. This paper deals with the configuration-interaction (CI) approach to compute the eigenvalues of the nonrelativistic Schrödinger equation. All findings in this paper are pertinent to relativistic CI calculations [1] as well.

Although CI has been known for many years [2], a substantial development in computers, software, and computational methods was necessary before atomic CI came of age [3]. The first mature CI calculations consisted of a thorough study of first-row-atom ground states [4], which essentially remained the last word in CI prowess for almost 20 years. Useful theoretical ideas which survived the test of time include the art of designing CI calculations which are balanced in the choice of approximations and basis sets [5], the partition of degenerate spaces into a hierarchy of interacting spaces [6], natural orbital transformations [7] to speed up the convergence of triple- and higher-excited configuration expansions [8], various estimates of energy contributions [9], and the use of some sort of patterns of convergence [10] for the radial and angular expansions [4,11,12]. Davidson's eigensolver [13], which evolved from closely related predecessors [9], was one of the essential tools that spurred so-called large-scale atomic CI [14] in the present decade.

Meanwhile, the numerical multiconfigurational Hartree-Fock (MCHF) method made its appearance [15] and quickly became established as the method of choice for atomic structures [16]. The advantages of the numerical MCHF method over CI come from the transparency and accuracy with which both occupied and correlation orbitals are obtained by solving MCHF equations when convergence problems do not occur. In CI, there also exists the problem of obtaining both accurate occupied orbitals and a compact correlation-effective basis of virtual orbitals without recurring to major human intervention.

Recently, a new generation of both MCHF and CI accurate calculations has been born [14,17-20]. The purpose of

this paper is to report on new CI techniques leading to considerably improved accuracy, exemplified by calculations on He, Li, Be, and Ne ground states.

Section II is concerned with the CI expansion and the construction of the CI Hamiltonian matrix. In Sec. III, we deal with construction of primitive basis sets of quality comparable to numerical MCHF orbitals. In Sec. IV, we examine multireference CI (MR-CI) and derive an estimate for the energy contribution of six-excited unlinked clusters. Finally, in Sec. V we summarize present achievements.

II. THEORY

There are basically two efficient approaches to the construction of the H matrix: the algebraic approach and the geometrical one. In Racah algebra [21] one may deal with fractional parentage coefficients and the algebraic manipulation of tensor operators. Alternatively, one may bypass fractional parentage coefficients and work directly on operators in the quantized space where all vectors satisfy the exclusion principle [22,23]. Most authors [23,24] use Racah algebra in an essential way.

In contrast with Racah's, the geometric approach, based on the use of projection operators [25], does require the explicit generation of symmetry eigenfunctions. Introduced in atomic physics calculations as early as 1931 [26], and further developed by Löwdin [27-29], the geometric approach attracted attention after the discovery [6,30,31] of selection rules that were not foreseen by the algebraic method. These selection rules allow a splitting of a symmetry-adapted Hilbert space into a hierarchy of interacting subspaces, corresponding to successive orders of perturbation theory [30], useful to systematize and simplify approximations to the full CI.

The merits of the geometric approach, however, transcend hierarchies of interacting spaces, as we shall examine below in connection with efficient wholesale evaluation of Hamiltonian matrix elements. A detailed theoretical treatment and computational description of projection operators in atomic electronic structure calculations has been given [32].

If $\{D_{ik}, i=1, \dots, n_k\}$ is the set of n_k Slater determinants

spanning configuration k , there will be g_k linearly independent Schmidt-orthonormalized configuration-state functions (CSF's), F_{gk} ,

$$F_{gk} = O(M^2; K) \sum_{i=1}^g D_{ik} b_i^g = \sum_{i=1}^{n_k} D_{ik} c_i^g, \quad g = 1, \dots, g_k, \quad (1)$$

where $O(M^2; K)$ is an idempotent, Hermitian, and symmetric projection operator for angular momentum, and $K(K+1)$ is the target eigenvalue of the angular momentum operator M^2 [29]. The atomic CI expansion is

$$\Psi = \sum_{k=1}^{k_x} \sum_{g=1}^{g_k} F_{gk} C_{gk}, \quad (2)$$

and its success relies on keeping the number of configurations k_x and the size g_k of each degenerate space as small as possible for a given accuracy. The corresponding CI-matrix eigenvalue equation is

$$\mathbf{HC} = \mathbf{EC}, \quad (3)$$

and, in practice, the maximum allowed CI size is determined indirectly by the maximum number of nonzero H -matrix elements that can be held in the auxiliary storage of the computer at hand.

The set of all configurations differing just in the labels of the virtual orbital radial functions is called a subclass [6]. Obviously, the b_i^g and c_i^g coefficients are the same for different configurations within a given subclass. The basic computational block for the evaluation of the H -matrix focuses on all nonzero matrix elements between two subclasses.

A general Hamiltonian matrix $H_{gk,hl}$ is traditionally given by

$$H_{gk,hl} = \langle F_{gk} | H | F_{hl} \rangle = \sum_{i=1}^{n_k} \sum_{j=1}^{n_l} \langle D_{ik} | H | D_{jl} \rangle c_i^g c_j^h, \quad (4)$$

however, one can use the hermiticity and idempotency of $O(M^2; K)$ [28] to drastically reduce the ranges in the summations of Eq. (4):

$$\begin{aligned} H_{gk,hl} &= \sum_{i=1}^g \sum_{j=1}^{n_l} \langle D_{ik} | H | D_{jl} \rangle b_i^g c_j^h \\ &= \sum_{i=1}^{n_k} \sum_{j=1}^h \langle D_{ik} | H | D_{jl} \rangle b_i^g c_j^h, \end{aligned} \quad (5)$$

thus bringing enormous savings in computational time.

Equations (5) are just an intermediate step in the reduction of $H_{gk,hl}$ to an efficient formula

$$H_{gk,hl} = \sum_s^{n_s} Q_s(ac) S_s^{gh} + \sum_t^{n_t} R_t(ac/bd) T_t^{gh}, \quad (6)$$

where $\{R_t(ac/bd), t=1, \dots, n_t\}$ is a list of radial two-electron integrals involving four radial functions $acbd$ in a way determined by subindex t , and $\{T_t^{gh}, t=1, \dots, n_t; g=1, \dots, g_k; h=1, \dots, h_l\}$ is the set of formula coefficients for one of many possible formulas; $Q_s(ac)$ and S_s^{gh} are analogous one-electron quantities. An equation similar to Eq.

(6) has been discussed for molecular electronic structure calculations [33]. When use is made of Racah techniques, one can also arrive to formulas identical with Eq. (6) [23,34,35]. In either case, the expressions for the formula coefficients of Eq. (6) must be derived symbolically by the computer program.

There are generally several formulas for each pair of subclasses, and each formula requires at least $g_k g_l n_t$ double precision words of program storage. When formulas are relatively expensive to compute [34], a ‘‘formula tape’’ containing all needed formulas is precomputed and held in auxiliary storage.

In the projection operator approach, once the b_i^g, c_i^g , and D_{ik} quantities of Eq. (1) are obtained and held in auxiliary storage, the evaluation of the set of all formulas for a pair of subclasses takes only a fraction of the time needed to replace actual R_t and T_t values in Eq. (6), contrary to common persuasion. Also, we verified that by using Eq. (6), instead of Eqs. (5), savings by a factor 5–10 are usually attained in complete H -matrix calculations with fairly large basis sets. In going from Eqs. (5) to (4), as in some codes still in use, the computational time of large-scale CI increases still by two additional orders of magnitude.

Summarizing, for large-scale atomic CI, the projection-operator-driven algorithm is so fast that formulas need not be kept in auxiliary storage once all work on a given pair of subclasses is finished, thus quite increasing the CI sizes that can be handled relative to implementations where use is made of a stored formula tape.

III. PRIMITIVE ONE-ELECTRON BASES

Any serious effort to close the basis set gap between CI and numerical MCHF methods will have to address the efficient construction of large energy-optimized bases. In this work we use Slater-type-orbital (STO) bases [36]. Of course, these primitive and nonorthogonal bases are orthogonalized to obtain basis orbitals. This orthogonalization may take several forms, *viz.*, a natural orbital transformation, that may be determinant for a satisfactory convergence towards the full CI.

Energy-optimized STO's are obtained using subroutine *autopt* [37] by fitting to a parabola three energy points as a function of a given orbital exponent, increasing a step size when energy lowerings are found, and vice versa after a local minimum is reached. An optimization attempt, for any sequence of STO's within a given irreducible representation (irrep), will be called an optimization cycle. The set of all cycles (one for each irrep) is called a macrocycle, and more than one macrocycle may be needed to complete an optimization process. Typically, for large bases, only two or three cycles are necessary to achieve energy optimization, contrasting with previous experience with bases of intermediate size, where many dozens of *macrocycles* may be necessary. Since a single optimization attempt for each orbital-exponent may demand between three and 20 CI calculations, a complete optimization process requires between six and 60 CI runs per basis function.

For each harmonic k , truncation errors $\delta \epsilon_k^{\text{SD}}$ can be evaluated via

$$\delta\epsilon_k^{\text{SD}} = E^{u(\text{SD})}(\text{improved } k) - E^{u(\text{SD})}, \quad (7)$$

where $E^{u(\text{SD})}(\text{improved } k)$ and $E^{u(\text{SD})}$ refer to a singles and doubles (SD) CI with a very large energy-optimized basis and with the actual basis one is settling for, respectively. (A SDCI is a CI including a single reference configuration and all singly and doubly excited configurations therefrom.) The SD qualification is to emphasize that there are non-negligible STO truncation energy errors beyond the SDCI approximation. The total STO truncation error δE_l^{SD} up to harmonic l will be the sum of all estimated $\delta\epsilon_k^{\text{SD}}$ up to $k=l$:

$$\delta E_l^{\text{SD}} = \sum_{k=0}^l \delta\epsilon_k^{\text{SD}}. \quad (8)$$

A SD angular energy limit E_l^{SD} is calculated as the sum of an upper bound $E_l^{u(\text{SD})}$ and its corresponding δE_l^{SD} :

$$E_l^{\text{SD}} = E_l^{u(\text{SD})} + \delta E_l^{\text{SD}}. \quad (9)$$

Naturally, δE_l for full CI will always be larger than δE_l^{SD} .

With higher and higher harmonics, CI calculations confront diminishing returns. Extrapolation of angular energy limits E_l^{SD} is a useful empirical procedure, first studied by Schwartz [10] and used successfully in the classic work of Sasaki and Yoshimine [4]. It was later refined for He [12] and for Li [38]. Here we use the functional

$$E_l^{\text{SD}} - E_{l-1}^{\text{SD}} = \Delta E_l^{\text{SD}} = a_4(l+1/2)^{-4} + a_5(l+1/2)^{-5} + a_6(l+1/2)^{-6}, \quad (10)$$

which was found to be satisfactory for He and Li [38].

We developed for Be ground state a STO basis [36] having, in the notation of Eq. (9), $E_{13}^{u(\text{SD})} = -14.663\,117\,83$ a.u., $\delta E_{\infty}^{\text{SD}} = -77(8)$ $\mu\text{hartree}$, and $E_{\infty}^{\text{SD}} = -14.663\,195(8)$ a.u. (Be). Making use of quadruple precision, the 8 $\mu\text{hartree}$ of uncertainty could be further reduced by one order of magnitude, at which stage other errors may come into play, such as deviations from additivity in angular energy errors. Analogously, for Ne ground state we constructed a STO basis [36] with $E_{13}^{u(\text{SD})} = -128.920\,5079$ a.u., $\delta E_{\infty}^{\text{SD}} = -622(28)$ $\mu\text{hartree}$, and $E_{\infty}^{\text{SD}} = -128.921\,130(28)$ a.u. (Ne). This $\delta E_{\infty}^{\text{SD}}$ turns out to be five times smaller than the -3435 $\mu\text{hartree}$ that may be inferred from the best previous SDCI calculation [39]. In trying to reduce this STO truncation error any further, one faces diminishing returns.

For He and Li, numerical bases [38,40–42] are the most accurate ones. It is thus of interest to examine analytic bases for two- and three-electron systems in order to assess the extent of this higher accuracy of numerical bases, even if far more accurate calculations using interparticle coordinates are available [43,44].

Angular energy limits E_l are well-defined quantities, however, the number of radial functions needed to capture some given fraction of E_l varies with the type of basis set. It is well known that for *small* one-electron bases, accurate natural orbitals (NO's) are superior to energy-optimized STO's. In fact, an old rationale [45] for using NO's was precisely to reduce basis size. We wish to investigate if there is a certain basis size after which STO's prevail over NO's.

In Table I we compare numerical MCHF [38,46,47], natural orbital expansions [12], and optimized STO results for He ground state obtained with one-electron bases of various sizes. It is seen, as expected, that the numerical MCHF method provides the fastest convergence. For small basis sizes, as ever taught, NO's come next, and the optimized STO's lag behind. Starting with ten s functions, however, STO's come unexpectedly ahead of accurate NO's. Thus energy-optimized STO sets of manageable size may compare favorably with the same number of accurate NO's.

At present, the patterns of convergence followed by numerical MCHF orbitals and by optimized STO's are unknown, in contrast with the energy contributions ΔE_{il} of radial NO's which are known to behave like $-A_l(i+l+\eta_l)^{-6}$ [11,12]. Recent work considered patterns of convergence for radial STO's [48] and for numerical MCHF orbitals [49] without much success.

In the last column of Table I, we show angular energy limits E_l . For $l=0$ we report the recent accurate value by Goldman [50]. Continuing up to $l \leq 11$ the E_l 's come from accurate NO expansions [12], while for $l > 11$ they are obtained by extrapolation from the previous ones, by use of Eq. (10). Beyond $l=0$, the MCHF, STO, and NO data represent best efforts at a given time. Our STO results, obtained with 12 radial functions for each irrep (except for the last three of them, where we used eleven, ten, and nine radial functions, respectively) also portray the farthest one can go with double precision arithmetic on workstations (16 figures). After $l=4$ the present results are the lowest CI upper bounds in the literature. The STO truncation error up to $l=15$ is only -3.01 $\mu\text{hartree}$, and the total truncation error is -9.23 $\mu\text{hartree}$, from which it may be concluded that it is not practical to seek truncation errors less than -10 $\mu\text{hartree}$ for highly correlated two-electron states.

Our Li calculations were essentially carried out at the full CI level with orbitals up to $l=13$. In Table II we present upper bounds E_{nr}^u and estimates E_{nr} of nonrelativistic energies for the Li ground state obtained by different authors. Only now it has been possible to match the pioneer 60-term Hylleraas-type expansion of Larsson [51] by means of a CI calculation. The results of Tong, Jönsson, and Fischer [52] showed that, in order to obtain a good extrapolated energy, it is more important to have accurate angular energy limits than holding the best upper bound. Comparison with the Drake-Yan result [44], obtained with a Hylleraas CI wave function and considered to be the converged result, shows that our STO truncation error δE_{∞} equals -35 $\mu\text{hartree}$, a sensible point to settle for. The angular energy limit for $l=15$ is 9 $\mu\text{hartree}$ away from E_{nr} , and the best one can hope for in a full thrust calculation would be an error around -6 $\mu\text{hartree}$ up to $l=15$, thus with the present programs and computers one may diminish the truncation error from -35 to -15 $\mu\text{hartree}$ but no more. (Our 1991 result [48] is seen to fall outside its stated margin of error; this can essentially be attributed to a faulty assessment of radial patterns of convergence of intershell STO truncation energy errors.)

In Table III we compare our angular energy limits for Li ground state with recent MCHF calculations [52]. MCHF, as expected, provides slightly more accurate orbitals for the first few angular energy limits. The improvement of numerical MCHF over CI orbitals, -2 $\mu\text{hartree}$, is about 5% of our

TABLE I. Comparison of MCHF, optimized STO's, and accurate NO's for the energy convergence of the He ground state, and extrapolated angular energy limits E_l ; energies in a.u.(He).

Basis	Energy (MCHF) ^a	Energy (STO's) ^b	Energy (NO's) ^c	E_l^c
1s	-2.861 799 956 ^d	-2.847 656 250	-2.861 531 102	
2s	-2.877 997 ^e	-2.876 887 488	-2.877 925 513	
3s	-2.878 871 ^e	-2.878 660 614	-2.878 844 046	
4s	-2.878 990 ^e	-2.878 942 134	-2.878 980 274	
5s		-2.879 001 967	-2.879 012 045	
6s		-2.879 020 057	-2.879 021 844	
7s			-2.879 025 502	
8s			-2.879 027 070	
9s			-2.879 027 816	
10s		-2.879 028 205	-2.879 028 201	
11s		-2.879 028 428	-2.879 028 413	
12s	-2.879 028 617	-2.879 028 556	-2.879 028 537	
13s		-2.879 028 627	-2.879 028 612	
14s			-2.879 028 659	
15s			-2.878 928 690	
∞_s	-2.879 028 732			-2.879 028 767 ^f
sp	-2.900 515 903	-2.900 515 774	-2.900 516 199	-2.900 516 220
spd	-2.902 766 775	-2.902 766 126	-2.902 766 777	-2.902 766 822
$l \leq 3$	-2.903 320 252	-2.903 320 110	-2.903 320 721	-2.903 321 079
$l \leq 4$	-2.903 517 316	-2.903 517 341	-2.903 518 165	-2.903 518 598
5	-2.903 603 864	-2.903 604 196	-2.903 600 34	-2.903 605 71
6		-2.903 648 18	-2.903 643 88	-2.903 649 88
7		-2.903 672 69	-2.903 668 05	-2.903 674 59
8		-2.903 687 41	-2.903 682 47	-2.903 689 47
9		-2.903 696 75	-2.903 691 23	-2.903 698 95
10		-2.903 702 96	-2.903 697 17	-2.903 705 27
11		-2.903 707 20	-2.903 701 16	-2.903 709 64
12		-2.903 710 19		-2.903 712 79 ^g
13		-2.903 712 37		-2.903 715 10
14		-2.903 713 96		-2.903 716 83
15		-2.903 715 15		-2.903 718 16
20				-2.903 721 62
100				-2.903 724 33
200				-2.903 724 35
∞				-2.903 724 35
Exact ^h				-2.903 724 38

^aReference [38].

^bThis work.

^cReference [12].

^dReference [47], $E = -2.861 799 956 115$. We get $E = -2.861 799 956 0$ for a relativistic Hartree-Fock wave function with five 1s STO's with orbital exponents 1.3834, 1.8113, 2.7368, 3.8252, and 7.4890.

^eReference [46].

^fReference [50].

^gStarting with this entry, extrapolated values using the 12 entries above and Eq. (10) with $a_4 = -0.075 772$, $a_5 = -0.008 187$, and $a_6 = -0.061 239$; this work.

^hReference [43].

final δE_∞ . For higher harmonics, CI faithfully continues to deliver results without undue effort, while MCHF data are not available. However, MCHF has also been used up to high- l values [49]. In conclusion, for the Li ground state, energy-optimized STO's are virtually equivalent to numerical MCHF orbitals.

When we tried to reproduce extrapolated energies from the MCHF data of Ref. [52] we found a slight discrepancy.

We carried out minimizations of pertinent functionals by means of the simplex algorithm embodied in Chandler's celebrated program [53]. Our recomputed angular energy limits from the MCHF data are shown in the last column of Table III. We obtain an extrapolated energy $E_\infty = -7.478 060 43$, 0.8 μ hartree below the one reported in the original paper [52], and in good agreement with the "exact" result [44]. The angular energy limits reveal the extent of monotonic

TABLE II. Upper bounds E_{nr}^u and estimates E_{nr} of nonrelativistic energies for the Li ground state obtained by different authors. The first four entries correspond to CI calculations; energies in a.u.(Li).

Authors	Year	E_{nr}^u	E_{nr}
Larsson ^a	1969	-7.478 025	
Jitrik and Bunge ^b	1991	-7.477 9066	-7.478 062 4(7)
Chung ^c	1991	-7.477 9251	-7.478 059 7(9)
Tong, Jönsson, and Fischer ^d	1993	-7.477 7741	-7.478 059 6
Tong, Jönsson, and Fischer ^e	1993	-7.477 9686	-7.478 060 9
	1995	-7.477 7741	-7.478 060 4 ^f
This work ^g	1995	-7.4780254	
Chakravorty <i>et al.</i> ^h	1993		-7.478 06
Drake and Yan ⁱ	1995	-7.478060321	-7.478 060 323 10(31)

^aHylleraas-type expansion, Ref. [51].

^bReference [48].

^cReference [17].

^dReference [52].

^eReference [52] with a different extrapolation formula.

^fRecomputed E_{nr} , Table III.

^gAn optimized $12s12p11d11f10g9h8i7k6l5m4n3o2q1r$ STO basis was used.

^hReference [62].

ⁱHylleraas-type expansion, Ref. [44].

degradation of our upper bound energies with higher harmonics.

IV. TOWARD FULL CI

Full CI for an N -electron system includes the reference configuration, singly excited substitutions, doubly excited ones, and all the way up to N -excited substitutions. For $N=2$ full CI is trivial, and for $N=3$ it is well within the reach of current CI technology. For $N \geq 4$, the factorial scaling properties of full CI with basis size [9] make it unmanageable for large atomic bases, prompting some sort of selection process.

Our aim is to get as close as possible to the full CI energy to within a computable and small margin of error. To this end we resort to multireference singles and doubles CI (MR-SDCI) [54,55]. A conventional MR-SDCI is built from a set of N_{ref} reference CSF's and all singly and doubly-excited configurations relative to this reference set. In principle, the CSF's of the reference set may contain excitations of any order.

The reference space for a MR-SDCI may be chosen from previous CI calculations truncated according to various criteria. We use an energy-contribution criterion [9]. Starting with SDCI, we select all CSF's F_{gk} with energy contributions $\Delta \epsilon_{gk}$ satisfying $|\Delta \epsilon_{gk}| \geq \Delta \epsilon_{\text{thr}}$. A value of $\Delta \epsilon_{\text{thr}}$ between 10^{-3} and 10^{-4} is usually satisfactory. After carrying out the first MR-SDCI, the reference space can be enlarged by letting in triply and quadruply excited CSF's with energy contributions above $\Delta \epsilon_{\text{thr}}$.

We will now introduce a selection technique that appears to be new. It concerns the use of the properties of average natural orbitals [56]. We use NO's χ_i not to reduce the basis size (as dictated by conventional wisdom), but rather to speed up the convergence of triply- and higher-excited configuration expansions [8], and also to reduce the number of Davidson's iterations in the eigensolver part [8]. Provided

the NO bases derived from the energy-optimized STO bases are not truncated, it is not very different to approximate the full CI using these NO's, or Brueckner orbitals [57] or even numerical MCHF orbitals. Natural orbitals become distinctly convenient, however, when the one-electron basis is trun-

TABLE III. Comparison of CI and MCHF upper bounds E_l^u for Li ground state. Extrapolated angular energy limits E_l from MCHF data with parameters $a_4 = -0.107 159$, $a_5 = -0.000 891$, and $a_6 = -0.044244$, in Eq. (10). An optimized $12s12p11d11f10g9h8i7k6l5m4n3o2q1r$ STO basis was used for the upper bounds in the first column; energies in a.u.(Li).

l	$E_l^u(\text{CI})^a$	$E_l^u(\text{MCHF})^b$	E_l^b
0		-7.448 667 06	-7.448 667 26
1	-7.473 835 09	-7.473 836 52	-7.473 837 10
2	-7.476 766 81	-7.476 768 66	-7.476 769 82
3	-7.477 506 35	-7.477 508 12	-7.477 510 11
4	-7.477 772 26	-7.477 774 08	-7.477 777 16
5	-7.477 889 50		-7.477 896 04 ^c
6	-7.477 948 48		-7.477 956 74
7	-7.477 980 83		-7.477 990 89
8	-7.477 999 70		-7.478 011 55
9	-7.478 011 13		-7.478 024 78
10	-7.478 018 09		-7.478 033 64
11	-7.478 022 22		-7.478 039 79
12	-7.478 024 46		-7.478 044 19
13	-7.478 025 39		-7.478 047 43
15			-7.478 051 72
100			-7.478 060 40
∞			-7.478 060 43

^aThis work.

^bReference [52].

^cStarting with this entry, extrapolated values using the five entries above; this work.

TABLE IV. Angular energy limits E'_l for Be ground state using upper bounds E_l^u found with a $13s12p11d11f10g9h8i7k6l5m5n4o3q2r$ basis and Eq. (14). For $l > 13$, Eq. (10) is used with parameters optimized for $l \leq 13$. Energies in a.u.(Be). Energy contributions from triples and quadruples appear under E^{TQ} in $\mu\text{hartree}$.

l	CI size	E_l^u	E'_l	$-E^{\text{TQ}}$
2	365 46	-14.665 551 48	-14.665 5621	4076.4
3	789 82	-14.666 580 66	-14.666 5951	4129.9
4	122 816	-14.666 945 28	-14.666 9653	4145.4
5	158 144	-14.667 103 42	-14.667 1294	4151.6
6	182 413	-14.667 180 90	-14.667 2132	4154.6
7	196 446	-14.667 222 21	-14.667 2605	4156.3
8	204 430	-14.667 245 27	-14.667 2890	4157.1
9	208 690	-14.667 258 26	-14.667 3070	4157.6
10	211 057	-14.667 266 47	-14.667 3189	4157.7
11	212 240	-14.667 271 02	-14.667 3268	4157.7
12	212 649	-14.667 273 80	-14.667 3323	4157.7
13	212 710	-14.667 275 57	-14.667 3364	4157.8
15			-14.667 3418	
20			-14.667 3478	
50			-14.667 3520	
100			-14.667 3523	
∞			-14.667 352(8)	

cated in calculations beyond a SDCI.

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

$$\gamma(1,1') = \sum n_i \chi_i^*(1) \chi_i(1'). \quad (11)$$

For each q -excited configuration k we calculate the product $P(q,k)$ of corresponding occupation numbers,

$$P(q,k) = \prod_{i=1}^q n_{k_i}, \quad (12)$$

and proceed to delete the whole configuration (all corresponding degenerate elements) if

$$P(q,k) \leq P_t(q,h), \quad (13)$$

where $P_t(q,h)$ is a threshold normally between 10^{-10} and 0 depending also on index h specifying the type of hole associated to k . We always use $P_t(1,h) = P_t(2,h) = 0$. A selection process based on Eqs. (12)–(13) is used at two levels: in the construction of the configuration list, where it avoids the generation of computer-expensive subclasses, and in the choice of the CSF's to be included in a CI expansion. In Table IV we present full CI angular energy limits E'_l ,

$$E'_l = E_l^u + \delta E_l^{\text{SD}}, \quad (14)$$

for the Be ground state. We used $P_t(3,h) = P_t(4,h) = 10^{-24}$ for all holes h . Instead of setting up a MR-SDCI, we started from straight full CI truncated by Eqs. (12)–(13) since, in a MR-SDCI, symmetry restrictions in $1s^2 2s^2$ Be would pre-

TABLE V. Upper bounds E_{nr}^u and estimates E_{nr} of nonrelativistic energies for the Be ground state obtained by different authors; energies in a.u.(Be).

Authors	Year	E_{nr}^u	E_{nr}
Bunge ^a	1976	-14.666 902	-14.667 328(25)
Olsen and Sundholm ^b	1989		-14.667 370(30)
Lindroth <i>et al.</i> ^c	1992		-14.667 353(2)
Chung, Zhu, and Wang ^d	1993	-14.667 051	-14.667 3492
Chakravorty <i>et al.</i> ^e	1993	-14.666 999	-14.666 36
Fischer ^f	1993	-14.667 113	-14.667 315
This work	1995	-14.667 276	-14.667 357(8)

^aReference [8].

^bReference [59].

^cReference [60].

^dReference [19].

^eReference [62].

^fReference [49].

clude energy-significant configurations, like *spdf*, until reaching a very large number of reference configurations.

The extrapolated energies in the fourth column were obtained using Eq. (14) with δE_l^{SD} taken from SDCI, thus they are also upper bounds since the δE_l 's for the full CI are more negative. The angular energy limits E'_2 and E'_4 agree remarkably well with the only ones we could find in the literature [8]. The value of E_∞^{SD} in Sec. III was obtained with reference Hartree-Fock orbitals. Using approximate NO's we obtain $E_\infty^{\text{SD}} = -14.663 244(8)$, in good agreement with the value reported in Table XII of Ref. [8], $E_\infty^{\text{SD}} = -14.663 241(20)$. Thus there is a lowering of 49.0 $\mu\text{hartree}$ when going from HF to NO's in the calculation of E_∞^{SD} .

The energy contributions of triple and quadruple excitations, given in the last column under E^{TQ} , appear to converge to $-4157.8 \mu\text{hartree}$, but they still need to be corrected by STO truncation energy errors. According to Ref. [8], the truncation error δE^{TQ} in the Be ground state E^{TQ} may be approximated by $c_{1s^2 2p^2}^2 \delta E_K$, where $c_{1s^2 2p^2} = 0.295$ [58] is the CI coefficient of the leading correction after the Hartree-Fock configuration, and δE_K is the STO truncation error in the K -shell correlation energy. Assuming $\delta E_K = E(\text{Be}^{2+})_{\text{ex}} - E(\text{Be}^{2+})_{\text{STO}}$, where the subindex ex means exact [43], and the subindex STO means calculated with present STO basis, we find $\delta E_K = -57 \mu\text{hartree}$, resulting in $\delta E^{\text{TQ}} = -5.0 \mu\text{hartree}$. The nonrelativistic energy E_{nr} of the Be ground state may then be written as

$$E_{\text{nr}} = E_\infty' + \delta E^{\text{TQ}} = -14.667 357(8) \text{ a.u.}(\text{Be}). \quad (15)$$

Alternatively, one may write

$$E_{\text{nr}} = E_\infty^{\text{SD}} + E^{\text{TQ}} + \delta E^{\text{TQ}}, \quad (16)$$

where $E^{\text{TQ}} + \delta E^{\text{TQ}} = -4162.8 \mu\text{hartree}$, and E_∞^{SD} may be taken from Sec. III with 8 $\mu\text{hartree}$ of uncertainty, or from future more accurate calculations. Actual angular energy limits E_l , not reported here, should be slightly below the E'_l values.

In Table V we summarize our Be results and compare

them with previous work. It is seen that the old 1976 $E_{nr} = -14.667\,328(25)$ [8] agrees with the present one, $E_{nr} = -14.667\,357(8)$, to within stated margins of error. The present result also agrees with the Olsen-Sundholm [59] result of $E_{nr} = -14.667\,37(3)$ [60], but it does not support the conclusion reached by Martensson-Pendrill *et al.* [61] that our 1976 result was too high by $45\ \mu\text{hartree}$. The downward correction we obtain is $29(8)\ \mu\text{hartree}$.

The extrapolated MCHF result of Fischer [49] is too high. Possible reasons may be CI truncation errors, or the use of an unsatisfactory extrapolation formula. An E_{nr} more accurate than that of Eq. (15) might be obtained through MCHF via Eq. (16) and extrapolation, with Eq. (10), of MCHF angular limits E_l^{SD} . The agreement with Chung, Zhu, and Wang [19] is remarkable in that these authors obtained the ionization potential of Be (and other Be-like systems) to within quoted experimental errors. There is also good agreement with the E_{nr} values of Lindroth *et al.* [60], and of Chakravorty *et al.* [62].

For Ne, things become much more complicated. We do have to use a MR-SDCI limited to singles and doubles in the reference space thus arbitrarily eliminating quintuply and higher-excited configurations, awaiting better methods to deal with very large CSF's spaces. Hence we are settling for a singles, doubles, triples, and quadruples CI (SDTQCI) and corresponding energies E^{SDTQ} . In the largest MR-CI, the reference space consisted of 83 CSF's, including the HF configuration and singles and doubles with energy contributions greater than $500\ \mu\text{hartree}$, in a space of 2703 determinants, yielding a 354 455-term CI and 33.8 million determinants.

The energy effect of these higher-than-quadruple excitations was investigated by Bauschlicher *et al.* [63] by means of full CI on the eight valence electrons and with small basis sets not exceeding $5s3p2d$ or $6s4p1d$. They found, for the 5-8 excited configurations, energy contributions around 0.08% of the computed correlation energy with the same basis, and a smaller effect with increasing basis size. Combining this result with a recent estimate of -0.3905 a.u. [62] for the correlation energy of Ne ground state, we obtain a value of $E^{(5-8)}$ of $-312\ \mu\text{hartree}$ for energy contributions beyond quadruple excitations. An alternative estimate of $E^{(5-8)}$ may be found by evaluating Davidson's correction [64] for a MR-SDCI wave function [65]

$$E^{(5-8)} \approx E^{(5-6)} = E^{\text{TQ}}(1 - C_R^2)/C_R^2 \quad (17)$$

where (5-8) excitations are assumed to be well given by (5-6) excitations; E^{TQ} is given by

$$E^{\text{TQ}} = E^{\text{SDTQ}} - E^{\text{SD}}, \quad (18)$$

and C_R is the coefficient of the SDCI contribution to the SDTQCI wave function. Using $E^{\text{TQ}} = -16\,000\ \mu\text{hartree}$ and $C_R^2 = 0.9990$, we obtain $\delta E^{(5-6)} = -16\ \mu\text{hartree}$, 20 times smaller than the value derived from full CI calculations [63], thus invalidating Eq. (17).

Let us derive an alternative expression for $E^{(5-8)}$ following Brown's estimate [9,66] for the energy contribution ΔE_k of a configuration k :

$$\Delta E_k = C_k^2(E - H_{kk})/(1 - C_k^2), \quad (19)$$

TABLE VI. Angular energy SDTQCI limits $E_l^{u(\text{SDTQ})} + T_l$ for the Ne ground state using upper bounds E_l^u found with a $12s12p11d10f10g9h8i7k6l5m4n3o3q3r$ basis. Energies in a.u.(Ne). Energy contributions from triples and quadruples appear under E^{TQ} in $\mu\text{hartree}$.

l	CI size	E_l^u	$E_l^u + T_l$	$-E^{\text{TQ}}$
1	115 011	-128.741 534	-128.741 589	6759
2	177 926	-128.874 661	-128.874 745(5)	12 942
3	341 249	-128.913 519	-128.913 651(7)	14 890
4	319 191	-128.927 176	-128.927 344(9)	15 231
5	325 198	-128.931 664	-128.931 874(11)	15 260
6	331 905	-128.933 654	-128.933 909(13)	15 319
7	353 400	-128.934 604	-128.934 904(14)	15 315
8	353 757	-128.935 120	-128.935 457(15)	15 312
9	354 012	-128.935 413	-128.935 784(16)	15 309
10	354 182	-128.935 588	-128.935 987(17)	15 306
11	354 284	-128.935 690	-128.936 116(18)	15 302
12	354 371	-128.935 757	-128.936 201(19)	15 298
13	354 455	-128.935 802	-128.936 257(20)	15 294
14			-128.936 319	
20			-128.936 414	
40			-128.936 444	
∞			-128.936 445	

where E is the total variational energy, C_k is a CI coefficient and H_{kk} is the corresponding diagonal Hamiltonian matrix element. If $ghijkl$ refer to occupied orbitals and $abcdef$ to virtual orbitals, one may write the energy contribution of a six-excited determinant D_{ghijkl}^{abcdef} as

$$\Delta E_{ghijkl}^{abcdef} = (C_{ghijkl}^{abcdef})^2 (E - H_{ghijkl}^{abcdef}) \quad (20)$$

in an obvious notation. The diagonal matrix element will be approximated by

$$H_{ghijkl}^{abcdef} \approx D_0 + H_{gh}^{ab} + H_{ijkl}^{cdef} \quad (21)$$

and

$$(C_{ghijkl}^{abcdef})^2 \approx (C_{gh}^{ab})^2 (C_{ijkl}^{cdef})^2, \quad (22)$$

from which Eq. (20) becomes

$$\Delta E_{ghijkl}^{abcdef} = (C_{gh}^{ab})^2 \Delta E_{ijkl}^{cdef} + (C_{ijkl}^{cdef})^2 \Delta E_{gh}^{ab}, \quad (23)$$

similarly as in earlier work [8]. Adding over all sets $ghijkl$ of sextuple-excitations and over all virtual orbitals, we obtain

$$E^{(5-8)} \approx E^6 \approx \sum_{H2, H4} C_{H2}^2 \Delta E_{H4} + C_{H4}^2 \Delta E_{H2}, \quad (24)$$

where $H2$ is a two-electron hole ($1s^2, 1s2s, 1s2p, 2s^2, 2s2p$ or $2p^2$ for the Ne ground state), and $H4$ is a four-electron hole so that the product of $H2$ and $H4$ gives an allowed six-electron hole. Equation (24) should yield a reasonable estimate of E^6 .

Triply and quadruply excited configurations of first-row atoms may be denoted by $K^m L_1^n L_2^p$, where indices m , n , and

TABLE VII. Upper bounds E_{nr}^u and estimates E_{nr} of nonrelativistic energies for the Ne ground state obtained by different authors; energies in a.u.(Ne). Other important nonvariational results are added at the bottom.

Authors	Year	E_{nr}^u	E_{nr}
Sasaki and Yoshimine ^a	1974	-128.9168	-128.9368
Rizzo, Clementi, and Sekiya ^b	1991	-128.9271	
Chakravorty <i>et al.</i> ^c	1993		-128.9376
Noro, Ohtsuki, and Sasaki ^d	1994	-128.9292	-128.9362
This work	1995	-128.9358	-128.9370 ^e
Lee, Dutta and Das ^f	1971		-128.9362
Jankowski, Rutkowska, and Rutkowski ^g	1982		-128.9306

^aReference [4].

^bReference [39].

^cReference [62].

^dReference [20].

^eEquation (28).

^fMany-body perturbation theory results; Ref. [67].

^gRayleigh-Schrödinger third-order energy; Ref. [68].

p denote the occupation numbers of holes in the K , L_1 , and L_2 shells, respectively. We identify four categories of holes: (h1) all L -shell $K^0L_1^nL_2^p$, $n=0,1$, (h2) $2s^2$ -like L -shell holes $K^0L_1^2L_2^p$, $p=1,2$, (h3) KL -shell holes $K^2L_1^mL_2^p$, $m+p=2$, and (h4) the remaining K^1L^2 , K^1L^3 , and K^2L^1 holes. E^{TQ} may be approximately expressed as

$$E^{\text{TQ}} \approx E(h1) + E(h2) + E(h3) + E(h4). \quad (25)$$

For Ne, it may be verified that

$$|E(h1)| > |E(h2)| > |E(h3)| > |E(h4)|, \quad (26)$$

suggesting the use of the following selection criterion for configurations:

$$P_i(q, h1) = a(q)P_i(q, h2) = b(q)P_i(q, h3) = c(q)P_i(q, h4), \quad (27)$$

with $a(q) > b(q) > c(q)$. We use $b(q) = a(q)^2$, $c(q) = b(q)^2$ and $a(q)$ is fixed to values $a(3) = 0.178$ and $a(4) = 0.1$.

The evaluation of angular energy limits at the SDTQCI level is approximated in various ways. First, by adjusting $P(q, h)$ values. Second, we verified the validity of the working hypothesis of Sasaki and Yoshimine [4] connecting one-electron basis errors in full SDCI and in full SDTQCI for $l=1$, and used it to obtain combined STO and CI truncation energy errors T_l for $l > 0$. Third, we considered the effect of subclasses with n_k in the range 5000–10 000 and g_k in the range 100–140 for $l \leq 3$. In Table VI we present results for the Ne ground state. Configurations with products of natural orbital occupation numbers less than $P_i(3, h4) = 3 \times 10^{-17}$ or $P_i(4, h4) = 3 \times 10^{-20}$ are not included in the CI expansions (these values are multiplied by 0.1 for $l \leq 3$); also, use is made of Eq. (27). In the third column we show variational SDTQCI upper bounds $E_i^{u(\text{SDTQ})}$. Approximate angular energy limits E_i^{SDTQ} are given in the fourth column, obtained by adding T_l to the third column results.

For $l > 13$, angular energy limits are extrapolated as before. The last column contains triple and quadruple energy

contributions E^{TQ} . $E^{(5-8)}$ up to $l=2$ can be taken as $-312 \mu\text{hartree}$, from the data of Bauschlicher *et al.* [63]. Alternatively, using Eq. (24) and up to $l=8$ we obtain $-410 \mu\text{hartree}$. E_{nr} for the Ne ground state becomes

$$E_{\text{nr}} = E_{\infty}^{u(\text{SDTQ})} + T_{\infty} + E^{(5-8)}, \quad (28)$$

which together with the data of Table VI yields -128.9370 a.u., in reasonable agreement with the estimate of Chakravorty *et al.* [62].

In Table VII we summarize our Ne results and compare them with previous work. The classic work of Sasaki and Yoshimine [4] used an $8s7p6d5f4g3h2i$ orbital basis and a CI matrix of order 1068, and yielded an extrapolated energy in good agreement with current estimates. For nearly two decades it represented the best balanced compromise between one-electron basis size and the size of the N -electron CI matrix. The improved results obtained in the last few years [20,39] reflect advances in computer power, better programs, and better one-electron bases. The first well-founded *ab initio* estimate of E_{nr} for the Ne ground state was made long ago by many-body perturbation theory [67]. Another remarkable old result was a Rayleigh-Schrödinger third-order energy [68] which went a long way toward convergence in the radial expansions.

V. CONCLUSIONS

After many years of protracted dormancy, atomic CI became almost forgotten and remarkably misunderstood. In Sec. II we suggest that the geometric approach provides fast algorithms for evaluation of H -matrix elements, as the derivation of Eq. (6) takes a fraction of the time needed to make use of it, in frank challenge to the well-established Racah techniques.

It is now possible, as shown in Sec. III, to construct compact STO bases *equally* good to numerical MCHF orbitals, even for high angular momenta. Thus, one may safely conclude that the basis set bottleneck of atomic CI has been overcome, and that atomic CI and numerical MCHF calcu-

lations are now on an equal footing for simple systems with well-differentiated electronic shells.

A notion widely diffused in scientific circles interested in computing vast amounts of atomic data holds that CI makes use of fixed orbitals [69], or of “mean-field” orbitals [70], neither of which are varied. This view may be traced back to a popular and highly useful CI code [71] that makes use of such orbitals, nevertheless, adequate orbitals have been used in CI for a long time [5]. If one is interested in many calculations, *viz.*, for the elucidation or interpretation of a given spectra, our results in Secs. II, III, and IV suggests that use of CI with energy-optimized bases should be comparable in cost and accuracy with the numerical MCHF method, but without the specter of convergence problems.

Over the years, analytic functions other than STO's have been tested, some with substantial success [72]. Our He and Li results prescribe requirements for superior analytic bases: (i) reducing the number of optimization steps, and (ii) providing better approximations to MCHF results. In any case, we are at the threshold of diminishing returns for energy

convergence, at least for standard CI, thus the new analytic functions will also have to reflect some other advantages, such as fulfilling the electron-nuclear coalescence cusp [73].

Multireference approximations to full CI were considered. A formula for the energy contributions of six-excited unlinked clusters was presented. If we wish to estimate atomic full CI energies for larger systems, with uncertainties comparable to those of basis set truncations, purely variational results will have to be supplemented by conventional variation-perturbation and perturbation calculations.

We presented a small selection of nonrelativistic atomic CI results. Excited states are equally amenable to calculation. Tables of angular energy limits E_l converging toward E_∞ [12,52], such as Tables I, III, IV and VI, may be regarded as a paradigm of atomic CI calculations. These calculations will become routine once they get to be sufficiently cheap. Since similar studies can also be carried out in a relativistic framework [1], its implications for atomic spectroscopy will surely be felt.

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