A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements

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The major source of errror in most *ab initio* calculations of molecular energies is the truncation of the one-electron basis set. A complete basis set model chemistry is defined to include corrections for basis set truncation errors. This model uses double zeta plus polarization level atomic pair natural orbital basis sets to calculate molecular self-consistent-field (SCF) energies and correlation energies. The small corrections to give the complete basis set SCF energies are then estimated using the l^{-6} asymptotic convergence of the multicenter angular momentum expansion. The calculated correlation energies of the atoms He, Be, and Ne, and of the hydrides LiH, BH_3, CH_4, NH_3, H_2O, and HF, using the double zeta plus polarization basis sets vary from 83.0% to 91.2% of the experimental correlation energies. However, extrapolation of each of the pair energies and pair-coupling terms to the complete basis set values using the asymptotic convergence of pair natural orbital expansions retrieves from $99.5 \pm 0.7\%$ to $101.1 \pm 0.6\%$ of the experimental correlation energies for these atoms and molecules. With the exception of ammonia which gave 101.1%, the calculated correlation energies agree with the experimental values to within the error limits of the experiments for all these atoms and molecules with more than four electrons. The total extrapolated energies ($E^{SCF} + E^{Correlation}$) are then in agreement with experiment to within ± 0.0014 hartree (root mean square deviation) and represent the most accurate total energy calculations yet reported for the molecules. The largest discrepancies with experiment occur for methane, where we obtain $E^{Total} = -40.5112$ hartree compared to $E^{Expt} = -40.514 \pm 0.002$ hartree, and ammonia, where we obtain $E^{Total} = -56.5659$ hartree compared to $E^{Expt} = -56.563 \pm 0.002$ hartree.

I. INTRODUCTION

Improvements in computers, numerical computer programs, and theoretical methods are making *ab initio* calculations including electron correlation increasingly available for small and even moderately large molecules.[1,2] Configuration interaction (CI)[2–4] and many-body perturbation theory (MBPT)[1,5–8] have become sufficiently refined that the major source of error in most *ab initio* calculations of molecular correlation energies is now the truncation of the one-electron basis set.[8,9] The slow convergence of pair energies with the basis set expansion [10–12] makes a method of extrapolation highly desirable. The standard approach to accelerating the convergence of infinite series is to develop an extrapolation based on the asymptotic form of the series.

In a recent series of articles [13–16] we have determined the asymptotic convergence for pair natural orbital[17] (PNO) expansions for pair correlation energies[18,19] and pair-coupling terms.[3] Using these asymptotic forms, we then developed a method[16,20] for extrapolating correlation energies from finite PNO basis set calculations to estimate the results that would be obtained from complete basis set (CBS) calculations. Beginning with only five PNOs for each pair, this CBS asymptotic extrapolation gave a total correlation energy for a neon atom (-390.4 mhartree) that was within 0.2% of the experimental value (-389.6 mhartree).[16] A similar calculation on the ground state of the water molecule gave a total correlation energy (-370.6 mhartree) that was within the error limits of the experimental value (-370 ± 3 mhartree).[20]

In this paper, we shall first define a complete *CBS theoretical model chemistry* in the sense of Pople.[5,21] We shall then begin the systematic application of this model to a series of test cases that include the complete range of chemical situations. In this first model, we shall make no unnecessary assumptions. For example, we shall include all electrons in the correlation energy. We can then examine later the consequences of such simplifying approximations as including only the valence shell correlation energy.

II. THE CBS $^{(\infty,3)}$ (FULL)/DZ+P APNO MODEL

A "theoretical model chemistry" is a complete algorithm for the calculation of the energy of any geometry of any molecular system.[5,21] It cannot involve subjective decisions in its application. It must be size consistent so that the energy of every molecular species is uniquely defined. Other criteria, such as satisfaction of the variational principle and invariance to unitary transformations among degenerate orbitals, are desirable but not required.[5,21] Our CBS model chemistry will then require: a set of basis functions for each atom, a method for obtaining the CBS SCF energy, and a

method for obtaining the CBS correlation energy. Our design goal for this CBS model is an accuracy of 0.0001 hartree for each PNO.

A. APNO basis sets

Although the description of molecular orbitals as linear combinations of atomic orbitals is at the foundation of molecular quantum chemistry, surprisingly few calculations have been reported using accurate atomic orbitals as a basis set for molecular calculations.[20,22,23] Sets of Slater type orbitals (STOs) and Gaussian type orbitals (GTOs) with continuously variable exponents form nondenumerable basis sets for the one-electron Hilbert space. However, the molecular pair natural orbitals (MPNOs) that we must describe with these basis sets form a denumerable one-electron subspace that can be used to construct the exact many-electron wave function. The atomic pair natural orbitals (APNOs) allow us to focus on a denumerable subspace[17] that leads to a rapidly convergent expansion of MPNOs.

A recent paper[24] by Schwenke and Truhlar compares SCF calculations on the HF molecule using a variety of the more common contracted GTO basis sets. The APNO expansion of the SCF orbitals (which are the leading MPNOs) is more rapidly convergent than the conventional contracted GTO expansions (Fig. 1), and gives a concise physical description relating molecular orbitals to atomic orbitals. The APNO expansion of low-lying MPNO excitations is also rapidly convergent. This allows extrapolation of pair correlation energies from small PNO calculations to estimate the CBS values that would be obtained with complete basis sets.

TABLE I. The atomic pair natural orbital basis sets. Each APNO was optimized for the excitation in which it appears in bold print.

Shell	Excitation
KK	$1s,1s \rightarrow 2s',2s'$ **2p',2p'**
KL	$1s,2s \rightarrow 2s',3s''$ **4p'',4p''**
	$1s,2p \rightarrow 2s',3p''$ **4p'',4d''**
LL	$2s,2s \rightarrow 3s'',3s''$ **3p'',3p''** **3d'',3d''**
	$2p,2p \rightarrow$ **3p'',3p''** **3d'',3d''**
LL'	$2s,2p \rightarrow 3s'',3p''$ **3p'',3d''**

When such extrapolations are carried out for all pair energies and pair-coupling terms, the resulting CBS total energy converges rapidly to the experimental total energy.[13-16,20]

We have developed APNO basis sets for the atoms, H through Ne, based on the optimized primitive Gaussian basis sets of Van Duijneveldt.[25] The orbital exponents and contraction coefficients are given in the Appendix. These basis sets represent a compromise between the two extremes of either using all primitives to describe each APNO or forming disjoint sets of the primitives for the contractions. If the DZ + P {*KK,KL,LL*} APNO basis set is used, the energy contribution from each SCF orbital and from each APNO excitatioin listed in bold print in Table I, will be accurate to 0.0001 hartree, our desired accuracy. If the more flexible DZ + P {*KK,KL,LL,LL'*} APNO basis set is used, every excitation in Table I should achieve this accuracy. The total energy error, including both the SCF energy and the correlation energy, is then approximately

$$\text{Error} \leqslant 0.0001 N_{Occ} + 0.0005 \sqrt{N_{Pairs}}, \tag{1}$$

where the number of independent pairs, N_{Pairs}, is $2N_{Occ}(2N_{Occ} - 1)/2$. Since the errors in the pair energies can be either positive or negative, they behave like random errors. The coefficient, 0.0005 assumes that a "typical" pair has five "important" excitations. The accuracy we anticipate for a ten electron system such as neon or methane is then: 0.0005 hartree for the SCF energy, and 0.0034 hartree for the correlation energy. The construction of the basis sets is explained in detail in the Appendix.

B. The SCF limit

Our conceptual framework for the determination of the molecular SCF limit is based on the standard simultaneous expansion in angular momentum contributions ΔE_l about all of the nuclei. Hence, for the molecule AH_n we first determine the SCF limit using only s and p basis functions on A and only s basis functions on H. Next, we determine the SCF
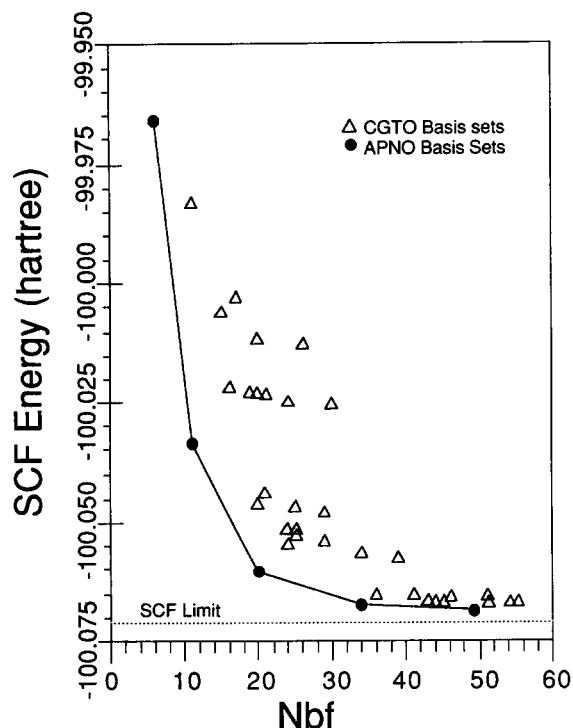

FIG. 1. The convergence of the SCF energy of HF as a function of NBF, the number of contracted basis functions. The numerical Hartree–Fock limit is indicated as a dotted line. The curve connecting the APNO basis sets appears to represent a lower bound for the SCF energy with a given size basis set.

limit using only s, p, and d basis functions on A and only s and p basis functions on H. However, rather than continue this process by including f functions on A and d functions on H, which would be very expensive, we instead shall use the asymptotic convergence of this angular momentum expansion to estimate the small contributions from the higher angular momentum terms. Expansion of a molecular orbital about a single center has been shown[26-28] to converge asymptotically as l^{-4}, if the orbital has a cusp displaced from the coordinate origin. However, orbitals without such cusps (e.g., the $1\pi_u$ orbital of H_2^+) converge[10] as l^{-6}. The latter form is appropriate in the present context, since our [spd,sp] limit already includes the cusp behavior at the nuclei.

Calculation of the CBS SCF energy using this approach requires three steps. First, we determine the [spd,sp] SCF limit. Then, we delete the [d,p] polarization functions to determine their contribution to the SCF energy. Finally, we use the increments $\Delta E(A)_d$ and $\Delta E(H)_p$ and the l^{-6} asymptotic convergence of ΔE_l to estimate the contributions of higher angular momentum basis functions to the molecular SCF energy. Note that since the [d,p] polarization functions make no contribution to atomic SCF energies, this l^{-6} extrapolation will correctly give zero for the estimated contribution of higher l terms to the atomic SCF energies.

To obtain the [spd,sp] SCF limits, the DZ + P APNO basis sets in the Appendix were modified in two ways. First, the $2s'$, $2p'$, $4p''$, and $4d''$ functions used to correlate the ($1s,1s$) and ($1s$, valence) pairs were deleted, since they make no significant contribution to the molecular SCF energy. Second, the contraction was relaxed so that the smallest two s primitives and the smallest three p and d primitives were used as individual Gaussian basis functions. Further relaxation of the contraction scheme changed the SCF energies by less than 0.0001 hartree. Therefore, these quadruple zeta plus triple polarization (QZ + TP) basis sets give molecular SCF energies for the AH_n isoelectronic molecules that are within 0.0005 hartree of the [spd,sp] limit.

The next step in the CBS SCF method attempts to separate the effects of polarization functions on each of the atoms. Such a separation is necessarily approximate, since a complete set of functions on any one center eliminates the need for basis functions on the others. Nevertheless, an approximate partition can be achieved. If we define the total polarization contribution as the difference between the [sp,s] limit and the [spd,sp] limit, then the individual atomic polarization contributions $\Delta E(A)_l$, can be obtained in the following way. First, we set the coefficients of the l-polarization functions on a particular center, A, equal to zero:

$$\varphi_i' = \sum_{j \neq A_l} C_{ij}\chi_j \,. \tag{2}$$

Then we perform a Schmidt orthogonalization of the occupied orbitals:

$$\varphi_1'' = \varphi_1' \,,$$
$$\varphi_i'' = \varphi_i' - \sum_{j=1}^{i-1} \langle \varphi_i' | \varphi_j'' \rangle \varphi_j'' \,; \quad i = 2,3,\dots,N_{\text{Occ}} \,,$$
$$\tag{3}$$

and normalize the orthogonalized orbitals:

$$\varphi_i(A)_l = \varphi_i'' / \langle \varphi_i'' | \varphi_i'' \rangle^{1/2} \,. \tag{4}$$

The atomic polarization contribution is then

$$\Delta E(A)_l$$
$$= \left\langle \mathscr{A}\left\{\prod_{i=1}^{\text{Occ}} \varphi_i(A)_l\right\} \middle| \mathscr{H} \middle| \mathscr{A}\left\{\prod_{i=1}^{\text{Occ}} \varphi_i(A)_l\right\} \right\rangle - E^{\text{SCF}} \,. \tag{5}$$

The sum of these atomic polarization contributions is very nearly equal to the total effect of polarization functions on the SCF energy:

$$\sum_A \Delta E(A)_l \cong E^{\text{SCF}}(spd,sp) - E^{\text{SCF}}(sp,s) \,. \tag{6}$$

For example, the sum of the atomic polarization contributions for HF[$\Delta E(F)_d = 0.010\,686$ hartree, $\Delta E(H)_p = 0.013\,395$ hartree] is 0.024 081 hartree, whereas the total effect of polarization functions on the SCF energy is 0.025 295 hartree. The success of this partition of the total polarization energy into atomic contributions allows us to estimate the effects from higher angular momentum functions.

We shall use the l^{-6} extrapolations[20]:

$$\Delta E(A) \cong \sum_{l=3}^{\infty} \left(\frac{2}{l}\right)^6 \Delta E(A)_d = 0.109\,939\Delta E(A)_d \tag{7}$$

and

$$\Delta E(H) \cong \sum_{l=2}^{\infty} \left(\frac{1}{l}\right)^6 \Delta E(H)_p = 0.017\,343\Delta E(H)_p \tag{8}$$

for the higher angular momentum contributions. Addition of these corrections to the [spd,sp] limit gives the CBS extrapolated Hartree–Fock limit:

$$E^{\text{SCF}}(\text{CBS}) \equiv E^{\text{SCF}}(spd,sp) + \sum_A \Delta E(A) + \sum_j \Delta E(H_j) \,. \tag{9}$$

In the case of HF, this extrapolation ($-100.070\,04$ hartree) agrees with the numerical Hartree–Fock limit ($-100.070\,82$ hartree) obtained by Sundholm, Pyykko, and Laaksonen[29] to within a factor of 2 of our design goal of 0.0005 hartree. Hence, the error in the l^{-6} extrapolation is comparable in magnitude to the error in the [spd,sp] limit obtained with the QZ + TP basis set ($-100.068\,63$ hartree).

C. Molecular PNOs

Calculation of the CBS correlation energy requires obtaining the molecular pair natural orbitals (MPNOs) for each pair of occupied molecular SCF orbitals. For each pair of occupied orbitals, ij, we must first determine the pair CI wave function:

$$\Psi_{ij}^{\text{CI}} = \sum_{ab}^{ij,\text{virt}} A_{ab}(i,j)\Phi_{ij}^{ab} \,, \tag{10}$$

where Φ_{ij}^{ab} is a configuration in which SCF orbitals i and j are replaced by virtual orbitals a and b, and $A_{ab}(i,j)$ is a variationally optimized coefficient. The pair energy and the optimized coefficients $\{A_{ab}\}$ are obtained with an iterative procedure developed by Pople, Seeger, and Krishnan.[30] This

algorithm avoids the full transformation of the electron repulsion integrals from the AO to the MO basis. This is important, since explicit calculation of the CI wave functions is by far the most time-consuming part of the CBS extrapolation.

Expanding the configurations Φ_{ij}^{ab} as antisymmetrized products of one-electron orbitals and rearranging gives

$$\Psi_{ij}^{CI} = \mathscr{A}\left\{\left[\prod_{k \neq ij}^{Occ} \varphi_k(k)\right]\left[\sum_{ab}^{ij,virt} \mathbf{A}_{ab}(i,j)\varphi_a(i)\varphi_b(j)\right]\right\}. \quad (11)$$

Since the only dependence on orbitals i and j occurs in the second term in square brackets, we can focus our attention on this two-electron term:

$$\psi_{ij}^{CI}(1,2) = \sum_{ab}^{ij,virt} \mathbf{A}_{ab}(i,j)\varphi_a(1)\varphi_b(2), \quad (12)$$

or, in matrix form:

$$\psi_{ij}^{CI} = \varphi \cdot \mathbf{A}\varphi, \quad (13)$$

where $\mathbf{A}$ is a square matrix. Its dimensions span the space of the virtual orbitals plus the ground state configuration for the pair. We seek a unitary transformation of the set of orbitals, $\{i,j,\{a,b\}\}$, such that the coefficient matrix $\mathbf{A}$ is "diagonal." The procedure varies somewhat for intraorbital pairs, $\alpha\beta$-interorbital pairs, and $\alpha\alpha$-interorbital pairs.

1. Intraorbital pairs

In the intraorbital case, the orbitals of the α and β electrons are spatially equivalent, so that excitations of the form $ii \rightarrow ab$ are physically the same as $ii \rightarrow ba$. Therefore, $\mathbf{A}$ is a symmetric matrix, and the diagonalization is a straightforward operation. A unitary matrix $\mathbf{U}$ is chosen such that

$$\mathbf{d} = \mathbf{U}^\dagger\mathbf{A}\mathbf{U}, \quad (14)$$

where $\mathbf{d}$ is a diagonal matrix, and this unitary transformation is also applied to the set of orbitals $\{i,j,\{a,b\}\}$:

$$\begin{aligned}{}^{\alpha\beta}\psi_{ii}^{CI} &= \varphi \cdot \mathbf{A}\varphi \\ &= \varphi \cdot (\mathbf{U}\mathbf{U}^\dagger)\mathbf{A}(\mathbf{U}\mathbf{U}^\dagger)\varphi \\ &= (\mathbf{U}^\dagger\varphi) \cdot (\mathbf{U}^\dagger\mathbf{A}\mathbf{U})(\mathbf{U}^\dagger\varphi) \\ &= \chi^{PNO} \cdot \mathbf{d}\chi^{PNO}, \end{aligned} \quad (15)$$

or

$$^{\alpha\beta}\psi_{ii}(1,2) = \sum_{k=1}^{N} d_{kk}(i)\chi_k(1)\chi_k(2), \quad (16)$$

where $\chi^{PNO} = \mathbf{U}^\dagger\varphi$, is by definition,[17] the vector of PNO's. The CI wave function is invariant to this unitary transformation of the orbitals and coefficients, but the PNO representation is necessary for understanding the convergence of the second-order pair energy[5,31]:

$$^{\alpha\beta}e_{ii}^{(2)}(\mathbf{N}_{ii}) = \sum_{k=2}^{N_{ii}} \frac{\langle\varphi_i\varphi_i|\mathbf{r}_{12}^{-1}|\chi_k\chi_k\rangle^2}{2\epsilon_{ii} - 2\langle\chi_k|\mathbf{F}|\chi_k\rangle}. \quad (17)$$

The asymptotic convergence of this PNO expansion for the pair energy[13-16,20]:

$$\lim_{N_{ii}\to\infty} {}^{\alpha\beta}e_{ii}^{(2)}(\mathbf{N}_{ii})$$

$$= {}^{\alpha\beta}e_{ii}^{(2)}(CBS) + \left(\frac{225}{4608}\right)(\mathbf{N}_{ii} + {}^{\alpha\beta}\delta_{ii})^{-1} \quad (18)$$

is insensitive to the particular chemical system under study and independent of our original choice of basis set.

2. $\alpha\beta$-interorbital pairs

Since an $\alpha\beta$ pair has an equal mixture of singlet and triplet components, the CI coefficient matrix $\mathbf{A}$ is *nonsymmetric*. The excitations $ij \rightarrow ab$ and $ij \rightarrow ba$ are not physically equivalent, so the elements $\{A_{ab}\}$ and $\{A_{ba}\}$ bear no simple relationship to one another. The overall many-electron wave function, $^{\alpha\beta}\Psi_{ij}^{CI}$ in Eq. (10), is still antisymmetric with respect to exchange of electronic coordinates, but the component for the pair ij, $^{\alpha\beta}\psi_{ij}^{CI}$ in Eq. (12), taken by itself, does not possess a simple pattern of spatial or spin symmetry. As a result of this lack of symmetry, there are twice as many independent off-diagonal elements in $\mathbf{A}$, and so two independent unitary transformations must be used to reduce $\mathbf{A}$ to diagonal form:

$$\mathbf{d} = \mathbf{U}_i^\dagger\mathbf{A}\mathbf{U}_j. \quad (19)$$

Each unitary transformation contains only $N(N+1)/2$ independent elements, since its column vectors are chosen to be orthonormal, and therefore two of them are necessary for the reduction of the $\alpha\beta$ matrix $\mathbf{A}$, where all N^2 coefficients are fully independent. We must now apply both unitary transformations to the set of orbitals, $\{i,j\{a,b\}\}$:

$$\begin{aligned}{}^{\alpha\beta}\psi_{ij}^{CI} &= \varphi \cdot \mathbf{A}\varphi \\ &= \varphi \cdot (\mathbf{U}_i\mathbf{U}_i^\dagger)\mathbf{A}(\mathbf{U}_j\mathbf{U}_j^\dagger)\varphi \\ &= (\mathbf{U}_i^\dagger\varphi) \cdot (\mathbf{U}_i^\dagger\mathbf{A}\mathbf{U}_j)(\mathbf{U}_j^\dagger\varphi) \\ &= \chi_i^{PNO} \cdot \mathbf{d}\chi_j^{PNO}, \end{aligned} \quad (20)$$

or

$$^{\alpha\beta}\psi_{ij}^{CI}(1,2) = \sum_{k=1}^{N_{ij}} d_{kk}(i,j)\chi_{ik}(1)\chi_{jk}(2), \quad (21)$$

where

$$\chi_i^{PNO} = \mathbf{U}_i^\dagger\varphi$$

and

$$\chi_j^{PNO} = \mathbf{U}_j^\dagger\varphi \quad (22)$$

are the two vectors of PNOs, one for each occupied orbital.

From a physical point of view, correlating the motion of two electrons requires that we move both electrons and that these movements be coordinated. The $(2s - 2p_x)$ pair of neon, for example, needs the flexibility to correlate in the radial, x, y, and z directions. This is accomplished through the $(2s,2p_x) \rightarrow (3s,3p_x)$ excitation in the radial direction, through the $(2s,2p_x) \rightarrow (3p_x,3d_{xx})$ excitation in the x direction, through the $(2s,2p_x) \rightarrow (3p_y,3d_{xy})$ excitation in the y direction, and through the $(2s,2p_x) \rightarrow (3p_z,3d_{xz})$ excitation in the z direction. That is, the $2s$ orbital and the $2p_x$ orbital must be simultaneously modified either in the radial direction, or in the x direction, or in the y direction, or in the z direction. In order to reduce the pair wave function for ij to diagonal form, two distinct sets of PNOs are required, one for the $2s$ orbital and another for the $2p_x$ orbital. Further-

more, the two sets must be ordered so that they combine to give the above excitations if we wish to introduce these correlations into the PNO wave function.

Two different sets of PNOs also arise naturally in the mathematical treatment of the diagonalization for the pair. The transformation of the nonsymmetric matrix $\mathbf{A}$ to its symmetric diagonal form requires that the inherent lack of symmetry in the wave function be moved from the array of CI coefficients to the excited orbitals themselves. The *singular-value decomposition*[32] of the matrix $\mathbf{A}$ leads to an appropriate diagonal form for $^{\alpha\beta}\psi_{ij}^{CI}$. It can be shown that an arbitrary $n \times n$ matrix $\mathbf{A}$ of rank k can be reduced to a diagonal matrix with k real eigenvalues by application of two unitary matrices $^1\mathbf{U}$ and $^2\mathbf{U}$:[32]

$$\mathbf{d} = {}^1\mathbf{U}^\dagger \mathbf{A}\, {}^2\mathbf{U}. \tag{23}$$

To obtain $^1\mathbf{U}$ and $^2\mathbf{U}$, we consider the diagonal matrix $\mathbf{D}$ which is the square of the diagonal form of $\mathbf{A}$:

$$\mathbf{D} = \mathbf{d}\mathbf{d}^\dagger = ({}^1\mathbf{U}^\dagger \mathbf{A}\, {}^2\mathbf{U})({}^2\mathbf{U}^\dagger \mathbf{A}^\dagger\, {}^1\mathbf{U})$$

$$= {}^1\mathbf{U}^\dagger(\mathbf{A}\mathbf{A}^\dagger)\, {}^1\mathbf{U} \tag{24}$$

and

$$\mathbf{D} = \mathbf{d}^\dagger \mathbf{d} = ({}^2\mathbf{U}^\dagger \mathbf{A}^\dagger\, {}^1\mathbf{U})({}^1\mathbf{U}^\dagger \mathbf{A}\, {}^2\mathbf{U})$$

$$= {}^2\mathbf{U}^\dagger(\mathbf{A}^\dagger \mathbf{A})\, {}^2\mathbf{U}. \tag{25}$$

Hence, if we diagonalize the product matrices, $\mathbf{A}\mathbf{A}^\dagger$ and $\mathbf{A}^\dagger\mathbf{A}$, which are symmetric matrices with the same set of positive eigenvalues, we shall obtain the required transformations $\mathbf{U}_1$ and $\mathbf{U}_2$.

The column vectors of the unitary transformations, $^1\mathbf{U}$ and $^2\mathbf{U}$, are not uniquely determined by Eqs. (24) and (25). The order of the column vectors obtained from diagonalization of $\mathbf{A}\mathbf{A}^\dagger$ and $\mathbf{A}^\dagger\mathbf{A}$ is arbitrary, but each column vector of $^1\mathbf{U}$ must be paired with a particular vector of $^2\mathbf{U}$ to satisfy Eq. (23). For example, the column vectors associated with the $(2s,2p_x)$ pair of neon must be ordered so that they combine the $3p_y$ column vector of $^1\mathbf{U}$ with the $3d_{xy}$ column vector of $^2\mathbf{U}$ to give the $(2s,2p_x) \rightarrow (3p_y,3d_{xy})$ PNO excitation, which separates the two electrons along the y coordinate. In the case of degenerate eigenvalues, the associated eigenvectors are not even uniquely defined for $^1\mathbf{U}$ and $^2\mathbf{U}$ separately. Therefore, the choice of the unitary matrices, $^1\mathbf{U}$ and $^2\mathbf{U}$, such that they diagonalize $\mathbf{A}\mathbf{A}^\dagger$ and $\mathbf{A}^\dagger\mathbf{A}$, respectively, is not a sufficient condition for the complete diagonalization of $\mathbf{A}$. We must also require that each column vector of $^1\mathbf{U}$ be related to a particular column vector of $^2\mathbf{U}$. We shall now show that the necessary relationship is[32]

$$^2U_{ij} = \frac{1}{\sqrt{D_{jj}}} \sum_k A^\dagger_{ik}\, {}^1U_{kj}, \tag{26}$$

where $^1\mathbf{U}$ satisfies Eq. (24). Then for each element d_{ij} of $\mathbf{d}$:

$$d_{ij} = [{}^1\mathbf{U}^\dagger \mathbf{A}\, {}^2\mathbf{U}]_{ij}$$

$$= \sum_{k,l} {}^1U^\dagger_{ik} A_{kl}\, {}^2U_{lj}. \tag{27}$$

Substitution of Eq. (26) for $^2U_{lj}$ then gives

$$d_{ij} = \sum_{kl} {}^1U^\dagger_{ik} A_{kl} \frac{1}{\sqrt{D_{jj}}} \sum_m A^\dagger_{lm}\, {}^1U_{mj}. \tag{28}$$

After reordering the summations:

$$d_{ij} = \sum_k {}^1U^\dagger_{ik} \sum_m \left[\sum_l A_{kl} A^\dagger_{lm} \right] {}^1U_{mj} \frac{1}{\sqrt{D_{jj}}}, \tag{29}$$

this simplifies to

$$d_{ij} = [{}^1\mathbf{U}^\dagger(\mathbf{A}\mathbf{A}^\dagger)\, {}^1\mathbf{U}]_{ij} \frac{1}{\sqrt{D_{jj}}}. \tag{30}$$

Substitution of Eq. (24) for D_{ij} then gives

$$d_{ij} = \frac{D_{ij}}{\sqrt{D_{jj}}}, \tag{31}$$

so that $\mathbf{d}$ is diagonal as required. Therefore, Eqs. (24) and (26) give the necessary and sufficient conditions for the diagonalization of $\mathbf{A}$ in Eq. (23) using the transformations $^1\mathbf{U}$ and $^2\mathbf{U}$.

The $\alpha\beta$-CI wave function is invariant to these unitary transformations of the orbitals and coefficients, but just as for intraorbital pairs, the PNO representation is necessary for understanding the convergence of the second-order pair energy[5,31]:

$$^{\alpha\beta}e_{ij}^{(2)}(\mathbf{N}_{ij}) = \sum_{k=2}^{N_{ij}} \frac{\langle \varphi_i\varphi_j | r_{12}^{-1} | \chi_{ik}\chi_{jk} \rangle \langle \chi_{ik}\chi_{jk} | r_{12}^{-1} | \varphi_i\varphi_j \rangle}{\epsilon_i + \epsilon_j - \langle \chi_{ik} | \mathbf{F} | \chi_{ik} \rangle - \langle \chi_{jk} | \mathbf{F} | \chi_{jk} \rangle}. \tag{32}$$

The asymptotic convergence of this PNO expansion for the $\alpha\beta$-interorbital pair energy[13–16,20]:

$$\lim_{\mathbf{N}_{ij} \to \infty} {}^{\alpha\beta}e_{ij}^{(2)}(\mathbf{N}_{ij})$$

$$= {}^{\alpha\beta}e_{ij}^{(2)}(\text{CBS}) + |S|_{ij}^2 \left(\frac{225}{4608} \right)(\mathbf{N}_{ij} + {}^{\alpha\beta}\delta_{ij})^{-1} \tag{33}$$

can now be used to estimate the CBS limit.

3. $\alpha\alpha$-Interorbital pairs

Once again, we need a diagonal form for the ij component of the CI wave function. The triplet wave function $^{\alpha\alpha}\psi_{ij}$ has an antisymmetric spatial component, so the triplet CI coefficient matrix $\mathbf{A}$ is antisymmetric:

$$A_{ab} = -A_{ba}. \tag{34}$$

On intuitive grounds, we expect to require only one unitary matrix $\mathbf{U}$ for the reduction of the wave function because the matrix $\mathbf{A}$ contains only $N(N+1)/2$ unique coefficients. An ordinary symmetric matrix has the same number of unique elements and requires only one unitary transformation for the reduction to N coefficients:

$$\mathbf{d} = \mathbf{U}^\dagger \mathbf{A}\mathbf{U}. \tag{35}$$

However, in the triplet case the reduced coefficient matrix $\mathbf{d}$ cannot be diagonal, since Eq. (34) requires that the diagonal elements be zero. Instead, we must be satisfied with a form for $\mathbf{d}$ that contains only N nonzero elements, but places them in off-diagonal positions. If we apply the unitary transformation that achieves this reduction to both the coefficient matrix $\mathbf{A}$ and the set of orbitals $\{i, j\{a,b\}\}$, we obtain the PNO representation of the two-electron triplet–pair wave function:

$$^{\alpha\alpha}\psi_{ij} = \varphi \cdot A\varphi$$

$$= (U^\dagger\varphi) \cdot (U^\dagger AU)(U^\dagger\varphi)$$

$$= \chi^{PNO} \cdot d\chi^{PNO} \tag{36}$$

or

$$^{\alpha\alpha}\psi_{ij}(1,2) = \sum_{k=1}^{N/2} d_{2k-1,2k}(i,j)[\chi_{2k-1}(1)\chi_{2k}(2)$$

$$- \chi_{2k-1}(2)\chi_{2k}(1)], \tag{37}$$

where the vector of PNOs:

$$\chi^{PNO} = U^\dagger\varphi \tag{38}$$

contains only N elements as in the intraorbital case, but they occur in $N/2$ associated pairs as in the $\alpha\beta$ case. The matrix d is a reduced form of A with antisymmetric 2×2 blocks arranged along the diagonal:

$$d = \begin{bmatrix} 0 & d_{12} & 0 & 0 \\ -d_{12} & 0 & 0 & 0 \\ 0 & 0 & 0 & d_{34} \\ 0 & 0 & -d_{34} & 0 \\ & & & & \ddots \\ & & & & & \ddots \end{bmatrix}. \tag{39}$$

To find the required unitary transformation U, we must

diagonalize the one-electron density matrix $AA^\dagger$ just as in the $\alpha\beta$ case:

$$D = dd^\dagger = (U^\dagger AU)(U^\dagger A^\dagger U)$$

$$= U^\dagger(AA^\dagger)U. \tag{40}$$

The density matrices $AA^\dagger$ and $A^\dagger A$ are equal in this case, so only one transformation is obtained. There is, however, one complication. If any two or more of the 2×2 blocks are degenerate, as they frequently are, then the diagonalization of the product matrix does not guarantee complete reduction of the matrix A. Since $dd^\dagger$ has been diagonalized, d is restricted to have both mutually orthogonal rows and columns. This condition is sufficient for the "diagonalization" of A in nondegenerate cases, but when degeneracies are present the procedure can fail to transform the $n \times n$ CI matrix into the form containing only N independent nonzero elements. For example, a twofold degeneracy will in general result in a "nondiagonal" form for d:

$$d = \begin{bmatrix} 0 & d_{12} & d_{13} & d_{14} \\ -d_{12} & 0 & d_{14} & -d_{13} \\ -d_{13} & -d_{14} & 0 & d_{12} \\ -d_{14} & d_{13} & -d_{12} & 0 \end{bmatrix} \tag{41}$$

which nevertheless gives a diagonal form for D:

$$D = dd^\dagger = \begin{bmatrix} d_{12}^2 + d_{13}^2 + d_{14}^2 & 0 & 0 & 0 \\ 0 & d_{12}^2 + d_{13}^2 + d_{14}^2 & 0 & 0 \\ 0 & 0 & d_{12}^2 + d_{13}^2 + d_{14}^2 & 0 \\ 0 & 0 & 0 & d_{12}^2 + d_{13}^2 + d_{14}^2 \end{bmatrix}. \tag{42}$$

This problem is easily solved by a procedure analogous to the standard method for obtaining eigenvectors associated with degenerate eigenvalues. If we modify d to split the degeneracy:

$$d' = \begin{bmatrix} 0 & d_{12}+\delta & d_{13} & d_{14} \\ -d_{12}-\delta & 0 & d_{14} & -d_{13} \\ -d_{13} & -d_{14} & 0 & d_{12}-\delta \\ -d_{14} & d_{13} & -d_{12}+\delta & 0 \end{bmatrix} \tag{43}$$

then

$$D' = d'd'^\dagger$$

$$= \begin{bmatrix} (d_{12}+\delta)^2 + d_{13}^2 + d_{14}^2 & 0 & -2\delta d_{14} & 2\delta d_{13} \\ 0 & (d_{12}+\delta)^2 + d_{13}^2 + d_{14}^2 & 2\delta d_{13} & 2\delta d_{14} \\ -2\delta d_{14} & 2\delta d_{13} & (d_{12}-\delta)^2 + d_{13}^2 + d_{14}^2 & 0 \\ 2\delta d_{13} & 2\delta d_{14} & 0 & (d_{12}-\delta)^2 + d_{13}^2 + d_{14}^2 \end{bmatrix} \tag{44}$$

is no longer diagonal. Diagonalization of D' will now remove the offending elements, d'_{13} and d'_{14} so that only N independent nonzero elements will remain in d'. The perturbation δ must be small compared to d_{12} so that the CI coefficients remain accurate, but large enough to effect the diagonalization of d. In practice, after reordering the eigenvectors so that $d_{12} > d_{1j}$ for all j, setting δ equal to $0.0002d_{12}$ has proven reliable.

The $\alpha\alpha$-CI wave function is invariant to these unitary transformations of the orbitals and coefficients, but the PNO representation is again necessary for understanding the convergence of the second-order $\alpha\alpha$-pair energy[5,31]:

$$^{\alpha\alpha}e_{ij}^{(2)}(N_{ij}) = \sum_{k=2}^{N_{ij}/2} \frac{\langle\varphi_i\varphi_j|r_{12}^{-1}|\chi_{2k-1}\chi_{2k} - \chi_{2k}\chi_{2k-1}\rangle^2}{\epsilon_i + \epsilon_j - \langle\chi_{2k-1}|F|\chi_{2k-1}\rangle - \langle\chi_{2k}|F|\chi_{2k}\rangle}. \tag{45}$$

The asymptotic convergence of this PNO expansion for the pair energy[16,20]:

$$\lim_{\mathbf{N}_{ij}\to\infty} {}^{\alpha\alpha}\mathbf{e}_{ij}^{(2)}(\mathbf{N}_{ij}) = {}^{\alpha\alpha}\mathbf{e}_{ij}^{(2)}(\text{CBS}) + {}^{\alpha\alpha}f_{ij}\left(\frac{225}{4608}\right)$$
$$\times (\mathbf{N}_{ij} + {}^{\alpha\alpha}\delta_{ij})^{-5/3} \qquad (46)$$

can be used to estimate the CBS limit.

D. Asymptotic extrapolations

The asymptotic extrapolations require the calculation of the second- and infinite-order pair energies with the appropriate molecular pair natural orbital (MPNO) basis sets. The extrapolation to the CBS values then uses the asymptotic forms for PNO expansions of these terms. In the absence of degeneracies, the dominant correction to finite basis set calculations will be the complete basis set extrapolation of the second-order pair energies.

The second-order CBS values for $\alpha\beta$-spin pairs are given by[13–16,20]

$$ {}^{\alpha\beta}\mathbf{e}_{ij}^{(2)}(\text{CBS}) = |S|_{ij}^2 \left(\frac{-255}{4608}\right)\frac{1}{1+{}^{\alpha\beta}\delta_{ij}}, \qquad (47)$$

where the exclusion parameters ${}^{\alpha\beta}\delta_{ij}$ are obtained from[16]

$$ {}^{\alpha\beta}\delta_{ij} = 1/2\left\{-(\mathbf{N}_{ij}+1) + \sqrt{(\mathbf{N}_{ij}+1)^2 - 4\left[\mathbf{N}_{ij} - \frac{(\mathbf{N}_{ij}-1)}{{}^{\alpha\beta}\mathbf{e}_{ij}^{(2)}(\mathbf{N}_{ij})}\left(\frac{-255}{4608}\right)|S|_{ij}^2\right]}\right\}. \qquad (48)$$

The value of the second-order pair energy calculated with $\mathbf{N}_{ij}$ MPNOs is ${}^{\alpha\beta}\mathbf{e}_{ij}^{(2)}(\mathbf{N}_{ij})$ and $|S|_{ij}$ is the absolute overlap integral[33–39]:

$$ |S|_{ij} = \int |\varphi_i\varphi_j| d\tau, \qquad (49)$$

where we place the indices outside the absolute value symbol to denote the integral of the absolute value, rather than the absolute value of the overlap integral, $|S_{ji}|$. Note that $|S|_{ij}$ cannot vanish unless the orbitals φ_i and φ_j are localized in disjoint regions of space. Hence for the orthogonal SCF orbitals, φ_i and φ_j, $|S|_{ij}$ will in general be nonzero. These integrals are conveniently evaluated by a Monte Carlo numerical integration incorporating importance sampling. The CBS extrapolation employing Eqs. (47) and (48) reduces the errors in the second-order $\alpha\beta$-pair energies of neon by one to two orders of magnitude.[16]

The analogous extrapolation for the $\alpha\alpha$-interorbital pair energies is[16,20]

$$ {}^{\alpha\alpha}\mathbf{e}_{ij}^{(2)}(\text{CBS}) = {}^{\alpha\alpha}f_{ij}\left(\frac{-225}{4608}\right)\frac{1}{(1+{}^{\alpha\alpha}\delta_{ij})^{5/3}}, \qquad (50)$$

where the triplet exclusion parameter ${}^{\alpha\alpha}\delta_{ij}$ is obtained from iterative solution of the transcendental equation:

$$ {}^{\alpha\alpha}\delta_{ij} = \left[(\mathbf{N}_{ij}+{}^{\alpha\alpha}\delta_{ij})^{-5/3} + \frac{{}^{\alpha\alpha}\mathbf{e}_{ij}^{(2)}(\mathbf{N}_{ij})}{{}^{\alpha\alpha}f_{ij}(-225/4608)}\right]^{-3/5} - 1, \qquad (51)$$

and the triplet overlap factor ${}^{\alpha\alpha}f_{ij}$ is given by[39]

$$ {}^{\alpha\alpha}f_{ij} = 2|S|_{ij}^2\left[\frac{1-|S|_{ij}^2}{1+|S|_{ij}^2}\right]. \qquad (52)$$

The relative accuracy of these triplet pair extrapolations for neon is about the same as that of the $\alpha\beta$-pair extrapolations.[16] However, the more rapid basis set convergence of the triplet-pairs leads to smaller absolute errors.

E. Closed shells of MPNOs

The asymptotic forms in Eqs. (18), (33), and (46) are, in principle, correct only for sets of PNOs that include complete shells (e.g., $\mathbf{N}_{1s^2} = 1, 5, 14, 30, 55, 91$, etc.).[13–16,20] In the case of polyatomic molecules, the number of PNOs required for a closed shell will vary from pair to pair and can even be a function of geometry. In order to have a well defined model chemistry, we must therefore define an algorithm that will select an appropriate number of MPNOs for each pair energy in the molecule. The nature of the required algorithm becomes obvious if we examine the convergence of the PNO expansion for a typical molecular pair energy (Fig. 2; also see Figs. 4, 5, and 6 in Ref. 16). Extrapolation with too few PNOs ($N = 2$ or 3) will result in an overestimate of the pair energy. Extrapolation with too many PNOs ($N = 7,8,9,...$) will result in an underestimate of the pair energy, since the modest DZ + P APNO basis set cannot describe these higher PNOs accurately [Fig. 2(b)]. The correct extrapolation is obtained by selecting a complete shell of PNOs. A closed shell creates a downward cusp in the figure and can therefore be recognized by its giving a minimum in the extrapolated pair energy:

$$ \mathbf{e}_{ij}^{(2)}\text{CBS} = \text{Min}\{\mathbf{e}_{ij}^{(2)}\text{CBS}(\mathbf{N}_{ij})\};$$
$$ \mathbf{N}_{ij} = 4,5,...,\mathbf{N}_{\text{BF}} - \mathbf{N}_{\text{occ}} + 1. \qquad (53)$$

For each $\alpha\beta$ pair, we first determine the extrapolated second-order pair energy using Eq. (47) with every possible value of $\mathbf{N}_{ij}$ in Eq. (48), and then select the $\mathbf{N}_{ij}$ that gave the most negative extrapolated second-order pair energy. For each $\alpha\alpha$ pair, we use Eqs. (50) and (51). Very small values of $\mathbf{N}_{ij}$ can lead to overestimates of pair energies (Fig. 2). Since our DZ + P APNO basis sets include at least five optimized APNOs for each intraorbital pair, we need only consider $\mathbf{N}_{ij} \geqslant 5$. Our basis sets are not of the same quality for interorbital pairs. In particular, to avoid excessively large basis sets, they contain no basis functions specifically optimized for the $(2s,2p)$ pairs. To compensate for this deficiency in the basis sets, we allow all $\mathbf{N}_{ij} \geqslant 4$.

In the present context of our $\text{CBS}^{(\infty,3)}$ DZ + P APNO model chemistry, the above algorithm is perfectly adequate. However, this algorithm does not constitute an extrapolation, since it will converge to a false value for $\mathbf{e}_{ij}^{(2)}$ as $\mathbf{N}_{\text{BF}}$ approaches infinity if $\mathbf{e}_{ij}^{(2)}\text{CBS}(\mathbf{N}_0)$ is less than the exact $\mathbf{e}_{ij}^{(2)}$. This is easily remedied by considering only those $\mathbf{N}_{ij}$ greater than a minimum size that is proportional to the size of the basis set, $\mathbf{N}_{\text{BF}}$:

$$\mathbf{e}_{ij}^{(2)}\mathrm{CBS} = \mathrm{Min}\{\mathbf{e}_{ij}^{(2)}\mathrm{CBS}(N_{ij})\};$$

$$\mathbf{N}_{ij} \geqslant \mathrm{Max}\{4, (\mathbf{N}_{\mathrm{BF}} + \mathbf{N}_{\mathrm{occ}})/2\mathbf{N}_{\mathrm{occ}}\}, \tag{54}$$

where we have made the minimum value for $\mathbf{N}_{ij}$ proportional to the number of basis functions per occupied orbital. This algorithm necessarily converges to the exact value for each pair energy as the basis set approaches completeness. However, the results will not be size consistent unless we fix the minimum value of $\mathbf{N}_{ij}$ for each basis set type (e.g., DZ + P $\{KK,KL,LL\}$APNO), and make this value the same for intraorbital pairs and interorbital pairs.

F. The CBS$^{(\infty,3)}$ correlation energy

The total CBS$^{(\infty,3)}$ correlation energy is the sum of the extrapolated infinite-order pair energies, $\mathbf{e}_{ij}^{(\infty)}(\mathrm{CBS})$, plus the extrapolated third-order pair coupling terms, $\mathbf{e}_{ij,kl}^{(3)}(\mathrm{CBS})$.

1. Infinite-order pair energies

Once we have determined the complete basis set second-order pair energies, the interference effect can be used to extrapolate the infinite-order pair energies[13–16,20]:

$$\mathbf{e}_{ij}(\mathrm{CBS})$$
$$= \mathbf{e}_{ij}(\mathbf{N}_{ij}) + \left(\sum_{\mu=1}^{N_{ij}} c_{\mu ij}\right)^2 [\mathbf{e}_{ij}^{(2)}(\mathrm{CBS}) - \mathbf{e}_{ij}^{(2)}(\mathbf{N}_{ij})]. \tag{55}$$

This extrapolation reduces the errors in the infinite-order pair energies of neon by about two orders of magnitude.[16]

2. Third-order pair-coupling terms

The extrapolation of the third-order pair-coupling terms to the complete basis set values is given by[16,20]

$$\sum_{kl \neq ij} \mathbf{e}_{ij,kl}^{(3)}(\mathrm{CBS})$$
$$= \sum_{kl \neq ij} \mathbf{e}_{ij,kl}^{(3)}(\mathbf{N}_{ij},\mathbf{N}_{kl}) \left[\frac{\mathbf{e}_{ij}(\mathrm{CBS}) - \mathbf{e}_{ij}^{(2)}(\mathrm{CBS})}{\mathbf{e}_{ij}(\mathbf{N}_{ij}) - \mathbf{e}_{ij}^{(2)}(\mathbf{N}_{ij})}\right], \tag{56}$$

so that the pair couplings are scaled by the same fraction as the higher-order contributions to the associated pairs. The results obtained with this extrapolation for neon using the DZ + P APNO pair energies and pair couplings are in fair agreement with the best estimates we have for the pair couplings. Although the relative errors are much larger than those for the pair extrapolations, the absolute errors are comparable (rms error = 0.1 mhartree for neon[16]).

3. Total correlation energy

There are two sources of error in the total CBS$^{(\infty,3)}$ correlation energy. The first is the residual error resulting from the use of a finite basis set. This error has been greatly reduced, but not eliminated by the CBS asymptotic extrapolations. It could be further reduced by using larger more complete basis sets. The second source of error is the use of the third-order pair-coupling terms. This error appears to be on the order of a few percent of the pair-coupling terms, and can

FIG. 2. The convergence of the PNO expansion of the bonding pair energy of hydrogen fluoride. The infinite basis set pair energy corresponds to the intercept in this graph using the inverse of the number N of PNOs as the abscissa. (a) The filled circles, from upper right to lower left, represent: N = 1 (the SCF energy), N = 6 (the first complete shell of PNOs, used for the CBS extrapolation), and N = ∞ (the extrapolated CBS pair energy). The open circles represent: N = 2,3,4,5 and N = 7,8,...,28, and N = 29, the limit with the DZ + P APNO basis set. (b) When the basis set is expanded with additional s, p, and d primitives, and $2f$ primitives, then a second complete shell of PNOs is obtained with N = 18.

be eliminated only by including successively higher orders of pair-coupling terms, $e_{ij,kl}^{(4)}$, etc., giving successively higher-order CBS methods $CBS^{(\infty,4)}$, etc.

III. The $CBS^{(\infty,3)}$ PROGRAM

The current CBS program is based upon a slightly modified version of the program, GAUSSIAN 82.[40] First, GAUSSIAN 82 is used to evaluate all necessary integrals and determine the SCF wave function and energy using a DZ + P APNO basis set. The modified version of GAUSSIAN 82 leaves the integral files and files with the SCF orbitals and eigenvalues on the disk. Then our CBS program determines the MNPO's using the integrals evaluated by GAUSSIAN 82 and performs the CBS extrapolation of the correlation energy. Since we use a larger QZ + TP frozen core basis set for the [*spd,sp*] limit SCF energies, they must be determined in a separate calculation. This is less convenient, but more efficient than using a basis set flexible enough to accurately determine both the SCF energy and the correlation energy in a single calculation. Once again, we use GAUSSIAN 82 to evaluate all necessary integrals and determine the SCF wave function and energy using a QZ + TP basis set. Then our CBS SCF program deletes the polarization functions from each atom in turn, recalculates the SCF energy using the integrals evaluated by GAUSSIAN 82, and finally performs the l^{-6} extrapolation to estimate the SCF limit. We plan to develop a modified version of GAUSSIAN 86 in which all this is done automatically as a standard CBS option.

All calculations reported in this paper were performed on a Digital Equipment Corporation Micro VAX-II computer. A more efficient version of our program designed to treat larger molecules using a Cray X-MP supercomputer is under development.

IV. RESULTS

Numerical results from the application of the $CBS^{(\infty,3)}$ (Full)/DZ + P APNO model to closed-shell atoms and hy-

drides of the first-row elements are presented in Tables II through VIII. The experimental geometries were used in all cases except BH_3 for which the $CBS^{(\infty,3)}$ optimum geometry ($R_{BH} = 1.2003$ Å, $\Theta_{HBH} = 120°$) was used. The DZ + P APNO basis sets in the Appendix were used to calculate the $CBS^{(\infty,3)}$ correlation energy (Tables V and VI) and the less contracted QZ + TP basis sets were used to calculate the CBS SCF energy (Table II) as described above.

A. The CBS SCF limit

The convergence of the SCF energy is indicated in Table II. The small change in going from the LL' basis set to the QZ + TP basis set suggests that our CBS SCF energies should all be accurate to 0.001 hartree. The best empirical estimates of the SCF limits from the literature confirm this accuracy (Table II). The rms error in the CBS SCF energies is 0.00014 hartree per occupied orbital, which is only slightly larger than our design goal ($0.0001 N_{occ}$ hartree) in Eq. (1). The error in the $CBS^{(\infty,3)}$ correlation energy is about twice as large as the CBS SCF error.

B. The $CBS^{(\infty,3)}$ correlation energy

A qualitative impression of the success of the method is presented in Fig. 3, which compares the direct calculation of the total correlation energy using the DZ + P {KK,KL,LL,LL'} APNO basis sets with the $CBS^{(\infty,3)}$ asymptotic extrapolations and with the "experimental correlation energies" (i.e., the experimental total energies of the atoms[41] + the experimental dissociation energies of the molecules[43-48] − the SCF energies of the molecules − the relativistic, mass, and Lamb corrections of the atoms[46]). The accuracy of the direct DZ + P APNO calculations shows a pronounced variation with the total number of basis functions in the CH_4, NH_3, H_2O, HF, Ne isoelectronic series, ranging from 80.4% of the exact correlation energy for Ne with 38 basis functions to 87.8% of the exact correlation energy for CH_4 with 74 basis functions (Fig. 4). In contrast,

TABLE II. Convergence of the SCF energy (in hartree a.u.) for closed-shell atoms and hydrides of first-row elements.

Method	Basis set	He	LiH	Be	BH₃	CH₄	NH₃	H₂O	HF	Ne
Direct E^{SCF}	DZ + P{*KK,LL*}APNO	− 2.861 62	− 7.893 65	− 14.572 99	− 26.398 74	− 40.207 64	− 56.212 78	− 76.054 26	− 100.061 85	− 128.546 45
(*spd,sp*)	DZ + P{*KK,KL,LL*}APNO		− 7.986 19	− 14.572 99	− 26.399 28	− 40.208 06	− 56.213 50	− 76.054 65	− 100.062 78	− 128.546 45
	DZ + P{*KK,KL,LL,LL'*}APNO	− 2.861 62	− 7.986 62	− 14.572 99	− 26.400 03	− 40.213 27	− 56.220 79	− 76.062 31	− 100.066 99	− 128.546 49
	QZ + TP	− 2.861 62	− 7.986 98	− 14.572 99	− 26.401 57	− 40.215 73	− 56.222 90	− 76.064 76	− 100.068 63	− 128.546 49
l^{-6} extrap.		0	− 0.000 07	0	− 0.001 31	− 0.001 81	− 0.002 24	− 0.002 25	− 0.001 41	0
Total CBS SCF		− 2.861 62	− 7.987 06	− 14.572 99	− 26.402 88	− 40.217 54	− 56.225 14	− 76.067 01	− 100.070 04	− 128.546 49
(Est. SCF limit)		(− 2.861 68)[a]	(− 7.987 31)[b]	(− 14.573 02)[a]	(− 26.403)[c]	(− 40.219)[d]	(− 56.226)[d]	(− 76.067 5)[c]	(− 100.070 82)[f]	(− 128.547 01)[a]

[a] Reference 41.
[b] Reference 42.
[c] Reference 43.
[d] Reference 44.
[e] Reference 49.
[f] Reference 29.

TABLE III. Convergence of the $E^{(2)}$, the direct second-order correlation energy (in hartree a.u.).

Component	Basis set	He	LiH	Be	BH$_3$	CH$_4$	NH$_3$	H$_2$O	HF	Ne
KK	DZ + P{*KK,LL*}APNO	− 0.028 70	− 0.031 18	− 0.031 29	− 0.031 92	− 0.032 10	− 0.032 05	− 0.031 84	− 0.031 49	− 0.031 14
	DZ + P{*KK,KL,LL*}APNO		− 0.031 58	− 0.032 15	− 0.032 70	− 0.033 10	− 0.032 94	− 0.032 67	− 0.032 35	− 0.032 27
	DZ + P{*KK,KL,LL,LL '*}APNO	− 0.030 15	− 0.031 59	− 0.032 15	− 0.033 19	− 0.033 38	− 0.033 42	− 0.033 09	− 0.032 78	− 0.032 42
KL	DZ + P{*KK,LL*}APNO		− 0.001 61	− 0.002 63	− 0.004 75	− 0.006 97	− 0.008 08	− 0.009 32	− 0.010 32	− 0.011 31
	DZ + P{*KK,KL,LL*}APNO		− 0.002 18	− 0.004 33	− 0.006 77	− 0.010 81	− 0.012 43	− 0.013 81	− 0.016 85	− 0.020 82
	DZ + P{*KK,KL,LL,LL '*}APNO		− 0.002 18	− 0.004 33	− 0.007 82	− 0.011 37	− 0.013 99	− 0.015 76	− 0.018 83	− 0.021 73
LL	DZ + P{*KK,LL*}APNO		− 0.024 64	− 0.026 10	− 0.042 19	− 0.048 37	− 0.065 30	− 0.067 55	− 0.069 72	− 0.064 87
	DZ + P{*KK,KL,LL*}APNO		− 0.024 74	− 0.026 40	− 0.042 90	− 0.049 27	− 0.066 61	− 0.069 04	− 0.072 11	− 0.068 62
	DZ + P{*KK,KL,LL,LL '*}APNO		− 0.025 94	− 0.027 72	− 0.045 06	− 0.051 22	− 0.070 98	− 0.074 00	− 0.077 47	− 0.073 43
LL '	DZ + P{*KK,LL*}APNO				− 0.054 92	− 0.123 14	− 0.135 03	− 0.153 27	− 0.157 69	− 0.154 64
	DZ + P{*KK,KL,LL*}APNO				− 0.056 02	− 0.125 68	− 0.138 14	− 0.156 55	− 0.163 35	− 0.165 96
	DZ + P{*KK,KL,LL,LL '*}APNO				− 0.059 50	− 0.130.99	− 0.148 99	− 0.170 32	− 0.178 87	− 0.178 06
Total	DZ + P{*KK,LL*}APNO	− 0.028 70	− 0.057 42	− 0.060 02	− 0.133 78	− 0.210 58	− 0.240 45	− 0.261 97	− 0.269 23	− 0.261 96
	DZ + P{*KK,KL,LL*}APNO		− 0.058 49	− 0.062 88	− 0.138 39	− 0.218 86	− 0.250 13	− 0.272 06	− 0.284 65	− 0.287 67
	DZ + P{*KK,KL,LL,LL '*}APNO	− 0.030 15	− 0.059 71	− 0.064 21	− 0.145 57	− 0.226 95	− 0.267 38	− 0.293 15	− 0.307 95	− 0.305 65
	(Expt.)	(− 0.042 04)[a] ± 0.000 00	(− 0.082 97)[b‑d] ± 0.000 05	(− 0.094 33)[b,c] ± 0.000 02	(− 0.195)[b,c,e] ± 0.005	(− 0.295)[b,c,f] ± 0.002	(− 0.337)[b,c,f] ± 0.002	(− 0.370)[b,c,f] ± 0.002	(− 0.3855)[b,c,g] ± 0.0005	(− 0.3896)[b,c] ± 0.001

[a]Reference 45.
[b]Reference 46.
[c]Using $[E^{\text{expt}}$ (atoms) from Ref. 41] $- (E^{\text{Rel}} + $ Mass Corr. + Lamb Corr. from Ref. 46) $+ De^{\text{expt}} - E^{\text{SCF}}$.
[d]Reference 47.
[e]De for BH$_3$ was taken from Ref. 43.
[f]Reference 44.
[g]Reference 48.

the error in the CBS$^{(\infty,3)}$ correlation energies is always less than 1.2%. Quantitatively, all examples studied so far satisfy the inequality in Eq. (1). Our design goal for the CBS$^{(\infty,3)}$ correlation energy has been satisfied. The CBS$^{(\infty,3)}$ total energies for LiH, BH$_3$, CH$_4$, NH$_3$, H$_2$O, and HF are the most accurate total nonrelativistic energies reported to date for these species. For example, the most accurate result for CH$_4$ was − 40.5063 hartree,[50] whereas we obtain − 40.5112 hartree and the experimental value is − 40.514 ± 0.002 hartree. The largest error occurred for ammonia, where we ob-

TABLE IV. Convergence of the direct higher-order contributions to the correlation energy (in hartree a.u.).

Component	Basis set	He	LiH	Be	BH$_3$	CH$_4$	NH$_3$	H$_2$O	HF	Ne
KK	DZ + P{*KK,LL*}APNO	− 0.007 22	− 0.004 71	− 0.003 55	− 0.002 83	− 0.002 31	− 0.001 96	− 0.001 68	− 0.001 47	− 0.001 30
	DZ + P{*KK,KL,LL*}APNO		− 0.004 64	− 0.003 49	− 0.002 75	− 0.002 26	− 0.001 91	− 0.001 64	− 0.001 44	− 0.001 27
	DZ + P{*KK,KL,LL,LL '*}APNO	− 0.006 89	− 0.004 64	− 0.003 49	− 0.002 71	− 0.002 23	− 0.001 89	− 0.001 63	− 0.001 42	− 0.001 26
KL	DZ + P{*KK,LL*}APNO		− 0.000 24	− 0.000 11	− 0.000 33	− 0.000 28	− 0.000 19	− 0.000 10	− 0.000 05	− 0.000 01
	DZ + P{*KK,KL,LL*}APNO		− 0.000 39	− 0.000 28	− 0.000 51	− 0.000 57	− 0.000 44	− 0.000 32	− 0.000 31	− 0.000 34
	DZ + P{*KK,KL,LL,LL '*}APNO		− 0.000 38	− 0.000 28	− 0.000 64	− 0.000 68	− 0.000 55	− 0.000 44	− 0.000 41	− 0.000 38
LL	DZ + P{*KK,LL*}APNO		− 0.008 61	− 0.019 42	− 0.010 33	− 0.007 22	− 0.009 67	− 0.007 56	− 0.006 57	− 0.004 59
	DZ + P{*KK,KL,LL*}APNO		− 0.008 46	− 0.019 15	− 0.010 20	− 0.007 06	− 0.009 46	− 0.007 29	− 0.006 25	− 0.004 08
	DZ + P{*KK,KL,LL,LL '*}APNO		− 0.009 08	− 0.017 94	− 0.009 86	− 0.007 24	− 0.009 06	− 0.006 96	− 0.005 81	− 0.003 73
LL '	DZ + P{*KK,LL*}APNO				− 0.015 44	− 0.021 20	− 0.015 98	− 0.010 33	− 0.004 78	− 0.002 71
	DZ + P{*KK,KL,LL*}APNO				− 0.015 30	− 0.020 83	− 0.015 58	− 0.009 88	− 0.004 17	− 0.001 95
	DZ + P{*KK,KL,LL,LL '*}APNO				− 0.014 95	− 0.021 83	− 0.015 74	− 0.010 22	− 0.004 40	− 0.002 42
Total	DZ + P{*KK,LL*}APNO	− 0.007 22	− 0.013 56	− 0.023 08	− 0.028 93	− 0.031 01	− 0.027 80	− 0.019 67	− 0.012 87	− 0.008 61
	DZ + P{*KK,KL,LL*}APNO		− 0.013 49	− 0.022 92	− 0.028 76	− 0.030 72	− 0.027 39	− 0.019 13	− 0.012 17	− 0.007 64
	DZ + P{*KK,KL,LL,LL '*}APNO	− 0.006 89	− 0.014 10	− 0.021 71	− 0.028 16	− 0.031 98	− 0.027 24	− 0.019 25	− 0.012 04	− 0.007 79

TABLE V. Convergence of the CBS$^{(2)}$ correlation energy (in hartree a.u.).

Component	Basis set	He	LiH	Be	BH$_3$	CH$_4$	NH$_3$	H$_2$O	HF	Ne
KK	DZ + P{KK,LL}APNO	−0.037 94	−0.039 65	−0.040 45	−0.041 07	−0.041 15	−0.041 12	−0.040 91	−0.040 59	−0.040 28
	DZ + P{KK,KL,LL}APNO		−0.039 58	−0.040 27	−0.040 98	−0.041 04	−0.041 02	−0.040 86	−0.040 52	−0.040 14
	DZ + P{KK,KL,LL,LL'}APNO	−0.037 59	−0.039 67	−0.040 27	−0.040 87	−0.041 05	−0.040 94	−0.040 79	−0.040 42	−0.040 12
KL	DZ + P{KK,LL}APNO		−0.002 01	−0.003 50	−0.006 39	−0.009 43	−0.011 12	−0.013 01	−0.014 66	−0.016 39
	DZ + P{KK,KL,LL}APNO		−0.002 63	−0.005 18	−0.008 22	−0.013 07	−0.015 21	−0.017 18	−0.020 96	−0.025 76
	DZ + P{KK,KL,LL,LL'}APNO		−0.002 64	−0.005 18	−0.009 27	−0.013 61	−0.016 81	−0.019 15	−0.022 88	−0.026 58
LL	DZ + P{KK,LL}APNO		−0.030 09	−0.031 77	−0.052 12	−0.060 53	−0.083 29	−0.087 90	−0.092 56	−0.090 40
	DZ + P{KK,KL,LL}APNO		−0.030 09	−0.031 79	−0.052 40	−0.060 86	−0.083 63	−0.088 08	−0.093 12	−0.090 78
	DZ + P{KK,KL,LL,LL'}APNO		−0.031 23	−0.031 82	−0.053 08	−0.061 45	−0.085 03	−0.089 80	−0.093 64	−0.090 99
LL'	DZ + P{KK,LL}APNO				−0.069 96	−0.156 26	−0.176 86	−0.204 71	−0.217 14	−0.218 60
	DZ + P{KK,KL,LL}APNO				−0.070 52	−0.157 10	−0.177 88	−0.205 49	−0.219 32	−0.223 11
	DZ + P{KK,KL,LL,LL'}APNO				−0.071 78	−0.158 14	−0.181 98	−0.210 74	−0.221 86	−0.224 75
Total	DZ + P{KK,LL}APNO	−0.037 94	−0.071 74	−0.075 72	−0.169 54	−0.267 37	−0.312 38	−0.346 53	−0.364 95	−0.365 84
	DZ + P{KK,KL,LL}APNO		−0.072 29	−0.077 24	−0.172 12	−0.272 07	−0.317 74	−0.351 62	−0.373 92	−0.379 79
	DZ + P{KK,KL,LL,LL'}APNO	−0.037 59	−0.073 54	−0.077 27	−0.175 00	−0.274 25	−0.324 75	−0.360 47	−0.378 80	−0.382 44
	(Expt.)	(−0.042 04)[a] ±0.000 00	(−0.082 97)[b-d] ±0.000 05	(−0.094 33)[b,c] ±0.000 02	(−0.195)[b,c,e] ±0.005	(−0.295)[b,c,f] ±0.002	(−0.337)[b,c,f] ±0.002	(−0.370)[b,c,f] ±0.002	(−0.3855)[b,c,g] ±0.0005	(−0.3896)[b,c] ±0.001

[a] Reference 45.
[b] Reference 46.
[c] Using $[E^{\text{Expt}} \text{ (atoms) from Ref. 41}] - (E^{\text{Rel}} + \text{Mass Corr.} + \text{Lamb Corr. from Ref. 46}) + DE^{\text{Expt}} - E^{\text{SCF}}$.
[d] Reference 47.
[e] De for BH$_3$ was taken from Ref. 43.
[f] Reference 44.
[g] Reference 48.

tain −56.5659 hartree and the experimental value is −56.563 ± 0.002 hartree.

It is important that an extrapolation, such as the CBS method, obtains the right answers for the right reasons. There are two definitive calculations in the literature that permit a detailed pair by pair examination of the accuracy of our CBS calculations for neon[51] and hydrogen fluoride.[52] In the Appendix, we have included a detailed comparison (Table XII) of our results for the neon atom with the definitive second-order calculations[51] of Jankowski and Malinowski. The rms error in our individual pair energies is only 0.00016 hartree, indicating that the small error (0.0015 hartree) in

TABLE VI. Convergence of the higher-order contributions to the CBS$^{(\infty,3)}$ correlation energy (in hartree a.u.).

Component	Basis set	He	LiH	Be	BH$_3$	CH$_4$	NH$_3$	H$_2$O	HF	Ne
KK	DZ + P{KK,LL}APNO	−0.004 31	−0.002 95	−0.002 19	−0.001 76	−0.001 45	−0.001 23	−0.001 05	−0.000 92	−0.000 80
	DZ + P{KK,KL,LL}APNO		−0.002 97	−0.002 23	−0.001 78	−0.001 48	−0.001 25	−0.001 06	−0.000 92	−0.000 82
	DZ + P{KK,KL,LL,LL'}APNO	−0.004 42	−0.002 89	−0.002 23	−0.001 80	−0.001 47	−0.001 23	−0.001 05	−0.000 93	−0.000 81
KL	DZ + P{KK,LL}APNO		−0.000 24	−0.000 13	−0.000 31	−0.000 27	−0.000 18	−0.000 11	−0.000 04	−0.000 01
	DZ + P{KK,KL,LL}APNO		−0.000 40	−0.000 32	−0.000 44	−0.000 57	−0.000 39	−0.000 31	−0.000 30	−0.000 32
	DZ + P{KK,KL,LL,LL'}APNO		−0.000 38	−0.000 32	−0.000 60	−0.000 57	−0.000 48	−0.000 36	−0.000 40	−0.000 35
LL	DZ + P{KK,LL}APNO		−0.005 61	−0.014 68	−0.055 99	−0.003 57	−0.005 50	−0.004 38	−0.003 98	−0.002 45
	DZ + P{KK,KL,LL}APNO		−0.005 54	−0.014 67	−0.006 05	−0.003 60	−0.005 51	−0.004 33	−0.003 93	−0.002 29
	DZ + P{KK,KL,LL,LL'}APNO		−0.005 86	−0.014 75	−0.006 36	−0.003 88	−0.005 18	−0.003 91	−0.003 96	−0.001 94
LL'	DZ + P{KK,LL}APNO				−0.011 08	−0.012 99	−0.010 36	−0.006 55	−0.002 41	−0.001 17
	DZ + P{KK,KL,LL}APNO				−0.011 11	−0.012 92	−0.010 17	−0.006 27	−0.001 94	−0.000 62
	DZ + P{KK,KL,LL,LL'}APNO				−0.011 41	−0.013 46	−0.009 12	−0.005 38	−0.002 01	+0.000 17
Total	DZ + P{KK,LL}APNO	−0.004 31	−0.008 81	−0.017 00	−0.019 15	−0.018 28	−0.017 27	−0.012 08	−0.007 34	−0.004 44
	DZ + P{KK,KL,LL}APNO		−0.008 92	−0.017 21	−0.019 41	−0.018 57	−0.017 32	−0.011 96	−0.007 07	−0.004 05
	DZ + P{KK,KL,LL,LL'}APNO	−0.004 42	−0.009 14	−0.017 30	−0.020 17	−0.019 38	−0.016 01	−0.010 71	−0.007 29	−0.002 92

TABLE VII. Convergence of the total calculated correlation energy (in hartree a.u.).

Method	Basis set	He	LiH	Be	BH_3	CH_4	NH_3	H_2O	HF	Ne
Direct	DZ + P{KK,LL}APNO	− 0.035 92	− 0.070 99	− 0.083 11	− 0.162 70	− 0.241 58	− 0.268 25	− 0.281 65	− 0.282 09	− 0.270 55
	DZ + P{KK,KL,LL}APNO		− 0.071 99	− 0.085 80	− 0.167 16	− 0.249 59	− 0.277 51	− 0.291 20	− 0.296 83	− 0.295 30
	DZ + P{KK,KL,LL,LL'}APNO	− 0.037 04	− 0.073 81	− 0.086 04	− 0.173 74	− 0.258 93	− 0.294 62	− 0.312 41	− 0.319 99	− 0.313 43
	(13s8p4d2f)/[5s6p4d2f]									− 0.352 60
$CBS^{(\infty,3)}$	DZ + P{KK,LL}APNO	− 0.042 24	− 0.080 55	− 0.092 72	− 0.188 69	− 0.285 64	− 0.329 65	− 0.358 61	− 0.372 29	− 0.370 10
	DZ + P{KK,KL,LL}APNO		− 0.081 21	− 0.094 45	− 0.191 53	− 0.290 64	− 0.335 06	− 0.363 58	− 0.380 99	− 0.383 83
	DZ + P{KK,KL,LL,LL'}APNO	− 0.042 01	− 0.082 67	− 0.094 64	− 0.195 17	− 0.293 63	− 0.340 76	− 0.371 18	− 0.386 10	− 0.385 36
	(13s8p4d2f)/[5s6p4d2f]									− 0.389 78
(Expt.)		(− 0.042 04)[a] ± 0.000 00	(− 0.082 97)[b-d] ± 0.000 05	(− 0.094 33)[b,c] ± 0.000 02	(− 0.195)[b,c,e] ± 0.005	(− 0.295)[b,c,f] ± 0.002	(− 0.337)[b,c,f] ± 0.002	(− 0.370)[b,c,f] ± 0.002	(− 0.3855)[b,c,g] ± 0.0005	(− 0.3896)[b,c] ± 0.001

[a]Reference 45.
[b]Reference 46.
[c]Using [E^{Expt} (atoms) from Ref. 41] − (E^{Rel} + Mass Corr. + Lamb Corr. from Ref. 46) + $De^{Expt} − E^{SCF}$.
[d]Reference 47.
[e]De for BH_3 was taken from Ref. 43.
[f]Reference 44.
[g]Reference 48.

the total CBS second-order correlation energy (Table XI) is the result of getting the individual pieces right rather than a fortuitous cancellation of errors.

Although there are no results of comparable accuracy for the polyatomic molecules, the landmark calculations[52] of Adamowicz and Bartlett provide a very valuable check on the accuracy of our calculations for hydrogen fluoride. They have determined the 193 most important MPNOs for hydrogen fluoride as numerical orbitals. Since their (no^2) cluster correlation energies are equivalent to our infinite-order no^2-

TABLE VIII. Components[a] of the total nonrelativistic energy (in hartree a.u.) for closed-shell atoms and hydrides of first-row elements.

Type	Component	He	LiH	Be	BH_3	CH_4	NH_3	H_2O	HF	Ne
E^{SCF}	E^{SCF}(spd,sp)	− 2.861 62	− 7.986 98	− 14.572 99	− 26.401 57	− 40.215 73	− 56.222 90	− 76 064 76	− 100.068 63	− 128.546 49
	l^{-6} extrap.	0	− 0.000 07	0	− 0.001 31	− 0.001 81	− 0.002 24	− 0.002 25	− 0.001 41	0
	Total CBS SCF	− 2.861 62	− 7.987 06	− 14.572 99	− 26.402 88	− 40.217 54	− 56.225 14	− 76.067 01	− 100.070 04	− 128 546 49
	(Est. SCF limit)	(− 2.861 68)[b]	(− 7.987 31)[c]	(− 14.573 02)[b]	(− 26.403)[d]	(− 40.219)[e]	(− 56.226)[e]	(− 76.067 5)[f]	(− 100.070 82)[g]	(− 128.547 01)[b]
E^{Corr}	K^2	− 0.042 01	− 0.042 62	− 0.042 46	− 0.042 63	− 0.042 50	− 0.042 17	− 0.041 84	− 0.041 34	− 0.040 92
	KL	0	− 0.002 88	− 0.005 31	− 0.009 58	− 0.013 88	− 0.017 29	− 0.019 26	− 0.022 92	− 0.026 59
	L^2	0	− 0.036 84	− 0.046 57	− 0.141 93	− 0.236 15	− 0.281 31	− 0.311 47	− 0.321 89	− 0.319 36
	Total CBS E^{Corr}	− 0.042 01	− 0.082 67	− 0.094 64	− 0.195 17	− 0.293 63	− 0.340 76	− 0.371 18	− 0.386 10	− 0.389 78
	(Expt.)	(− 0.042 04)[h]	(− 0.082 97)[h-k]	(− 0.094 33)[i,j]	(− 0.195)[i,j,l]	(− 0.295)[e,i,j]	(− 0.337)[e,i,j]	(− 0.370)[e,i,j]	(− 0.385 5)[i,j,m]	(− 0.389 6)[i,j]
Total	CBS	− 2.903 63	− 8.069 73	− 14.667 63	− 26.598 05	− 40 511 17	− 56.565 90	− 76.438 19	− 100.456 14	− 128.936 25
	(Expt.)	(− 2.903 724)[h] ± 0.000 000	(− 8.070 28)[i,k,n] ± 0.000 05	(− 14.667 35)[i,n] ± 0.000 02	(− 26.598)[i,l,n] ± 0.005	(− 40.514)[e,i,n] ± 0.002	(− 56.563)[e,i,n] ± 0.002	(− 76.437)[e,i,n] ± 0.002	(− 100.456 3)[i,m,n] ± 0.0005	(− 128.936 6)[i,n] ± 0.001

[a]The L^2 component includes the LL intraorbital valence-shell pairs and the LL' interorbital valence-shell pairs.
[b]Reference 41.
[c]Reference 42.
[d]Reference 43.
[e]Reference 44.
[f]Reference 49.
[g]Reference 29.
[h]Reference 45.
[i]Reference 46.
[j]Using [E^{Expt} (atoms) from Ref. 41] − (E^{Rel} + Mass Corr. + Lamb Corr. from Ref. 46) + $De^{Expt} − E^{SCF}$.
[k]Reference 47.
[l]De for BH_3 was taken from Ref. 43.
[m]Reference 48.
[n]Using [E^{Expt} (atoms) from Ref. 41) − (E^{Rel} + Mass Corr. + Lamb Corr. from Ref. 46) + De^{Expt}.
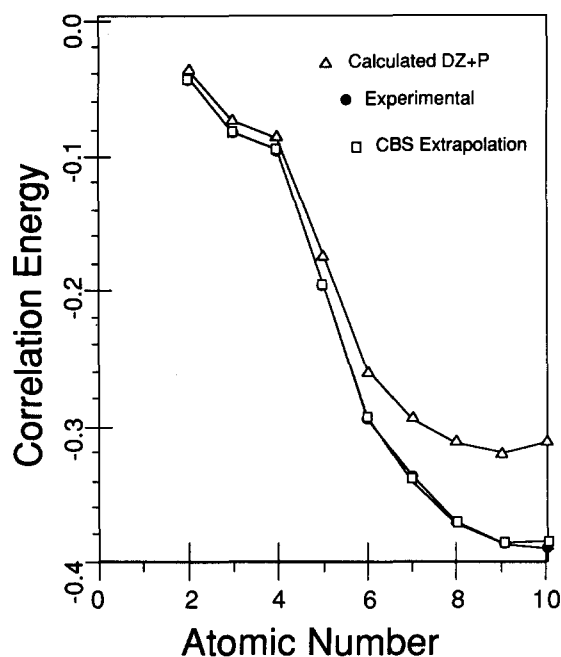
FIG. 3. Comparison of directly calculated DZ + P APNO correlation energies, CBS$^{(\infty,3)}$ extrapolated correlation energies, and "experimental" correlation energies for closed-shell atoms and hydrides of first-row elements.
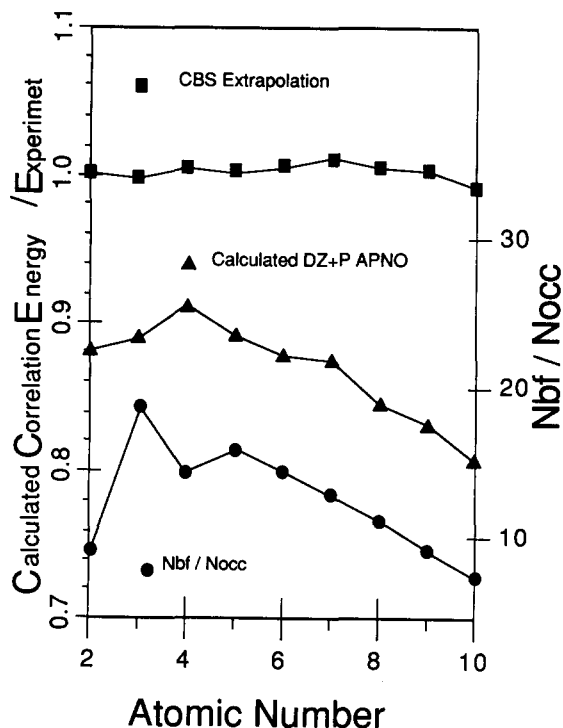

FIG. 4. The fraction of the experimental correlation energies of closed-shell atoms and hydrides of first-row elements that is calculated directly with the DZ + P APNO basis sets and the fraction obtained with the CBS$^{(\infty,3)}$ extrapolation. The number of basis functions, N_{BF}, per occupied SCF orbital (N_{bf}/N_{occ}) shows a moderate correlation with the fraction of the correlation energy obtained by direct calculation except in the case of LiH where a full valence basis set is needed for only one occupied valence orbital and Be where the $(2s,2p)$ near degeneracy makes the $(2s,2s)$ pair rapidly convergent.

intraorbital pair energies, a direct comparison is possible for these pairs (Table IX). In fact, Adamowicz and Bartlett report the natural orbitals used in each pair calculation, so that a CBS extrapolation of their results is possible if we estimate the trace of the pair CI coefficient matrix, $\Gamma(c_{ij})$, and use our values for the δ_{ij} (Fig. 5). The rms deviation between the CBS extrapolated pair energies obtained with our [$4s5p3d,3s2p$] APNO basis set and the CBS extrapolated pair energies obtained with the [$45\sigma40\pi26\delta8\phi$] numerical MPNO basis set of Adamowicz and Bartlett is only 0.000 14 hartree (Table IX). The close agreement for the $3\sigma^2$-bonding pair (− 0.033 10 vs − 0.033 04 hartree) in particular, indicates that MPNOs can indeed be very accurately described as linear combinations of APNOs. The general agreement increases our confidence in the CBS extrapolations.

Adamowicz and Bartlett also report[52] all the second-order pair energies calculated with a [$28\sigma23\pi17\delta7\phi$] numerical MPNO basis set. Although we have insufficient information for a CBS extrapolation of these MPNO pair energies, comparison with our APNO results (Table X) makes it clear that our CBS extrapolated pair energies are an order of magnitude more accurate than our direct pair energies obtained with our APNO basis set.

TABLE IX. Calculated and extrapolated infinite-order (i.e., IEPA) σ-intraorbital pair energies for hydrogen fluoride.

| Pair | δ_{ij} | [$4s5p3d, 3s2p$] APNO | | | | [$45\sigma\,40\pi\,26\delta\,8\phi$] MPNO | | | |
		N_{ij}	$\Gamma^2(c_{ij})$	$e^{(\infty)}{}_{ij}(N_{ij})$	$e^{(\infty)}{}_{ij}$(CBS)	N_{ij}	$\Gamma^2(c_{ij})$	$e^{(\infty)}{}_{ij}(N_{ij})$	$e^{(\infty)}{}_{ij}$(CBS)
$1\sigma^2$	0.2079	5	0.9374	− 0.032 56	− 0.041 35	25[a]	0.9064[b]	− 0.039 59[a]	− 0.041 35[c]
$2\sigma^2$	2.7957	10	0.7957	− 0.010 55	− 0.013 58	19[a]	0.7427[b]	− 0.012 15[a]	− 0.013 81[c]
$3\sigma^2$	0.6827	6	0.6756	− 0.028 17	− 0.033 10	24[a]	0.5416[b]	− 0.031 97[a]	− 0.033 04[c]
rms error[d]				0.006 10	0.000 14				0.001 53

[a] Reference 52, Table I.
[b] Estimated using the $N^{-1/2}$ convergence $\Gamma(c)$ found in Fig. 8 of Ref. 16.
[c] Using Eqs. (18) and (55). The large values of N_{ij} ensure that the approximation of $\Gamma(c_{ij})$ and δ_{ij} will affect $e^{(\infty)}{}_{ij}$ (CBS) by less than 10% of the correction (i.e., less than 0.000 153 hartree).
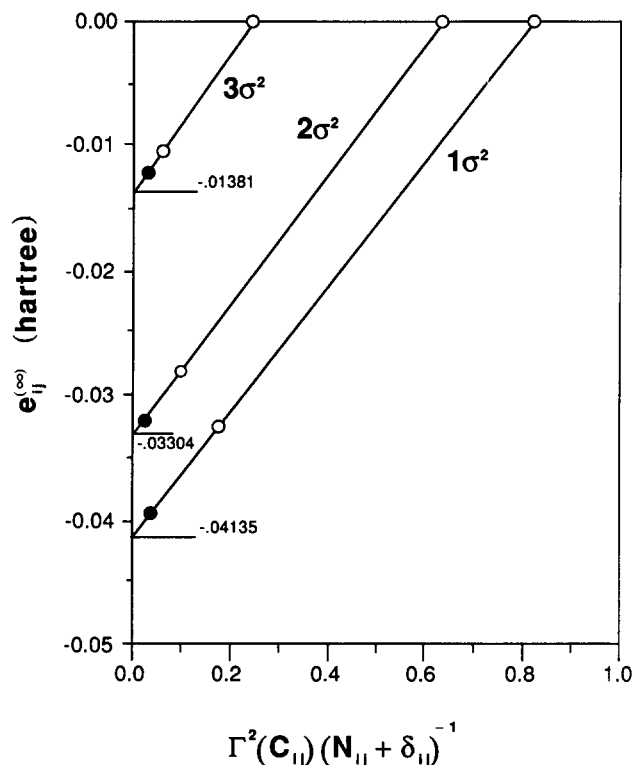[d] The error is measured with respect to the CBS/MPNO pair energies.

FIG. 5. The convergence of the PNO expansions of the σ^2-intraorbital pair energies of hydrogen fluoride including the numerical MPNO calculations (Ref. 52) of Adamowicz and Bartlett ($\bullet$). The numerical data are in Table IX.

In order to better understand the details of the effects of our basis sets, we have partitioned the correlation energy into a KK, core–core component:

$$E^{\text{Corr}}_{KK} = e^{(\infty)}_{1s,1s}, \qquad (57)$$

a KL, core–valence component:

$$E^{\text{Corr}}_{KL} = \sum_{l} e^{(\infty)}_{1s,2l} + \sum_{l,m,n} e^{(3)}_{1s,2l,m,n}, \qquad (58)$$

an LL, valence–valence intraorbital component:

$$E^{\text{Corr}}_{LL} = \sum_{l} e^{(\infty)}_{2l,2l} + \sum_{l,m,n} e^{(3)}_{2l,2l,m,n}, \qquad (59)$$

and an LL', valence–valence interorbital component:

$$E^{\text{Corr}}_{LL'} = \sum_{l} e^{(\infty)}_{2l,2l'} + \sum_{l,m,n} e^{(3)}_{2l,2l',m,n}. \qquad (60)$$

The directly calculated second-order energies in Table III show the well known slow convergence with the basis set. The DZ + P $\{KK,LL\}$ APNO basis sets include only the intraorbital APNOs and even when the higher-order contributions (Table IV) are included these basis sets give only 69.4% (Ne) to 88.1% (Be) of the experimental correlation energies without extrapolation (Table VII). The CBS$^{(\infty,3)}$ extrapolation with these basis sets (Tables V and VI) gives from 95.0% (Ne) to 100.5% (He) of the experimental correlation energies (Table VII). When the $\{KL\}$ APNO's are added to the basis sets, the $(1s,2p)$ pair energies improve markedly as discussed in the Appendix. The resulting DZ + P $\{KK,KL,LL\}$ APNO basis sets give from 75.8% (Ne) to 91.0% (Be) of the experimental correlation energies in the direct calculations and from 98.5% (Ne) to 100.5% (He) for the CBS$^{(\infty,3)}$ extrapolation (Table VII). The improvement over the smaller $\{KK,LL\}$ basis sets occurs primarily in the KL, core–valence, pair energies (Tables III and V). Further improvement can be achieved by making the valence portion of the basis sets more flexible. The less contracted DZ + P $\{KK,KL,LL,LL'\}$ APNO basis sets affect the valence-shell interorbital pair energies more than the other components (Tables III and V), which indi-

TABLE X. Calculated and extrapolated second-order pair energies for hydrogen fluoride.

Shell	Pair(s)	[4s5p3d, 3s2p] APNO		[28σ 23π 17δ 7φ] MPNO	
		$e^{(2)}_{ij}$ (calc.)	$e^{(2)}_{ij}$ (CBS)	$e^{(2)}_{ij}$ (calc.)	$e^{(2)}_{ij}$ (est.)
KK	$(1\sigma,1\sigma)$	− 0.032 78	− 0.040 42	− 0.038 89[a]	− 0.039 84[b]
KL	$(1\sigma,2\sigma)$	− 0.004 20	− 0.004 95	− 0.005 02[a]	− 0.005 15[b]
	$(1\sigma,3\sigma)$	− 0.004 21	− 0.005 16	− 0.005 17[a]	− 0.005 32[b]
	$(1\sigma,1\pi)$	− 0.010 42	− 0.012 76	− 0.013 02[a]	− 0.013 42[b]
LL	$(2\sigma,2\sigma)$	− 0.010 11	− 0.012 86	− 0.012 25[a]	− 0.012 58[b]
	$(3\sigma,3\sigma)$	− 0.024 76	− 0.029 02	− 0.028 25[a]	− 0.028 79[b]
	$(1\pi,1\pi)^c$	− 0.082 62	− 0.097 64	− 0.096 14[a]	− 0.098 24[b]
LL'	$(2\sigma,3\sigma)$	− 0.020 99	− 0.029 65	− 0.027 58[a]	− 0.028 60[b]
	$(2\sigma,1\pi)$	− 0.039 98	− 0.058 32	− 0.054 45[a]	− 0.056 70[b]
	$(3\sigma,1\pi)$	− 0.077 88	− 0.088 01	− 0.087 11[a]	− 0.088 55[b]
Total		− 0.307 95	− 0.378 80	− 0.367 88	(− 0.3772)
rms error[d]		0.008 82	0.000 73	0.001 19	···

[a]Reference 52, Table II.
[b]$e^{(2)}_{ij}$(MPNO) + $[e^{(2)}_{ij}$(MPNO) − $e^{(2)}_{ij}$(APNO)] $[E_{\text{corr}}$ (expt) − E_{corr} (MPNO)]/ $[E_{\text{corr}}$ (MPNO) − E_{corr} (APNO)].
[c]This includes the $(1\pi_x,1\pi_y)$-interorbital pair energies.
[d]The error is measured with respect to $e^{(2)}_{ij}$(est.).

cates that the extra basis functions serve their intended purpose and thereby justifies our notation for the three types of APNO basis sets. They are all DZ + P APNO basis sets in the sense that they provide for one radial and three Cartesian directions of electron correlation for each pair of occupied SCF orbitals that is indicated by the name. The DZ + P $\{KK,KL,LL,LL'\}$ APNO basis sets give from 80.4% (Ne) to 91.2% (Be) of the experimental correlation energies in the direct calculations and from $98.9 \pm 0.3\%$ (Ne) to $101.1 \pm 0.6\%$ (NH_3) for the $CBS^{(\infty,3)}$ extrapolation (Table VII). The rms error in the $CBS^{(\infty,3)}/DZ + P$ $\{KK,KL,LL,LL'\}$ APNO correlation energies is $0.000\,28\sqrt{N_{Pairs}}$ hartree which is somewhat better than our design goal ($0.0005\sqrt{N_{Pairs}}$ hartree) in Eq. (1).

The lowest percentage of the exact correlation energy is consistently obtained for the neon atom which has the smallest number of basis functions per occupied orbital. The neon $CBS^{(\infty,3)}$ correlation energy can be improved further by use of a very flexible ($13s8p4d\,2f$)/[$5s6p4d\,2f$] basis set which recovers 90.5% of the experimental correlation energy in the direct calculation and $100.05 \pm 0.26\%$ in the $CBS^{(\infty,3)}$ extrapolation (Table VII). However, the need for f functions is precisely what the CBS extrapolation is designed to avoid, so we did not pursue the use of such a large basis set for the molecular examples. The neon results are sufficient to demonstrate that the $CBS^{(\infty,3)}$ correlation energies obtained with the DZ + P $\{KK,KL,LL,LL'\}$ APNO basis sets will change by less than 1% with further expansion of the basis sets.

If we combine the $CBS^{(\infty,3)}$ total correlation energies obtained with the largest basis sets in Table VII with the CBS SCF energies in Table II, we obtain the total energies in Table VIII. In every case, these total energies agree with experiment to within 1% of the correlation energy. Therefore the partition of the correlation energy into K^2, KL, and L^2 contributions as obtained from these calculations can be used as benchmarks to evaluate more approximate methods.

The KK and LL intraorbital pair energies (Table V) change very little as the basis set becomes more flexible, indicating that the molecular PNO's are primarily linear combinations of the corresponding atomic PNO's. In fact, the KK pair energies decrease very slightly as the basis set is expanded. This is a result of our use of MCSCF orbitals for APNO basis functions rather than true natural orbitals.

There would be little point to including the KK, core–core correlation energy, without also including the KL, core–valence correlation energy, since it is the latter that can change in chemical reactions. For example, in the Ne, HF, H_2O, NH_3, CH_4 isoelectronic series, the KK component varies by only 0.001 58 hartree, whereas the KL component varies by 0.012 71 hartree (Table VIII). It is therefore important to note that we cannot obtain accurate KL effects without using specific KL, core–valence basis functions, with exponents intermediate in size between the large exponent core functions and the small exponent valence functions.

Calculations such as those in Table VIII will provide us with accurate valence-shell correlation energies for comparison with more approximate calculations, and a more complete analysis of these results will provide a basis for detailed estimates of the errors in such approximations as order-by-order MBPT expansions of the correlation energy using complete basis sets. For example, the $CBS^{(2)}$ correlation energy (Table V) varies from as little as 81.9% of the total correlation energy in the beryllium atom with its ($2s,2p$) near degeneracy, to as much as 99.2% of the total correlation energy in the neon atom where the higher-order pair contributions are almost completely canceled by positive pair-coupling contributions. It is clearly necessary to include higher-order contributions to obtain reliable results for molecules with low-lying excited states. However, the results in Table VI suggest that the $CBS^{(\infty,3)}$ extrapolation of the higher-order contributions converges more rapidly with basis set than the $CBS^{(2)}$ contributions in Table V. The rms relative error in the total correlation energies calculated with the smallest, $\{KK,LL\}$ basis sets, is 3.04% (Table VII). This is reduced to 1.37% with the $\{KK,KL,LL\}$ basis sets and 0.58% with the $\{KK,KL,LL,LL'\}$ basis sets. A hybrid method using the smallest, $\{KK,LL\}$ basis sets, to calculate the higher-order contributions (Table VI) and the largest, $\{KK,KL,LL,LL'\}$ basis sets to calculate the $CBS^{(2)}$ contributions (Table V) gives a rms relative error of 0.73%. Hence, virtually all of the improvement from using a larger basis set occurs in second order and the hybrid method can substantially reduce computer time without significantly affecting the results. Such an analysis is at present tentative, since the critical question is how much truncation of the basis set affects the chemistry, and we must examine more examples to answer this question.

V. CONCLUSIONS

We appear to have met our design goal of developing a model chemistry for which the errors satisfy the inequality in Eq. (1). Now we must expand the range of test cases to firmly establish the limitations of the method and provide a data base to quantitatively measure the accuracy of less expensive calculations using smaller basis sets and incorporating such simplifications as the frozen-core approximation. Additional systems currently being studied include the homonuclear diatomics which provide examples of multiple bonds (N_2), valence shell lone-pair lone-pair repulsions (F_2), and weak van der Waals interactions (Be_2). We shall also determine complete $CBS^{(\infty,3)}$ potential energy curves to establish the accuracy of the method for studies of chemical reactions and solvation.

APPENDIX: APNO BASIS SETS

Although there are many studies of basis sets in the literature, the rules are somewhat different for CBS calculations. We must describe the low-lying MPNOs accurately if the CBS extrapolation is to succeed. Whether we include parts of the higher MPNOs will have no effect on our results, since we truncate the MPNO expansion before extrapolating. We have therefore developed a series of contracted Gaussian type orbital (CGTO) basis sets that are specifically designed for CBS extrapolations. It is important to have a well defined series of basis sets available, since the safest approach to any problem is to continue to improve the basis set until the property of interest has converged. The convergence of the CBS correlation energy with this series of CGTO basis sets is illustrated in Table XI for the neon atom. The neon atom is a good example to examine in detail, since Jankowski and Malinowski have determined the individual second-order pair energies to within 0.000 01 hartree.[51]

Our design goal for these basis sets was an accuracy of 0.0001 hartree for each PNO, including the occupied SCF orbitals. We began with the optimized primitive Gaussian basis sets of Van Duijneveldt.[25] For each atom from H through Ne, the minimum number of primitive Gaussians that would meet our design goal for the atomic SCF energy was selected. We then added polarization primitives with exponents that were optimized for the intraorbital pair energies. The minimum number of these functions that would meet our design goal for the pair energies was selected, and the basis set was contracted to include only the intraorbital APNO's in Table I. This gives a small CGTO basis set that nevertheless includes the energetically most important APNO's. For example, for neon we arrived at a $(13s8p3d)/[4s3p1d]$ CGTO basis set which gave the first row of results in Table XI.

The CBS extrapolation of the second-order pair energies using the $[4s3p1d]$ basis set recovers over 96% of every intraorbital pair energy, but less than 50% of the $(1s,2p)$ α,β-interorbital pair energy (Table XII). The underestimation of interorbital pair energies with this basis set results in a total CBS correlation energy that is only 95% of the experimental value (Table XI). Addition of a single p primitive and a single d primitive with exponents optimized for the $(1s,2p)$ pairs gives a $(13s8p4d)/[4s4p2d]$ CGTO basis set for which the largest error in a CBS extrapolated pair energy is 0.0006 hartree (Table XII), which is only slightly larger than our design goal of 0.0001 hartree for each PNO or 0.0005 hartree for each pair energy. The total CBS correlation energy obtained with this basis set is 98.5% of the experimental value (Table XI). This error can be further reduced by addition of s, p, d, and f primitives (Tables XI and XII), but such a large basis set is impractical for studies of polyatomic molecules. In fact, the need for f functions is

TABLE XI. Basis set convergence of the total correlation energy (in mhartree) for the neon atom.

Basis set	Method		
	Direct $E^{(2)}$	CBS$^{(2)}$	CBS$^{(\infty,3)}$
$(13s8p3d)/[4s3p1d]$	-261.96	-365.84	-370.10
$(13s8p4d)/[4s4p2d]$	-287.67	-380.33	-383.83
$(13s8p4d)/[4s5p3d]$	-305.65	-382.44	-385.36
$(13s8p4d\,2f)/[5s6p4d\,2f]$	-343.83	-386.38	-389.78
$l<9$[a]	-387.9 ± 0.1	-387.9 ± 0.1	$\cdots$
Experiment	$\cdots$	$\cdots$	-389.6 ± 1.0

[a] Reference 51.

TABLE XII. Extrapolated CBS second-order pair correlation energies (in mhartree) for neon.

Spin	Basis set	Pair						
		$1s^2$	$2s^2$	$2p_x^2$	$1s,2s$	$1s,2p$	$2s,2p$	$2p_x,2p_y$
$\alpha\beta$	$4s3p1d$	-40.28	-11.64	-26.26	-2.01	-0.95	-10.50	-13.49
	$4s4p2d$	-40.15	-11.91	-26.32	-2.06	-1.87	-10.94	-13.55
	$4s5p3d$	-40.12	-12.00	-26.33	-2.09	-1.93	-11.27	-13.41
	$5s6p4d\,2f$	-40.12	-12.02	-26.51	-2.12	-1.95	-11.55	-13.49
	$l<9$[a]	-40.22	-12.02	-26.90	-2.25	-2.14	-11.55	-13.64
$\alpha\alpha$	$4s3p1d$				-0.40	-0.99	-2.72	-9.74
	$4s4p2d$				-0.54	-1.56	-2.95	-9.82
	$4s5p3d$				-0.58	-1.61	-3.00	-9.78
	$5s6p4d\,2f$				-0.60	-1.63	-3.16	-9.78
	$l<9$[a]				-0.53	-1.56	-2.98	-9.71

[a] Reference 51.

precisely what the CBS method is designed to avoid. A reasonable compromise is instead to add one additional primitive which is the smallest exponent of the highest occupied SCF orbital and one additional primitive which is the smallest exponent of the valence shell polarization function. This provides flexibility in the valence shell for the formation of molecules and complexes without a major increase in computer time over the [$4s4p2d$] basis set.

Comparison of the second-order correlation energies obtained with this series of basis sets provides an unambiguous measure of the ability of CBS extrapolations to accelerate the convergence of basis set expansions (Table XI). The ratio of the CBS$^{(2)}$ error to the direct $E^{(2)}$ error decreases as the basis set increases. This is to be expected, since the CBS extrapolations are asymptotically correct as the basis set becomes complete. However, examination of the convergence of the individual pair energies in Table XII reveals that the improvement over the smallest, [$4s3p1d$] basis set, that is obtained with the [$4s4p2d$] basis set is primarily found in the ($1s,2p$) pair energies, and the further improvement obtained with the [$4s5p3d$] basis set is mainly in the ($2s,2p$) pair energies. We can therefore designate these basis sets as {KK,LL}, {KK,KL,LL}, and {KK,KL,LL,LL'} respectively. They are all DZ + P APNO in the sense that they provide for one radial and three Cartesian directions of correlation for each pair of occupied SCF orbitals that is indicated by the name. For example, the DZ + P {KK,LL} APNO basis set is DZ + P for both the ($1s,1s$) pair and the valence shell intraorbital pair energies.

Although the larger basis sets are only useful for benchmark test cases, we plan extensive applications of the smaller basis sets. It is therefore important to construct them in an efficient way. Expansion of each APNO using all primitives of appropriate symmetry would be straightforward, but result in excessively large computation times for polyatomic molecules. At the other extreme, disjoint contractions in which each Gaussian primitive is used in only one contracted Gaussian type orbital (CGTO) are very efficient for integral evaluation, but cannot achieve the level of accuracy we seek without a substantial increase in the number of con-
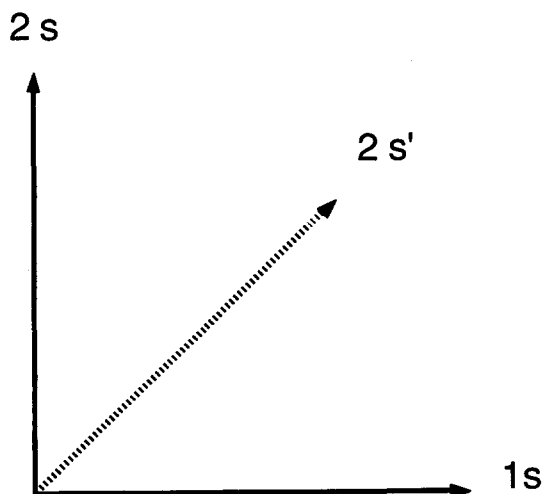
FIG. 6. Contraction of the 2s' APNO.

TABLE XIII. Double zeta plus polarization basis set for the hydrogen atom.

H
6330
1

1S S6 1.00	
0.8263637400E + 02	0.2006000000E − 02
0.1240955800E + 02	0.1534500000E − 01
0.2823854000E + 01	0.7557700000E − 01
0.7976700000E + 00	0.2569220000E + 00
0.2580530000E + 00	0.4973790000E + 00
0.8989100000E − 01	0.2960700000E + 00

2S' S3 1.00	
0.7976700000E + 00	0.2442926000E + 00
0.2580530000E + 00	− 0.7684522000E + 00
0.8989100000E − 01	− 0.3923966000E + 00

2P' P3 1.00		
0.1848000000E + 01	0.0000000000E + 00	0.7208160000E − 01
0.7056000000E + 00	0.0000000000E + 00	0.3202558000E + 00
0.2720000000E + 00	0.0000000000E + 00	0.2246452000E + 00

Hydrogen negative ion
7449
1

1S S7 1.00	
0.8263637400E + 02	0.1413409000E − 02
0.1240955800E + 02	0.1090111800E − 01
0.2823854000E + 01	0.5143712600E − 01
0.7976700000E + 00	0.1672287900E + 00
0.2580530000E + 00	0.2772890200E + 00
0.8989100000E − 01	0.3537735600E + 00
0.2000000000E − 01	0.3877925300E + 00

2S' S4 1.00	
0.7976700000E + 00	0.7468018300E − 01
0.2580530000E + 00	0.1825695200E + 00
0.8989100000E − 01	− 0.7133159300E + 00
0.2000000000E − 01	− 0.1348413000E + 01

2P' P4 1.00		
0.1848000000E + 01	0.0000000000E + 00	0.2802707300E − 01
0.7056000000E + 00	0.0000000000E + 00	0.1207351400E + 00
0.2720000000E + 00	0.0000000000E + 00	0.4940790300E + 00
0.8710000000E − 01	0.0000000000E + 00	0.5044991700E + 00

TABLE XIV. Double zeta plus polarization basis set for the helium atom.

He
8330
1

1S S8 1.00	
0.1149270536E + 04	0.3583000000E − 03
0.1720445690E + 03	0.2779500000E − 02
0.3908046500E + 02	0.1430850000E − 01
0.1103617300E + 02	0.5601700000E − 01
0.3564152000E + 01	0.1634618000E + 00
0.1240443000E + 01	0.3324932000E + 00
0.4473160000E + 00	0.4166511000E + 00
0.1642060000E + 00	0.1877220000E + 00

2S' S3 1.00	
0.3564152000E + 01	− 0.2186853500E + 00
0.4473160000E + 00	0.1398736400E + 01
0.1642060000E + 00	0.8025910000E + 00

2P' P3 1.00		
0.4982992000E + 01	0.0000000000E + 00	0.1429287100E + 00
0.1350244000E + 01	0.0000000000E + 00	0.6907588200E + 00
0.3823840000E + 00	0.0000000000E + 00	0.3108120500E + 00

TABLE XV. Double zeta plus polarization basis set for the lithium atom.

Li
822313111110
1
1*S S* 8 1.00

$0.2072040929E + 04$	$0.4990000000E - 03$
$0.3110337170E + 03$	$0.3842000000E - 02$
$0.7121536500E + 02$	$0.1939200000E - 01$
$0.2047780600E + 02$	$0.7220600000E - 01$
$0.6843695000E + 01$	$0.1944470000E + 00$
$0.2533132000E + 01$	$0.3545300000E + 00$
$0.1023091000E + 01$	$0.3675980000E + 00$
$0.4366880000E + 01$	$0.1470870000E + 00$

2*S S* 2 1.00

$0.1023091000E + 01$	$- 0.5028300100E - 01$
$0.4366880000E + 00$	$- 0.6492685800E - 01$

3*S'' S* 2 1.00

$0.7643800000E - 01$	$0.5490419400E + 00$
$0.2892700000E - 01$	$0.5494853600E + 00$

2*S' S* 3 1.00

$0.2533132000E + 01$	$0.4393963600E + 00$
$0.1023091000E + 01$	$0.1947637800E + 01$
$0.4366880000E + 00$	$0.7222343400E + 00$

4*S'' S* 1 1.00

$0.1827000000E + 00$	$0.1000000000E + 01$

2*P' P* 3 1.00

$0.1400000000E + 02$	$0.0000000000E + 00$	$0.1075725300E + 00$
$0.4080000000E + 01$	$0.0000000000E + 00$	$0.5691751400E + 00$
$0.1400000000E + 01$	$0.0000000000E + 00$	$0.4474109900E + 00$

2*P'' P* 1 1.00

$0.1615490000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

3*P'' P* 1 1.00

$0.6228300000E - 01$	$0.0000000000E + 00$	$0.1000000000E + 01$

4*P'' P* 1 1.00

$0.4500000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

3*D'' D* 1 1.00

$0.1435610000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

4*D'' D* 1 1.00

$0.3758540000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

tracted basis functions. A systematic compromise was developed based on the fact that it is not necessary to actually use APNO's as basis functions, but only to use a contracted basis set that contains the APNOs to the prescribed level of accuracy:

$$\varphi_j^{\mathrm{APNO}} \approx \mathbf{U}_j \cdot \varphi^{\mathrm{CGTO}}, \tag{A1}$$

where

$$|\langle \varphi_j^{\mathrm{APNO}} | \hat{\mathbf{f}}_j | \varphi_j^{\mathrm{APNO}} \rangle - \langle \mathbf{U}_j \cdot \varphi^{\mathrm{CGTO}} | \hat{\mathbf{f}}_j | \mathbf{U}_j \cdot \varphi^{\mathrm{CGTO}} \rangle |$$
$$\leqslant 0.0001 \text{ hartree.} \tag{A2}$$

If the molecular pair natural orbitals (MPNOs) are then expanded in this CGTO basis set:

$$\varphi^{\mathrm{MPNO}} = \mathbf{C} \varphi^{\mathrm{CGTO}} \tag{A3}$$

the expansion of the MPNOs in the APNOs can readily be obtained:

$$\varphi^{\mathrm{MPNO}} = \mathbf{C} \mathbf{U}^{-1} \varphi^{\mathrm{APNO}}, \tag{A4}$$

provided that the transformation **U** is nonsingular.

Starting with the 1*s* CGTO, we form a 2*s'* orbital in the 1*s*,2*s* plane, but not necessarily equal to the 2*s* AO and therefore not necessarily orthogonal to the 1*s* CGTO (Fig. 6). The number of primitive Gaussian functions used for both the 1*s* CGTO and the 2*s'* CGTO was the minimum number that could satisfy Eq. (A2). This procedure was continued for the 2*p* CGTO, the 2*s'*, the 2*p'*, etc. until each of the basis functions in the tables was determined.

The DZ + P {*KK,KL,LL*} APNO basis sets for the atoms H through Ne are given in Tables XIII through XXII in the format appropriate for input to the program, GAUSSIAN 82. The {*KK,LL*} and {*KK,KL,LL,LL '*} basis sets are readily obtained by either deleting the 4*p''* and 4*d ''* functions or adding the smallest exponent *p* and *d* Gaussian functions as primitives. Each APNO was optimized for the excitation in which it appears in boldface in Table I.

These basis sets as well as the QZ + TP SCF basis sets

TABLE XVI. Double zeta plus polarization basis set for the beryllium atom.

Be
287441351119
1

CUSP *S* 2 1.00			
$2.2631589258E + 04$	$0.0530000000E - 00$		
$0.3372318148E + 04$	$0.4180000000E - 00$		
1*S S* 8 1.00			
$0.7603584860E + 03$	$0.2227000000E - 02$		
$0.2117404760E + 03$	$0.9558000000E - 02$		
$0.6722346900E + 02$	$0.3484200000E - 01$		
$0.2337217700E + 02$	$0.1058370000E - 00$		
$0.8721373000E + 01$	$0.2460990000E - 00$		
$0.3460891000E + 01$	$0.3867760000E - 00$		
$0.1452144000E + 01$	$0.3092290000E - 00$		
$0.6086150000E + 00$	$0.6440100000E - 01$		
2*S S* 7 1.00			
$0.8721373000E + 01$	$-0.0051823000E - 00$		
$0.3460891000E + 01$	$-0.0216101000E - 00$		
$0.1452144000E + 01$	$-0.0747816000E - 00$		
$0.6086150000E + 00$	$-0.0399696000E - 00$		
$0.2576960000E + 00$	$0.2716238000E - 00$		
$0.1041760000E + 00$	$0.5822183000E - 00$		
$0.4242700000E - 01$	$0.2874280000E - 00$		
2*S' S* 4 1.00			
$0.8721373000E + 01$	$0.2796841000E + 00$		
$0.3460891000E + 01$	$-0.1313164700E + 01$		
$0.1452144000E + 01$	$-0.1434063500E + 01$		
$0.6086150000E + 00$	$-0.3475495000E + 00$		
3*S'' S* 4 1.00			
$0.3460891000E + 01$	$-0.1007309000E - 00$		
$0.1452144000E + 01$	$-0.3430305000E - 00$		
$0.2576960000E + 00$	$0.2263099400E + 01$		
$0.1041760000E + 00$	$0.8821435000E - 00$		
4*S'' S* 1 1.00			
$0.1500000000E + 01$	$0.1000000000E + 01$		
2*P' P* 3 1.00			
$0.3000000000E + 02$	$0.0000000000E + 00$	$0.9484720000E - 01$	
$0.7500000000E + 01$	$0.0000000000E + 00$	$0.6158136000E + 00$	
$0.2500000000E + 01$	$0.0000000000E + 00$	$0.4147793000E + 00$	
2*P'' P* 5 1.00			
$0.9920000000E + 01$	$0.0000000000E + 00$	$0.7435000000E - 02$	
$0.2160000000E + 01$	$0.0000000000E + 00$	$0.3200730000E - 01$	
$0.6100000000E + 00$	$0.0000000000E + 00$	$0.1817440000E - 00$	
$0.1920000000E + 00$	$0.0000000000E + 00$	$0.6287937000E - 00$	
$0.7000000000E - 01$	$0.0000000000E + 00$	$0.2992105000E - 00$	
3*P'' P* 1 1.00			
$0.1150000000E + 01$	$0.0000000000E + 00$	$0.1000000000E + 01$	
3*D'' D* 1 1.00			
$0.2025796400E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$
4*D'' D* 1 1.00			
$0.5716000000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

TABLE XVII. Double zeta plus polarization basis set for the boron atom.

B
286448331310
1

CUSP *S* 2 1.00

$0.3336021657E + 05$	$0.5800000000E - 01$
$0.4972095217E + 04$	$0.4560000000E + 00$

1*S S* 8 1.00

$0.1125641723E + 04$	$0.2409000000E - 02$
$0.3164913560E + 03$	$0.1016100000E - 01$
$0.1020072560E + 03$	$0.3609200000E - 01$
$0.3629587300E + 02$	$0.1059500000E + 00$
$0.1397141000E + 02$	$0.2395670000E + 00$
$0.5741156000E + 01$	$0.3734070000E + 00$
$0.2496268000E + 01$	$0.3079370000E + 00$
$0.1114202000E + 01$	$0.7845500000E - 01$

2*S S* 6 1.00

$0.1397141000E + 02$	$0.7032000000E - 02$
$0.5741156000E + 01$	$0.2176550000E - 01$
$0.2496268000E + 01$	$0.7660100000E - 01$
$0.4215490000E + 00$	$- 0.2888420000E + 00$
$0.1696330000E + 00$	$- 0.5260364000E + 00$
$068535000000E - 01$	$- 0.2403703000E + 00$

2*S' S* 4 1.00

$0.1397141000E + 02$	$0.2868968000E + 00$
$0.5741156000E + 01$	$- 0.1339225700E + 01$
$0.2496268000E + 01$	$- 0.1369082000E + 01$
$0.1114202000E + 01$	$- 0.5074138000E + 00$

3*S" S* 4 1.00

$0.5741156000E + 01$	$0.2324524000E + 00$
$0.2496268000E + 01$	$0.5707554000E + 00$
$0.4215490000E + 00$	$- 0.2011113000E + 01$
$0.1696330000E + 00$	$- 0.1198731800E + 01$

2*P P* 8 1.00

$0.5500000000E + 02$	$0.0000000000E + 00$	$0.1124000000E - 02$
$0.1336610100E + 02$	$0.0000000000E + 00$	$0.8162000000E - 02$
$0.4135394000E + 01$	$0.0000000000E + 00$	$0.3598300000E - 01$
$0.1481256000E + 01$	$0.0000000000E + 00$	$0.1115140000E + 00$
$0.6021360000E + 00$	$0.0000000000E + 00$	$0.2455830000E + 00$
$0.2556340000E + 00$	$0.0000000000E + 00$	$0.3710130000E + 00$
$0.1111510000E + 00$	$0.0000000000E + 00$	$0.3404030000E + 00$
$0.4764800000E - 01$	$0.0000000000E + 00$	$0.1213950000E + 00$

2*P' P* 3 1.00

$0.5500000000E + 02$	$0.0000000000E + 00$	$0.7519750000E - 01$
$0.1336610100E + 02$	$0.0000000000E + 00$	$0.6228454000E + 00$
$0.4135394000E + 01$	$0.0000000000E + 00$	$0.4546343000E + 00$

3*P" P* 3 1.00

$0.2556340000E + 00$	$0.0000000000E + 00$	$0.4069872000E + 00$
$0.1111510000E + 00$	$0.0000000000E + 00$	$0.1299967600E + 01$
$0.4764800000E - 01$	$0.0000000000E + 00$	$0.6263062000E + 00$

4*P" P* 1 1.00

$0.6021360000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

3*D" D* 3 1.00

$0.1139250000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1146185000E + 00$
$0.4134380000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.6032253000E + 00$
$0.1696030000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.5559864000E + 00$

4*D" D* 1 1.00

$0.2778000000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

TABLE XVIII. Double zeta plus polarization basis set for the carbon atom.

C			
286448331310			
1			
CUSP S 2 1.00			
$0.5055750067E + 05$	$0.5500000000E + 00$		
$0.7524785601E + 04$	$0.4340000000E + 01$		
1S S 8 1.00			
$0.1694327599E + 04$	$0.2316000000E - 02$		
$0.4728227890E + 03$	$0.9872000000E - 02$		
$0.1517107520E + 03$	$0.3521700000E - 01$		
$0.5391874600E + 02$	$0.1041840000E + 00$		
$0.2065931100E + 02$	$0.2412550000E + 00$		
$0.8383976000E + 01$	$0.3839290000E + 00$		
$0.3577015000E + 01$	$0.3082190000E + 00$		
$0.1547118000E + 01$	$0.6852700000E - 01$		
2S S 6 1.00			
$0.2065931100E + 02$	$0.7366300000E - 02$		
$0.8383976000E + 01$	$0.2793400000E - 01$		
$0.3577015000E + 01$	$0.8429620000E - 01$		
$0.6130130000E + 00$	$- 0.3652309000E + 00$		
$0.2460680000E + 00$	$- 0.5565053000E + 00$		
$0.9908700000E - 01$	$- 0.2123800000E + 00$		
2S' S 4 1.00			
$0.2065931100E + 02$	$0.2830128000E + 00$		
$0.8383976000E + 01$	$- 0.1399510100E + 01$		
$0.3577015000E + 01$	$- 0.1418703200E + 01$		
$0.1547118000E + 01$	$- 0.0275905000E + 00$		
3S'' S 4 1.00			
$0.8383976000E + 01$	$0.2590898000E + 00$		
$0.3577015000E + 01$	$0.6268001000E + 00$		
$0.6130130000E + 00$	$- 0.2302777000E + 01$		
$0.2460680000E + 00$	$- 0.1602082200E + 01$		
2P P 8 1.00			
$0.8333315500E + 02$	$0.0000000000E + 00$	$0.1254000000E - 02$	
$0.1955761100E + 02$	$0.0000000000E + 00$	$0.9640000000E - 02$	
$0.6080365000E + 01$	$0.0000000000E + 00$	$0.4287300000E - 01$	
$0.2179317000E + 01$	$0.0000000000E + 00$	$0.1351080000E + 00$	
$0.8651500000E + 00$	$0.0000000000E + 00$	$0.2822960000E + 00$	
$0.3619440000E + 00$	$0.0000000000E + 00$	$0.3801440000E + 00$	
$0.1547400000E + 00$	$0.0000000000E + 00$	$0.3049210000E + 00$	
$0.6542900000E - 01$	$0.0000000000E + 00$	$0.8720800000E - 01$	
2P' P 3 1.00			
$0.8333315500E + 02$	$0.0000000000E + 00$	$0.7439130000E - 01$	
$0.1955761100E + 02$	$0.0000000000E + 00$	$0.6342891000E - 00$	
$0.6080365000E + 01$	$0.0000000000E + 00$	$0.4482495000E - 00$	
3P'' P 3 1.00			
$0.3619440000E + 00$	$0.0000000000E + 00$	$0.4605295000E + 00$	
$0.1547400000E + 00$	$0.0000000000E + 00$	$0.1635004500E + 01$	
$0.6542900000E - 01$	$0.0000000000E + 00$	$0.1418009000E + 00$	
4P'' P 1 1.00			
$0.8651500000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$	
3D'' D 3 1.00			
$0.1550000000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.2138883000E + 00$
$0.5625000000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.7733625000E + 00$
$0.2307520000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1071692000E + 00$
4D'' D 1 1.00			
$0.3780000000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

TABLE XIX. Double zeta plus polarization basis set for the nitrogen atom.

N
287448331310
1

CUSP S 2 1.00

$0.7476171511E + 05$	$0.5000000000E - 01$
$0.1112365381E + 05$	$0.3940000000E + 00$

$1S$ S 8 1.00

$0.2512685697E + 04$	$0.2088000000E - 02$
$0.7037772850E + 03$	$0.8906000000E - 02$
$0.2254787930E + 03$	$0.3208100000E - 01$
$0.7961581000E + 02$	$0.9742400000E - 01$
$0.3023728300E + 02$	$0.2317280000E + 00$
$0.1226362200E + 02$	$0.3775400000E + 00$
$0.5265086000E + 01$	$0.3186230000E + 00$
$0.2333471000E + 01$	$0.8257800000E - 01$

$2S$ S 7 1.00

$0.3023728300E + 02$	$0.6720200000E - 02$
$0.1226362200E + 02$	$0.2775370000E - 01$
$0.5265086000E + 01$	$0.7955420000E - 01$
$0.2333471000E + 01$	$0.7646100000E - 02$
$0.9018560000E + 00$	$- 0.3547078000E + 00$
$0.3583360000E + 00$	$- 0.5289566000E + 00$
$0.1410930000E + 00$	$- 0.2188159000E + 00$

$2S'$ S 4 1.00

$0.3023728300E + 02$	$0.3129792000E + 00$
$0.1226362200E + 02$	$- 0.1278886500E + 01$
$0.5265086000E + 01$	$- 0.1446746800E + 01$
$0.2333471000E + 01$	$- 0.5130825000E + 00$

$3S''$ S 4 1.00

$0.1226362200E + 02$	$- 0.2470182000E + 00$
$0.5265086000E + 01$	$- 0.6414619000E + 00$
$0.9018560000E + 00$	$0.2412430900E + 01$
$0.3583360000E + 00$	$0.1360799400E + 01$

$2P$ P 8 1.00

$0.1266665670E + 03$	$0.0000000000E + 00$	$0.1152000000E - 02$
$0.2983738900E + 02$	$0.0000000000E + 00$	$0.9016000000E - 02$
$0.9394038000E + 01$	$0.0000000000E + 00$	$0.4081400000E - 01$
$0.3405104000E + 01$	$0.0000000000E + 00$	$0.1301010000E + 00$
$0.1350000000E + 01$	$0.0000000000E + 00$	$0.2776970000E + 00$
$0.5576960000E + 00$	$0.0000000000E + 00$	$0.3807360000E + 00$
$0.2324490000E + 00$	$0.0000000000E + 00$	$0.3149660000E + 00$
$0.9426400000E - 01$	$0.0000000000E + 00$	$0.9449800000E - 01$

$2P'$ P 3 1.00

$0.1266665670E + 03$	$0.0000000000E + 00$	$0.5900340000E - 01$
$0.2983738900E + 02$	$0.0000000000E + 00$	$0.5793235000E + 00$
$0.9394038000E + 01$	$0.0000000000E + 00$	$0.5141121000E + 00$

$3P''$ P 3 1.00

$0.5576960000E + 00$	$0.0000000000E + 00$	$0.5137303000E + 00$
$0.2324490000E + 00$	$0.0000000000E + 00$	$0.1215746300E + 01$
$0.9426400000E - 01$	$0.0000000000E + 00$	$0.5080717000E + 00$

$4P''$ P 1 1.00

$0.1350000000E + 01$	$0.0000000000E + 00$	$0.1000000000E + 01$

$3D''$ D 3 1.00

$0.2411111000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1746983000E + 00$
$0.8750000000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.6206678000E + 00$
$0.3589440000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.3956690000E + 00$

$4D''$ D 1 1.00

$0.5880000000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

TABLE XX. Double zeta plus polarization basis set for the oxygen atom.

O
286448331310
1

CUPS *S* 2 1.00			
$0.1053749453E + 06$	$0.4590000000E - 01$		
$0.1567924033E + 05$	$0.3607000000E + 00$		
1*S S* 8 1.00			
$0.3534544676E + 04$	$0.1919600000E - 02$		
$0.9873651600E + 03$	$0.8206000000E - 02$		
$0.3159787520E + 03$	$0.2972500000E - 01$		
$0.1116542810E + 03$	$0.9045200000E - 01$		
$0.4269945100E + 02$	$0.2174020000E + 00$		
$0.1739559600E + 02$	$0.3687200000E + 00$		
$0.7438309000E + 01$	$0.3372770000E + 00$		
$0.3222862000E + 01$	$0.9680800000E - 01$		
2*S S* 6 1.00			
$0.4269945100E + 02$	$- 0.7105000000E - 02$		
$0.1739559600E + 02$	$- 0.2313500000E - 01$		
$0.7438309000E + 01$	$- 0.8931500000E - 01$		
$0.1253877000E + 01$	$0.3414650000E + 00$		
$0.4951550000E + 00$	$0.5655150000E + 00$		
$0.1916650000E + 00$	$0.2305500000E + 00$		
2*S' S* 4 1.00			
$0.4269945100E + 02$	$- 0.3402461000E + 00$		
$0.1739559600E + 02$	$0.1129588900E + 01$		
$0.7438309000E + 01$	$0.1515109000E + 01$		
$0.3222862000E + 01$	$0.5982731000E + 00$		
3*S'' S* 4 1.00			
$0.7438309000E + 01$	$- 0.2836830000E + 00$		
$0.3222862000E + 01$	$0.2547639000E + 00$		
$0.1253877000E + 01$	$0.2507299300E + 01$		
$0.4951550000E + 00$	$0.8819984000E + 00$		
2*P P* 8 1.00			
$0.2000000000E + 03$	$0.0000000000E + 00$	$0.8920000000E - 03$	
$0.4653336700E + 02$	$0.0000000000E + 00$	$0.7351000000E - 02$	
$0.1462180900E + 02$	$0.0000000000E + 00$	$0.3486300000E - 01$	
$0.5313064000E + 01$	$0.0000000000E + 00$	$0.1148770000E + 00$	
$0.2102525000E + 01$	$0.0000000000E + 00$	$0.2559830000E + 00$	
$0.8502230000E + 00$	$0.0000000000E + 00$	$0.3742360000E + 00$	
$0.3375970000E + 00$	$0.0000000000E + 00$	$0.3440420000E + 00$	
$0.1288920000E + 00$	$0.0000000000E + 00$	$0.1302970000E + 00$	
2*P' P* 3 1.00			
$0.2000000000E + 03$	$0.0000000000E + 00$	$0.3809830000E - 01$	
$0.4653336700E + 02$	$0.0000000000E + 00$	$0.4802138000E + 00$	
$0.1462180900E + 02$	$0.0000000000E + 00$	$0.6093604000E + 00$	
3*P'' P* 3 1.00			
$0.8502230000E + 00$	$0.0000000000E + 00$	$0.3808123000E + 00$	
$0.3375970000E + 00$	$0.0000000000E + 00$	$0.1261123900E + 01$	
$0.1288920000E + 00$	$0.0000000000E + 00$	$0.6115835000E + 00$	
4*P'' P* 1 1.00			
$0.2102525000E + 01$	$0.0000000000E + 00$	$0.1000000000E + 01$	
3*D'' D* 3 1.00			
$0.3424300000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.2023154000E + 00$
$0.1210000000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.7092042000E + 00$
$0.4620000000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.3939832000E + 00$
4*D'' D* 1 1.00			
$0.8470000000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$1.0000000000E + 00$

TABLE XXI. Double zeta plus polarization basis set for the fluorine atom.

F			
287448331310			
1			
CUSP S 2 1.00			
$0.1031094642E + 06$	$0.6400000000E - 02$		
$0.1528100672E + 05$	$0.5030000000E - 01$		
1S S 8 1.00			
$0.3441539198E + 04$	$0.2668000000E - 02$		
$0.9670948300E + 03$	$0.1120000000E - 01$		
$0.3140353380E + 03$	$0.3909700000E - 01$		
$0.1134422960E + 03$	$0.1122630000E + 00$		
$0.4464472700E + 02$	$0.2471990000E + 00$		
$0.1894287400E + 02$	$0.3680040000E + 00$		
$0.8532743000E + 01$	$0.2908640000E + 00$		
$0.3919401000E + 01$	$0.7816500000E - 01$		
2S S 7 1.00			
$0.4464472700E + 02$	$0.9566200000E - 02$		
$0.1894287400E + 02$	$0.3153070000E - 01$		
$0.8532743000E + 01$	$0.8295300000E - 01$		
$0.3919401000E + 01$	$- 0.2124730000E - 01$		
$0.1568157000E + 01$	$- 0.3601384000E + 00$		
$0.6232900000E + 00$	$- 0.5214862000E + 00$		
$0.2408610000E + 00$	$- 0.2151514000E + 00$		
2S' S 4 1.00			
$0.4464472700E + 02$	$0.2626626000E + 00$		
$0.1894287400E + 02$	$- 0.1541765200E + 01$		
$0.8532743000E + 01$	$- 0.1269559000E + 01$		
$0.3919401000E + 01$	$- 0.5661412000E + 01$		
3S'' S 4 1.00			
$0.1894287400E + 02$	$- 0.4059084000E + 00$		
$0.8532743000E + 01$	$- 0.9040563000E + 00$		
$0.1568157000E + 01$	$0.2594556900E + 01$		
$0.6232900000E + 00$	$0.1980563200E + 00$		
2P P 8 1.00			
$0.2453302870E + 03$	$0.0000000000E + 00$	$0.9850000000E - 03$	
$0.5691900500E + 02$	$0.0000000000E + 00$	$0.8257000000E - 02$	
$0.1760456800E + 02$	$0.0000000000E + 00$	$0.4061100000E - 01$	
$0.6274995000E + 01$	$0.0000000000E + 00$	$0.1344250000E + 00$	
$0.2447030000E + 01$	$0.0000000000E + 00$	$0.2788670000E + 00$	
$0.9950600000E + 00$	$0.0000000000E + 00$	$0.3649280000E + 00$	
$0.4039730000E + 00$	$0.0000000000E + 00$	$0.3187010000E + 00$	
$0.1548100000E + 00$	$0.0000000000E + 00$	$0.1234750000E + 00$	
2P' P 3 1.00			
$0.2453302870E + 03$	$0.0000000000E + 00$	$0.4186640000E - 01$	
$0.5691900500E + 02$	$0.0000000000E + 00$	$0.5166282000E + 00$	
$0.1760456800E + 02$	$0.0000000000E + 00$	$0.5882624000E + 00$	
3P'' P 3 1.00			
$0.9950600000E + 00$	$0.0000000000E + 00$	$0.5182824000E + 00$	
$0.4039730000E + 00$	$0.0000000000E + 00$	$0.1230326000E + 01$	
$0.1548100000E + 00$	$0.0000000000E + 00$	$0.5399739000E + 00$	
4P'' P 1 1.00			
$0.2447030000E + 01$	$0.0000000000E + 00$	$0.1000000000E + 01$	
3D'' D 3 1.00			
$0.4146426000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1816708000E + 00$
$0.1658571000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.4739219000E + 00$
$0.6910720000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.3951536000E + 00$
4D'' D 1 1.00			
$0.9950000000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

TABLE XXII. Double zeta plus polarization basis set for the neon atom.

Ne
286448331319
1

CUSP S 2 1.00			
$0.1661650806E + 06$	$0.4700000000E - 01$		
$0.2310752423E + 05$	$0.4010000000E + 00$		
1S S 8 1.00			
$0.5060153856E + 04$	$0.2193000000E - 02$		
$0.1384612313E + 04$	$0.9588000000E - 02$		
$0.4365125760E + 03$	$0.3507400000E - 01$		
$0.1534714760E + 03$	$0.1046520000E + 00$		
$0.5938908700E + 02$	$0.2377160000E + 00$		
$0.2486196700E + 02$	$0.3696030000E + 00$		
$0.1101570400E + 02$	$0.3061760000E + 00$		
$0.4965175000E + 01$	$0.8418000000E - 01$		
2S S 6 1.00			
$0.5938908700E + 02$	$0.7736200000E - 02$		
$0.2486196700E + 02$	$0.3408820000E - 01$		
$0.1101570400E + 02$	$0.7595410000E - 01$		
$0.1936503000E + 01$	$- 0.3934813000E + 00$		
$0.7657280000E + 00$	$- 0.5374908000E + 00$		
$0.2955380000E + 00$	$- 0.2109040000E + 00$		
2S' S 4 1.00			
$0.5938908700E + 02$	$0.2899956000E + 00$		
$0.2486196700E + 02$	$- 0.1377763800E + 01$		
$0.1101570400E + 02$	$- 0.1494484900E + 01$		
$0.4965175000E + 01$	$- 0.5452027000E + 00$		
3S'' S 4 1.00			
$0.2486196700E + 02$	$0.3216765000E + 00$		
$0.1101570400E + 02$	$0.8413431000E + 00$		
$0.1936503000E + 01$	$- 0.2679910800E + 01$		
$0.7657280000E + 00$	$- 0.1722005400E + 01$		
2P P 8 1.00			
$0.2349450000E + 03$	$0.0000000000E + 00$	$0.1575000000E - 02$	
$0.5507738500E + 02$	$0.0000000000E + 00$	$0.1249600000E - 01$	
$0.1738954900E + 02$	$0.0000000000E + 00$	$0.5665000000E - 01$	
$0.6389537000E + 01$	$0.0000000000E + 00$	$0.1664550000E + 00$	
$0.2542082000E + 01$	$0.0000000000E + 00$	$0.3063630000E + 00$	
$0.1033764000E + 01$	$0.0000000000E + 00$	$0.3654580000E + 00$	
$0.4187880000E + 00$	$0.0000000000E + 00$	$0.2780540000E + 00$	
$0.1646270000E + 00$	$0.0000000000E + 00$	$0.8817200000E - 01$	
2P' P 3 1.00			
$0.2349450000E + 03$	$0.0000000000E + 00$	$0.8057140000E - 01$	
$0.5507738500E + 02$	$0.0000000000E + 00$	$0.6452554000E + 00$	
$0.1738954900E + 02$	$0.0000000000E + 00$	$0.4367269000E + 00$	
3P'' P 3 1.00			
$0.1033764000E + 01$	$0.0000000000E + 00$	$0.7643508000E + 00$	
$0.4187880000E + 00$	$0.0000000000E + 00$	$0.1111486500E + 01$	
$0.1646270000E + 00$	$0.0000000000E + 00$	$0.3756675000E + 00$	
3P'' P 1 1.00			
$0.2542082000E + 01$	$0.0000000000E + 00$	$0.1000000000E + 01$	
3D'' D 3 1.00			
$0.5250000000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.2464363000E + 00$
$0.2100000000E + 01$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.6254835000E + 00$
$0.8750000000E + 00$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.4728295000E + 00$
4D'' D 1 1.00			
$0.1202712000E + 02$	$0.0000000000E + 00$	$0.0000000000E + 00$	$0.1000000000E + 01$

can be obtained as files readable by GAUSSIAN 82 by connecting to our MicroVAX at (203)344-7941 at 1200 baud, Username: APNO, Password: Basis_Sets, and using Kermit to transfer the files.

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