Correlation energy extrapolation by intrinsic scaling. IV. Accurate binding energies of the homonuclear diatomic molecules carbon, nitrogen, oxygen, and fluorine

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Additional information on J. Chem. Phys.

Correlation energy extrapolation by intrinsic scaling. IV. Accurate binding energies of the homonuclear diatomic molecules carbon, nitrogen, oxygen, and fluorine

Laimutis Bytautas[a)] and Klaus Ruedenberg
Department of Chemistry and Ames Laboratory USDOE, Iowa State University, Ames, Iowa 50011

The method of *extrapolation by intrinsic scaling*, recently introduced to obtain correlation energies, is generalized to multiconfigurational reference functions and used to calculate the binding energies of the diatomic molecules C_2, N_2, O_2, and F_2. First, accurate approximations to the full configuration interaction energies of the individual molecules and their constituent atoms are determined, employing Dunning's correlation consistent double-, triple- and quadruple ζ basis sets. Then, these energies are extrapolated to their full basis set limits. Chemical accuracy is attained for the binding energies of all molecules. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1869493]

I. INTRODUCTION

Approaching the exact solution of the electronic Schrödinger equation[1] in molecules with as low a computational cost as possible remains a challenge for current work in quantum chemistry.

Early on, Hylleraas[2] pioneered the construction of accurate compact wave functions through the explicit inclusion of the internuclear distance r_{12}. Later developments along these lines have been the transcorrelated wave functions of Boys and Handy,[3–9] the Gaussian geminal methods by a number of authors,[10–12] and the linear R12 method of Kutzelnigg and Klopper.[13,14] While high accuracy has been achieved by the latter method, in particular in conjunction with coupled-cluster[15–18] and multireference configuration interaction (CI) approaches,[19–21] the computational costs are still high.

Without the help of the complicating r_{12} terms, i.e., by using only orbital-based configurations, the attainment of chemical accuracy encounters computational limitations due to the excessive lengths of the CI expansions in the full configuration spaces of the necessary basis sets. Therefore, efficient configuration-based treatments as well as effective extrapolations to the full basis set limit are needed. A number of developments have led to substantial progress in treating the full CI problem.[22,23] Fundamental recastings of the configuration-based approach have been introduced by the coupled-cluster methods,[24] in the density matrix renormalization group approach,[25] and in variational density matrix theory.[26] Of these, the coupled-cluster approach has proven to be very effective and has found wide use. On the other hand, considerable success has been achieved with regard to the methods for extrapolating to the complete basis set (CBS) limit.[27–38]

An approach towards theoretical predictions of molecular properties with chemical accuracy at *moderate* computational cost is that of the model chemistries. These methods combine *ab initio* electronic structure methods with the introduction of certain judiciously chosen adjustable parameters, which are then determined by minimizing the errors in the atomization energies, ionization potentials, etc., for selected large training sets of molecular systems. Examples are the GN methods of Pople and co-workers,[39,40] the CBS suite of methods by Petersson and co-workers[41,42] and the WN theories of Martin and co-workers.[43,44] The marked successes of the model chemistry methods notwithstanding however, work on rigorous parameterless electronic structure methods remains important. Even systematic improvements of model chemistry descriptions are dependent upon benchmark-quality *ab initio* results.

By virtue of their variational character, full configuration interaction (FCI) calculations[45] furnish results that can serve as *ab initio* benchmarks. The problem is, as mentioned above, that they suffer from the need for excessively long configurational expansions. Even with the progress achieved in Refs. 22–26, problems remain, notably when the zeroth-order reference function has multiconfigurational character, as is often the case for instance along reaction paths. A number of authors have therefore explored yet another path towards reducing the computational effort, namely, the use of suitable extrapolation procedures to approximate the FCI energy for a given basis[46–51] within chemical accuracy.

A new extrapolation method for obtaining FCI energies was introduced in two recent publications[49,50] by the present authors: The *correlation energy extrapolation by intrinsic scaling* (*CEEIS*). In a third investigation,[51] the implications for compact wave functions were discussed. Using Dunning's correlation consistent basis sets,[52–54] such CEEIS extrapolations were found to yield accurate approximations to the (valence) FCI energies for a number of prototype systems with a considerably reduced computational effort.

In the present investigation, we generalize the CEEIS method to multiconfigurational reference functions and use it

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a)On leave from Institute of Theoretical Physics and Astronomy, Vilnius University, Gostauto 12, Vilnius 2600, Lithuania.

122, 154110-1
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to predict the binding energies of the diatomic molecules, C_2, N_2, O_2, and F_2. These systems are often chosen as test cases for new computational approaches (see, e.g., Refs. 29, 55, and 56) since their electronic structures embody serious challenges for achieving high accuracy by *ab initio* methods. We use the CEEIS method to determine accurate approximations to the full CI energies for Dunning's correlation consistent polarized valence X-tuple zeta (cc-pVXZ) basis sets with $X = 2, 3, 4$ and, then, extrapolate these energies to the CBS limit by means of established techniques.[29,56–78] The predicted binding energies are found to agree with the experimental data within the chemical accuracy of 1 kcal/mol.

II. EXTRAPOLATION TO THE FULL CI ENERGY BY INTRINSIC SCALING

Since the basic CEEIS method has been described in detail in Ref. 49, we shall sketch here only briefly the basic notions and definitions. We shall however generalize the method to the case of a multiconfigurational reference function. While the method is manifestly applicable to all electrons, we use it here only to recover the correlations within valence shells, i.e., with the core shells assumed to be closed.

A. Resolution of the full CI energy

1. Expansion in terms of contributions from successive excitations

The CEEIS method presumes the prior determination of a "zeroth-order configuration space" that is generated from a set of M_R reference valence orbitals, called "occupied." This zeroth-order reference space does not have to be limited to a single Hartree–Fock-type determinant, but can be multiconfigurational. The reference orbitals are presumed to be close to those that would result from the multiconfigurational self-consistent-field (MCSCF) optimization in this zeroth-order configuration space. In the present investigation, we use the *full* configurational reference space that is generated by the occupied molecular orbitals (MOs). Let there be M *additionally* available valence orbitals, called "virtual" or "correlating," so that the total number of valence, i.e., noncore orbitals is $M_R + M$. Substituting virtual valence orbitals in place of occupied valence orbitals generates the additional correlating determinants. They are classified as single, double, triple, etc., excitations, the set of x-tuple excitations being defined as consisting of all determinants containing x correlating and $(N-x)$ occupied valence orbitals, where N is the number of valence electrons. (We mention in passing that other reference space choices are also compatible with the CEEIS method.)

Let $E(x)$ denote the CI energy obtained by using *all* configurations containing up to x excited electrons in the virtual orbital space. Thus, $E(0)$ is the reference energy of the zeroth-order wave function, $E(1)$ represents the singles, i.e., S-CI energy, $E(2)$ is the SD-CI energy, $E(3)$ is the SDT-CI energy, $E(4)$ is the SDTQ-CI energy, etc. The CI energy in the full configuration space can then be denoted as $E(f)$, where f is the smaller of $2M$ and N.

Our method is based on the resolution of the total energy improvement over the zeroth-order energy in the full space, viz. ΔE, as a sum of excitation contributions $\Delta E(x)$:

$$\Delta E = [E(f) - E(0)] = \Delta E(1) + \Delta E(2) + \cdots + \Delta E(f), \tag{1}$$

with the increments

$$\Delta E(x) = E(x) - E(x-1), \quad x = 1, 2, \ldots, f. \tag{2}$$

If f is even, ΔE can also be decomposed as

$$\Delta E = [E(f) - E(0)] = \Delta E(1,2) + \Delta E(3,4) + \Delta E(5,6) + \cdots + \Delta E(f-1,f), \tag{3}$$

where

$$\Delta E(x, x-1) = E(x) - E(x-2) = \Delta E(x) + \Delta E(x-1), \tag{4}$$

$$x = 1, 2, \ldots, f.$$

The individual terms in the series expansion of Eq. (1), which correspond to the successive excitations, are independent on the choice of the correlating orbitals that generate the configurations, as long as all M correlating orbitals are used at each excitation level. *For small systems involving the atoms hydrogen to neon, the expansion given by Eq. (1) has always been found to converge rapidly when the zeroth-order space is near-optimized*: millihartree accuracy is usually reached for $x=6$, in some cases for $x=4$ and rarely requiring $x=8$.

It is the expansion of each $\Delta E(x)$ in terms of determinants that converges very slowly. These determinantal expansions, in particular those for higher excitations, are responsible for the excessive lengths of CI expansions, and they are the object of the present approach.

2. Choice of orbitals

The convergence of the expansion of each excitation contribution $\Delta E(x)$ in terms of determinants depends on the choice of the molecular orbitals. It is therefore important to make an optimal choice of the configuration-generating orbitals and to order them according to their decreasing importance. A good set of correlating virtual orbitals would be the natural orbitals (NOs) of the full CI solution,[79,80] ordered by occupation numbers, if they were available. An effective practical alternative is provided by the NOs of the SD-CI calculation.[45] The present analysis is therefore based on wave functions and energies generated using these SD-NOs for all orbitals. The M_R strongly occupied orbitals, which are similar to the SCF or MCSCF orbitals, are used as the reference orbitals, while the M weakly occupied orbitals are used as the correlating orbitals.

This choice entails, of course, that the zeroth-order energy $E(0)$ is slightly higher than what is found when the reference orbitals are taken equal to the SCF or MCSCF orbitals and the correlating orbitals are obtained from diagonalizing only the projection of the SD density matrix in the virtual orbital space. In the molecules studied here, this is also found to be the case for the singles-plus-doubles energy $E(2)$. The energy differences resulting from the two orbital

choices become however uniformly less than 0.05 millihartree at the SDTQ excitation level.

3. Orbital contributions to a given excitation level

To analyze the expansions of $\Delta E(x)$ in terms of determinants, let us define as "$\{x|m\}$-*CI calculations*" those CI calculations that include excitations up to level x, *but where only the first m of the set of ordered virtual correlating orbitals are utilized*. The resulting energy values will be denoted as $E(x|m)$. They manifestly converge to the energy $E(x)$ as $m \to M$, and the energy in the full orbital space will be $E(f|M)$ with $f = \min\{N, 2M\}$.

In analogy to Eq. (1), the energy $E(x|m)$ from an $\{x|m\}$-CI calculation can be decomposed as

$$E(x|m) = E(0|m) + \Delta E(1|m) + \Delta E(2|m) + \cdots + \Delta E(x|m),$$

(5)

where

$$\Delta E(x|m) = [E(x|m) - E(x-1|m)]$$

(6)

or, for x=even, by

$$E(x|m) = E(0|m) + \Delta E(1,2|m) + \Delta E(3,4|m)$$
$$+ \cdots + \Delta E(x-1,x|m)$$

(7)

with

$$\Delta E(x-1,x|m) = [E(x|m) - E(x-2|m)]$$
$$= \Delta E(x|m) + \Delta E(x-1|m).$$

(8)

For for $m \to M$, one manifestly has

$$\Delta E(x|M) = \Delta E(x), \quad \Delta E(x,x-1|M) = \Delta E(x,x-1).$$

(9)

as defined by Eqs. (2) and (4).

B. Extrapolation of excitation contributions

The CEEIS method[49,50] is deduced from the observation that certain similarities exist in the way the energies $\Delta E(x|m)$ and $\Delta E(x+2|m)$, *considered as functions of m*, converge towards their respective full values $\Delta E(x)$ and $\Delta E(x+2)$. In fact, for m larger than a certain threshold value m_0, *the linear relationships*

$$\Delta E(x|m) = a_x \Delta E(x-2|m) + c_x$$

(10)

were found to give quite accurate representations of these similarities for x=4,5,6 and higher x values. Using these relations, several implementation schemes were developed and described in detail in Ref. 49. Here we focus on two of them.

1. Scheme I

Equation (10) permits the extrapolative determination of the desired end value $\Delta E(x) = \Delta E(x|M)$ from the *known* end value $\Delta E(x-2|M)$ provided the values of a_x and c_x are known. Since the latter vary not only with x, but also from system to system, they must be determined in each case. This is accomplished by computing the values of the two quantities $\Delta E(x|m)$ and $\Delta E(x-2|m)$ for a given x value and *for a set of low m values, defined say by $m_0 \leq m \leq m_1 < M$, termed*

the *"fitting range."* The constants a_x and c_x are then determined by least mean squares (LMSQ) fitting Eq. (10) to the data in the fitting range.

This fitting-plus-extrapolation procedure is used to deduce the contributions for x=4,6,8 from $\Delta E(2)$ and the contributions for x=5,7,9 from $\Delta E(3)$.

2. Scheme II

Here, $\Delta E(4|M)$ is obtained as in Scheme I. But, for $x \geq 5$ one uses the relationships

$$\Delta E(x-1,x|m) = [E(x|m) - E(x-2|m)]$$
$$= A_x \Delta E(1,2|m) + B_x \Delta E(3|m) + C_x,$$

(11)

which are readily derived form Eq. (10). In this case, values of the three quantities $\Delta E(1,2|m)$, $\Delta E(3|m)$, and $\Delta E(x-1,x|m)$ are calculated in a certain fitting range (m_0, m_1) for a given x value. For each x, the constants A_x, B_x, C_x are then determined by LMSQ fit and $\Delta E(x|M)$ is obtained from $\Delta E(1,2|M)$ and $\Delta E(3|M)$.

3. Error prediction

Since our objective is to obtain correlation energies in systems where calculations with full bases (i.e., for $m=M$) are not feasible, the ability to estimate the possible error of the extrapolation is relevant. We have shown in Ref. 49 how such an estimate can be deduced from the quality of the LMSQ fit discussed above. Consider, for instance, the use of Eq. (10) in Scheme I. Let the values of $\Delta E(x-2|m)$ at the borders of the fitting range be denoted by $\Delta E(x-2|m_0) = \eta_0$ and $\Delta E(x-2|m_1) = \eta_1$. Let furthermore the full value $\Delta E(x-2)$ be denoted by $\Delta E(x-2|M) = \eta_M$. Let the uncertainty of $\Delta E(x|m)$ inherent in the LMSQ *fit within the fitting range* be characterized by the quantity δ, which can be chosen either as the root-mean-square deviation or as the maximum deviation of the fit in the range. Then, the uncertainty in the extrapolated value for $\Delta E(x|M)$ is predicted to be $\pm\varepsilon$ with

$$\varepsilon = \delta[1 + 2(\eta_M - \eta_1)/(\eta_1 - \eta_0)].$$

(12)

For those cases where we knew the accurate values, we found the root-mean-square choice for δ to yield reliable estimates for ε most of the time. The maximum-deviation choice for δ is of course more conservative, but usually too much so. Both estimates of ε will be listed in some of the subsequent tables.

III. FULL VALENCE CI ENERGIES FOR C_2, N_2, O_2, AND F_2

A. Zeroth-order wave functions

For the molecules C_2, N_2, F_2, the zeroth-order wave functions can be taken as the dominating single determinants

$$C_2 \ (^1\Sigma_g^+): \ \mathcal{A}\{\text{core}^4(2\sigma)^2(2\sigma^*)^2(2\pi x)^2(2\pi y)^2(\alpha\beta)^6\},$$

$$N_2 \ (^1\Sigma_g^+): \ \mathcal{A}\{\text{core}^4(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(2\pi x)^2(2\pi y)^2(\alpha\beta)^7\},$$

F_2 ($^1\Sigma_g^+$): $\mathcal{A}\{core^4(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(2\pi x)^2(2\pi y)^2$

$\qquad \times (2\pi x^*)^2(2\pi y^*)^2(\alpha\beta)^9\}$,

where $\mathcal{A}$ denotes the respective antisymmetrizers. The number of reference valence orbitals for C_2, N_2, F_2 is $M_R = 4, 5, 7$, respectively. Since, in the cc-pVQZ basis, the total number of valence orbitals is $M_R + M = 108$ in all cases, the number of correlation valence orbitals is $M = 104, 103, 101$, respectively.

As regards C_2, it is however well known that the ground state full-valence-space MCSCF wave function contains about a 20% admixture of the second configuration

C_2 ($^1\Sigma_g^+$): $\mathcal{A}\{core^4(2\sigma)^2(3\sigma)^2(2\pi x)^2(2\pi y)^2(\alpha\beta)^6\}$,

and it is in fact this strong zeroth-order multiconfigurational character which is the cause of the difficulties that coupled-cluster methods encounter in trying to deal with this molecule. From the point of view of the CEEIS methodology, one wonders which is the more effective choice for our zeroth-order function: The single determinant mentioned in the preceding paragraph, or the small full configuration space generated by the *five* ($M_R = 5$) reference valence orbitals 2σ, $2\sigma^*$, 3σ, $2\pi x$, $2\pi y$. In $^1\Sigma_g^+$ symmetry, this space is spanned by seven determinants (which contain the two mentioned above) and all excitations are then generated with respect to this seven-dimensional reference space. The CEEIS procedure works for both approaches without problems and we shall investigate and compare both quantitatively below.

For O_2 on the other hand, because of the single occupancy of the π^* orbitals, the zeroth-order function is necessarily a linear combination of the two determinants

O_2 ($^3\Sigma_g^-$): $\Psi_1 = \mathcal{A}\{core^4(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(2\pi x)^2(2\pi y)^2$

$\qquad\qquad \times (2\pi x^*)(2\pi y^*)(\alpha\beta)^7\alpha\alpha\}$

$\Psi_2 = \mathcal{A}\{core^4(2\sigma)^2(2\sigma^*)^2(3\sigma)^2(2\pi x^*)^2(2\pi y^*)^2(2\pi x)$

$\qquad \times (2\pi y)(\alpha\beta)^7\alpha\alpha\}$,

which are the only 12-electron functions of $^3\Sigma_g^-$ symmetry in the full configuration space generated by the $M_R = 7$ occupied valence orbitals. The ORMAS (Ref. 23) code determines the optimal linear combination of Ψ_1 and Ψ_2 simultaneously with the coefficients of the excited configurations. The reference multiconfigurational (MC)-function is found to contain about a 5% admixture of Ψ_2. For O_2, we have $M = 101$ so that again $M_R + M = 108$.

B. CEEIS procedure for quadruple-ζ basis sets

We illustrate the working of the CEEIS method by documenting the extrapolation to the FCI energies of the molecules C_2, N_2, O_2, and F_2 for the largest basis sets used here, viz., cc-pVQZ.[52] The calculations were executed using the GAMESS program suite,[81] notably the ORMAS code.[23] They were performed at the experimental equilibrium distances, as given by Huber and Herzberg,[82] except for C_2, where the value of Douay *et al.*[83] was used.

The results for the four molecules are exhibited in Tables I–IV. The calculations for N_2 and F_2, reported in Tables II

and IV, were performed with the single-determinant reference functions given in Sec. III A. The calculations for O_2, reported in Table III, were performed with the two-determinant zeroth-order reference functions given in Sec. III A. The calculations for C_2, reported in Table I, were performed using as zeroth-order reference function the *dominant single determinant* given in the beginning of Sec. III A. The calculations based on the seven-determinant reference function proceeded just as smoothly and the results will be commented upon in Sec. V A.

In each of the four tables, the first section documents the resolution of the total valence-correlation energy in terms of the contributions from the single+double excitations, the triple excitations, and the remaining excitations. *Note that the first row of this section is not the quantity* $\Delta E(1,2)$ *defined by Eq. (4) for* $x=2$, *but the slightly different quantity*

$$\Delta E_{HF}(1,2) = E(2) - E_{HF} = \Delta E(1,2) + E(0) - E_{HF}, \quad (13)$$

where E_{HF} *is the independently calculated Hartree–Fock energy*, which differs slightly from $E(0)$ because we have chosen to work with the SD-NOs as reference orbitals, as has been discussed in Sec. II A 2. We list $\Delta E_{HF}(1,2)$ rather than $\Delta E(1,2)$ in order that the total becomes in fact the conventionally defined valence-correlation energy and can be compared with the results of other work. Note also that, while the CEEIS procedure in O_2 of Table III is based on a two-determinant zeroth-order reference function, the term E_{HF} in Eq. (13) is here defined as the energy of the *optimized single determinant* Ψ_1 discussed in Sec. III A. The second row of the first section in Tables I–IV contains the contribution $\Delta E(3) = \Delta E(3|M)$ just as defined by Eq. (2) for $x=3$.

The determination of the correlation contributions of the excitation levels $x = 4 - 8$ by the CEEIS extrapolation is documented in the second section of each of the Tables I–IV. The first three parts of this section contain the results for the contributions of excitations $x = 4, 5, 6$ respectively, as calculated by Scheme I. The next part lists the results for the total contribution of the excitations $x = 5 + 6$, calculated in two ways, viz., by adding the preceding results as well as by direct application of Scheme II. The final part contains the results for the contribution of excitations $x = 7 + 8$, calculated by Scheme II. The contributions of the excitations $x = 9$ and higher manifestly become negligibly small.

The first two columns in the second section identify the fitting ranges by specifying the values $\{m_0, m_1\}$. The third column lists the *calculated* value of $\Delta E(x|m_1)$, i.e., from the largest CI calculation made for this x value, and the fourth column gives the *extrapolated* result for $\Delta E(x) = \Delta E(x|M)$. The last two columns show the uncertainties predicted by Eq. (12) for the extrapolations, using the root-mean-square deviation as well as the maximum deviation for δ.

The contributions $\Delta E(4-8|M)$ in the first section of the table are obtained by adding up those excitation contributions in the second section that are identified by bold print.

It is apparent that the quantitative results shown in these tables are very similar for the four molecules. The energies obtained by different extrapolations for $\Delta E(4)$ of any given molecule are always within a few tenths of a millihartree of each other, indicating the reliability of the method. The same

TABLE I. Contributions of the various excitation levels to the FCI valence-correlation energy of the C_2 ground state in cc-pVQZ basis (in millihartree).

$\Delta E_{HF}(1,2\vert104)$	317.99		Calculated exactly, Eq. (13)
$\Delta E(3\vert104)$,	25.48		Calculated exactly, Eqs. (6) and (9)
$\Delta E(4-8\vert104)$	53.55 ± 0.3		Extrapolated, see below
Total valence-correlation energy	397.02 ± 0.3		Eqs. (1) and (13)

Fitting range		Energy contributions		Estimated abs. error, using	
m_0	m_1	$-\Delta E(x\vert m_1)$	$-\Delta E(x\vert104)$	δ(RMSQ)	δ(max)
Excitations $x=4$					
Extrapolation to $\Delta E(4\vert104)$ by Scheme I					
14	50	44.10	44.72	0.15	0.45
18	50	44.10	44.86		
25	50	44.10	44.85		
25	60	44.31	**44.84**	**0.09**	**0.22**
Excitations $x=5$					
Extrapolation to $\Delta E(5\vert104)$ by Scheme I					
23	36	5.52	**5.78**	**0.01**	**0.02**
Excitations $x=6$					
Extrapolation to $\Delta E(6\vert104)$ by Scheme I					
26	28	2.39	2.63		
21	28	2.39	**2.73**	**0.03**	**0.04**
Excitations $x=5+6$					
Sum of Scheme I extrapolations for $x=5$ and $x=6$					
	$\Delta E(5\vert104)+\Delta E(6\vert104)$		**8.51**	**0.04**	**0.06**
Extrapolation to $\Delta E(5,6\vert104)$ by Scheme II					
12	28	7.68	8.48		
15	28	7.68	8.48		
17	28	7.68	8.54	0.02	0.03
Excitations $x=7+8$					
Extrapolation to $\Delta E(7,8\vert104)$ by Scheme II					
9	20	0.16	0.20		
12	20	0.16	0.21		
13	20	0.16	**0.20**	**0.004**	**0.008**

holds for the extrapolations by Scheme I and by Scheme II for the contributions $\Delta E(5,6\vert M)$, which yield nearly identical estimates which lie within the predicted uncertainties of each other. The contribution $\Delta E(7,8\vert M)$ is always less than 0.1 mh except for C_2 where it is 0.2 millihartree.

C. Full CI energies for double-, triple-, and quadruple-ζ bases and comparison with coupled-cluster results

We determined very accurate FCI energy estimates also for the double-ζ (cc-pVDZ) and triple-ζ bases (cc-pVTZ), either directly or by using the CEEIS procedure when the direct FCI calculations were out of reach. In Table V, we compare all of these near-FCI energies with energies obtained from coupled-cluster methods including at least triple excitations. The CCSD(T) and CCSD[T] results[84–91] were obtained using a code due to Piecuch and co-workers[91] in GAMESS and they were determined at the same geometries as the CEEIS-FCI calculations, viz., the experimental internuclear distances. Also listed are the results of the CCSDT

calculations reported by Feller and Sordo[29] for optimized internuclear distances. The higher level, viz., CCSD(TQ) and CCSDT(Q) results were obtained by McGuire and Piecuch,[92] also at the experimental distances, and kindly given to the present authors.

In as much as the CEEIS-FCI results are accurate within fractions of millihartees, they can be considered as benchmarks for the coupled-cluster calculations. The deviations of the coupled-cluster values from the CEEIS-FCI result are indicated in parentheses (in millihartree) in Table V.

The overall observation is that these coupled-cluster energies differ from the full CI results in the millihartree range, with the CCSDT theory, exhibiting the largest errors for the better basis sets [even though very good optimized geometries can be obtained already at CCSD(T) level of theory[93]]. The CCSD[T] approximation shows the smallest errors (occasionally less than 1 millihartree). In C_2, however, the CCSD[T] results drop *below* the FCI energies, while all other CC energies in all molecules lie above the FCI energies.

All coupled-cluster results are in fact worst for the molecule C_2, the errors of the CCSDT calculations being 2.06, 3.93, 4.44 millihartree corresponding to the double- triple-

TABLE II. Contributions of the various excitation levels to the FCI valence-correlation energy of the N_2 ground state in cc-pVQZ basis (in millihartree).

$\Delta E_{HF}(1,2 \mid 103)$	364.76	Calculated exactly, Eq. (13)
$\Delta E(3 \mid 103)$	16.95	Calculated exactly, Eqs. (6) and (9)
$\Delta E(4-8 \mid 103)$	32.94 ± 0.1	Extrapolated, see below
Total valence-correlation energy	414.65 ± 0.1	Eqs. (1) and (13)

Fitting range		Energy contributions		Estimated absolute error, using	
m_0	m_1	$-\Delta E(x \mid m_1)$	$-\Delta E(x \mid 103)$	$\delta(\text{RMSQ})$	$\delta(\text{max})$
Excitations $x=4$					
Extrapolation to $\Delta E(4 \mid 103)$					
13	25	25.64	29.80		
13	29	26.28	29.73	0.08	0.16
16	29	26.28	29.70		
16	50	28.51	**29.65**	**0.05**	**0.12**
Excitations $x=5$					
Extrapolation to $\Delta E(5 \mid 103)$ by Scheme I					
6	20	1.63	2.37	0.04	0.08
15	20	1.63	2.42	0.05	0.09
18	20	1.63	**2.23**	**0.001**	**0.001**
Excitations $x=6$					
Extrapolation to $\Delta E(6 \mid 103)$ by Scheme I					
6	17		0.85	0.016	0.057
15	17		**0.99**	**0.007**	**0.009**
Excitations $x=5+6$					
Sum of Scheme I extrapolations for $x=5$ and $x=6$					
$\Delta E(5 \mid 103) + \Delta E(6 \mid 103)$			**3.22**	**0.008**	**0.010**
Extrapolation to $E(5,6 \mid 103)$ by Scheme II					
5	12	1.52	3.21		
5	14	1.72	3.14		
5	17	2.11	3.17	0.04	0.08
Excitations $x=7+8$					
Extrapolation to $\Delta E(7,8 \mid 103)$ by Scheme II					
5	13	0.03	**0.07**	**0.002**	**0.003**

and quadruple-ζ bases, respectively. In view of the geometry optimizations, the CCSDT energies would deviate from the FCI energies even more at the experimental internuclear distance. Even the CCSDT(Q) calculation entails an error of 2.16 millihartree. Since the deviations are also substantial for the CCSD(T) and CCSD[T] approximations, it is likely that the reason for these errors is the partial multireference character of the C_2 ground state wave function.

One furthermore notes that the deviations of the CC energies from the FCI energies are typically nearly constant when going from the cc-pVTZ to the cc-pVQZ basis sets and they also maintain the same sign.

Finally, one observes that CCSD(TQ) and CCSDT(Q) methods[91,92] provide a better accuracy than CCSD[T] and CCSD(T) approaches, especially in the case of the F_2 molecule, as indeed they should. Nevertheless, the C_2 molecule appears to remain a problem case even for CCSD(TQ) and CCSDT(Q) methods. The inclusion of higher CC excitations is expected to improve the CC results further.[94,95]

IV. EXTRAPOLATION TO THE COMPLETE BASIS SET LIMIT

A. Approach of cc-pVXZ energies to the CBS limit

As mentioned in the Introduction, chemical accuracy may be achievable without extrapolations when the linear-R12 methodology is used in conjunction with MCSCF reference functions and *very* large basis sets.[17–21] Chemically accurate determinations of electronic energies by the straight CI approach require, however, extrapolations of the full CI energies to the CBS limit. Considerable work has therefore been done in developing physically appropriate as well as computationally efficient extrapolation techniques[56–78] for energies obtained with sequences of various basis set types. One result of the theoretical analyses is that the soundest procedure is to extrapolate the Hartree–Fock energy and the correlation energy separately.

For sequences of Dunning's correlation consistent cc-pVXZ basis sets, the Hartree–Fock energy for the X-tuple-ζ

TABLE III. Contributions of the various excitation levels to the FCI valence-correlation energy of the O_2 ground state in cc-pVQZ basis (in millihartree).

$\Delta E_{HF}(1,2\|101)$		469.35		Calculated exactly, Eq. (13)	
$\Delta E(3\|101)$		25.30		Calculated exactly, Eqs. (6) and (9)	
$\Delta E(4-8\|101)$		16.89±0.02		Extrapolated, see below	
Total valence-correlation energy		511.54±0.02		Eqs. (1) and (13)	

Fitting range		Energy contributions		Estimated absolute error, using	
m_0	m_1	$-\Delta E(x\|m_1)$	$-\Delta E(x\|101)$	δ(RMSQ)	δ(max)
Excitations $x=4$					
Extrapolation to $\Delta E(4\|101)$					
18	28	11.86	15.02		
26	28	11.86	15.09		
18	37	13.04	15.14	0.05	0.08
26	37	13.04	15.27		
28	37	13.04	**15.29**	**0.005**	**0.007**
Excitations $x=5$					
Extrapolation to $\Delta E(5\|101)$ by Scheme I					
8	21	0.78	1.19	0.03	0.05
12	21	0.78	1.24		
16	21	0.78	**1.27**	**0.003**	**0.005**
Excitations $x=6$					
Extrapolation to $\Delta E(6\|101)$ by Scheme I					
8	18	0.20	0.30	0.006	0.009
12	18	0.20	**0.31**	**0.002**	**0.003**
Excitations $x=5+6$					
Sum of Scheme I extrapolations for $x=5$ and $x=6$					
	$\Delta E(5\|101)+\Delta E(6\|101)$		**1.58**	**0.005**	**0.008**
Extrapolation to $\Delta E(5,6\|101)$ by Scheme II					
7	14	0.65	1.34		
9	14	0.65	1.38		
7	18	0.91	1.59		
9	18	0.91	1.62	0.03	0.05
Excitations $x=7+8$					
Extrapolation to $\Delta E(7,8\|101)$ by Scheme II					
7	11	0.01	**0.02**	**0.0006**	**0.0007**

basis approaches its CBS limit according to the exponential law[78]

$$E_{HF}(X) = E_{HF}(CBS) + a \exp(-\alpha X). \quad (14)$$

The correlation energy, on the other hand, has been shown to approach its CBS limit according to an inverse power law, the most likely candidate being

$$E_{COR}(X) = E_{COR}(CBS) + aX^{-3} + bX^{-5}, \quad (15)$$

where the power (-3) is due to singlet-coupled terms and the power (-5) to triplet-coupled terms.[17,96,97] But it has been observed that only a small error seems to be introduced by omitting of the (-5) term in Eq. (15).[64,65]

On the other hand, it has been generally found that the double-ζ $(X=2)$ energies do not fit well into the extrapolation process and are better omitted from the procedure.

We confirmed these generally accepted inferences by explicit calculations on the neon atom, which are discussed below in Sec. IV D.

B. CBS extrapolation of the Hartree–Fock energy

Formula (14) contains three unknowns [$E_{HF}(CBS)$, a, α]. Three Hartree–Fock (HF) energies are therefore required to determine the desired $E_{HF}(CBS)$ value. Since our calculations did not go beyond quadruple-ζ bases, we were forced to use the energies for $X=2$ as well as those for $X=3,4$. It is however a relatively simple matter to determine HF-CBS limits accurately by going to larger bases sets, and they have indeed been reported in the literature for the atoms C, N, O, F (Refs. 98–100) and for the molecules C_2, N_2, O_2, F_2 (Refs. 99 and 100). We pursued both avenues and found that, in fact, the listed accurate HF-CBS limits and those obtained by using our results for $X=2,3,4$ never differed by more than 1 millihartree. Substitution of the accurate HF-CBS limit, when comparing with experiment, entails of course a more stringent test for the correlation energies and, hence, also for the CEEIS method.

A slight complication arose, in the case of the atoms, from the fact that, long before we came to this point, we had

TABLE IV. Contributions of the various excitation levels to the FCI valence-correlation energy of the F_2 ground state in cc-pVQZ basis (in millihartree).

$\Delta E_{HF}(1,2\vert 101)$	528.27		Calculated exactly, Eq. (13)
$\Delta E(3\vert 101)$	16.70		Calculated exactly, Eqs. (6) and (9)
$\Delta E(4-8\vert 101)$	46.87 ± 0.2		Extrapolated, see below
Total valence-correlation energy	591.84 ± 0.2		Eqs.(1) and (13)

Fitting range		Energy contributions		Estimated absolute error, using	
m_0	m_1	$-\Delta E(x\vert m_1)$	$-\Delta E(x\vert 101)$	δ(RMSQ)	δ(max)
Excitations $x=4$					
Extrapolation to $\Delta E(4\vert 101)$					
14	26	34.00	43.12		
14	33	36.29	43.15	0.15	0.28
14	40	38.23	43.15		
33	40	38.23	43.10		
25	40	38.23	**43.29**	**0.08**	**0.14**
Excitations $x=5$					
Extrapolation to $\Delta E(5\vert 101)$ by Scheme I					
10	16	0.68	1.99	0.083	0.18
10	20	1.04	2.01	0.037	0.09
16	20	1.04	**2.05**	**0.007**	**0.01**
Excitations $x=6$					
Extrapolation to $\Delta E(6\vert 101)$ by Scheme I					
10	16	0.89	**1.48**	**0.006**	**0.01**
Excitations $x=5+6$					
Sum of Scheme I extrapolations for $x=5$ and $x=6$					
$\Delta E(5\vert 101)+\Delta E(6\vert 101)$			**3.53**	**0.013**	**0.02**
Extrapolation to $\Delta E(5,6\vert 101)$ by Scheme II					
7	16	1.57	3.36		
8	16	1.57	3.47	0.09	0.15
Excitations $x=7+8$					
Extrapolation to $\Delta E(7,\vert 101)$ by Scheme II					
7	11	0.02	**0.05**	**0.001**	**0.002**

chosen to determine the Hartree–Fock energies for these open-shell atoms by restricted open shell Hartree-Fock (ROHF) calculations with *nonequivalent px, py, pz* orbitals. The quoted references report however only CBS limits for the case of equivalent orbitals. Our deduction of the corresponding CBS limits for nonequivalent orbitals is explained by Table VI. For each atom, the left side of this table contains the following Hartree–Fock energies for the case of *equivalent* orbitals: The cc-pVQZ energy, the CBS limit and, in the third numerical column, the difference between them (in millihartree). Adding this difference to the cc-pVQZ Hartree–Fock energy for nonequivalent orbitals, listed in the fourth numerical column, we obtained the estimate of the HF-CBS limit for nonequivalent orbitals, which is listed in the last column.

C. CBS extrapolation of the correlation energy

The determination of the three constants in Eq. (15) for the correlation energy would require the use of $X=2$ as well as $X=3,4$. But, as mentioned in Sec. IV A, the inclusion of double-ζ energies typically degrades the CBS extrapolation of the correlation energy. Much better results are indeed ob-

tained by omitting the (-5) term and determining the two constants using only $X=3,4$, which is also in agreement with the observations by others mentioned in Sec. IV A. [It might be mentioned in passing that omitting the (-5) term, but retaining $X=2$ together with $X=3,4$ and determining the two constants by least-mean-squares fitting also worsens the CBS extrapolation.]

Accordingly we adopt here the following two standard CBS extrapolation forms:

$$CBS\text{-}1A = Hartree – Fock\ by\ Eq.\ (14),\ with\ X$$
$$= 2,3,4.\ Correlation\ by\ Eq.\ (15)\ without\ X^{-5},$$
$$using\ X = 3,4, \qquad (16)$$

$$CBS\text{-}1B = Exact\ Hartree – Fock\ CBS\ limit.$$
$$Correlation\ by\ Eq.\ (15)\ without\ X^{-5},$$
$$using\ X = 3,4. \qquad (17)$$

If the energies for quintuple-ζ bases ($X=5$) are also available, then application of the full Eq. (15) may yield the best results for the CBS extrapolation of FCI energies.

TABLE V. Comparison of FCI and coupled-cluster energies for C_2, N_2, O_2, F_2. Total energies in hartree. Deviations from CEEIS-FCI energies in parentheses in millihartree.

	R	VDZ	VTZ	VQZ
		C_2 ($^1\Sigma_g^+$)		
CEEIS-FCI	Expt.	−75.728 55	−75.784 97	−75.802 80
CCSD[T]	Expt.	−75.730 72(−2.17)	−75.787 43(−2.46)	−75.805 26(−2.46)
CCSD(T)	Expt.	−75.726 69(1.86)	−75.783 07(1.90)	−75.800 81(1.99)
CCSDT	Optimized	−75.726 49(2.06)	−75.781 04(3.93)	−75.798 39(4.41)
CCSD(TQ)	Expt.	−75.727 41(1.14)	−75.783 37(1.60)	−75.801 03(1.77)
CCSDT(Q)	Expt.	−75.727 65(0.90)	−75.783 18(1.79)	−75.800 64(2.16)
Experimental R_{CC}[a] (Å)		1.242 44	1.242 44	1.242 44
Optimized R_{CC}[b] (Å)		1.270 7	1.250 6	1.245 5
		N_2 ($^1\Sigma_g^+$)		
CEEIS-FCI	Expt.	−109.276 98	−109.375 30	−109.405 73
CCSD[T]	Expt.	−109.275 93(1.05)	−109.374 68(0.62)	−109.405 25(0.48)
CCSD(T)	Expt.	−109.275 25(1.73)	−109.373 84(1.46)	−109.404 37(1.36)
CCSDT	Optimized	−109.276 51(0.46)	−109.373 64(1.67)	−109.403 97(1.76)
CCSD(TQ)	Expt.	−109.276 18(0.80)	−109.374 25(1.05)	−109.404 75(0.98)
CCSDT(Q)	Expt.	−109.276 70(0.28)	−109.374 56(0.74)	−109.404 97(0.76)
Experimental R_{NN}[c] (Å)		1.097 7	1.097 7	1.097 7
Optimized R_{NN}[b] (Å)		1.118 5	1.103 1	1.099 6
		O_2 ($^3\Sigma_g^-$)		
CEEIS-FCI	Expt.	−149.987 87	−150.130 55	−150.175 53
CCSDT	Optimized	−149.986 02(1.85)	−150.128 99(1.56)	−150.173 81(1.72)
Experimental R_{OO}[c] (Å)		1.207 52	1.207 52	1.207 52
Optimized R_{OO}[b] (Å)		1.215 9	1.211 7	1.207 4
		F_2 ($^1\Sigma_g^+$)		
CEEIS-FCI	Expt.	−199.099 35	−199.297 38	−199.360 11
CCSD[T]	Expt.	−199.097 92(1.43)	−199.296 81(0.57)	−199.359 71(0.40)
CCSD(T)	Expt.	−199.097 48(1.87)	−199.296 10(1.28)	−199.358 91(1.20)
CCSDT	Optimized	−199.098 69(0.66)	−199.296 10(1.28)	−199.358 84(1.27)
CCSD(TQ)	Expt.	−199.098 80(0.55)	−199.296 75(0.63)	−199.359 45(0.66)
CCSDT(Q)	Expt.	−199.099 30(0.05)	−199.297 16(0.22)	−199.359 87(0.24)
Experimental R_{FF}[c] (Å)		1.411 93	1.411 93	1.411 93
Optimized R_{FF}[b] (Å)		1.457 7	1.415 4	1.412 4

[a]Reference 83.
[b]Reference 29.
[c]Reference 82.

D. CBS extrapolation of the total energy

A number of authors have pragmatically applied extrapolation formulas to the *total* (HF+correlation) energies,[66,67,69,70] typically using one of the formulas

$$E_{TOT}(X) = E_{TOT}(CBS) + A \exp(-\alpha X) \tag{18}$$

$$E_{TOT}(X) = E_{TOT}(CBS) + B(X+b)^{-\beta} + C(X+c)^{-\gamma}. \tag{19}$$

TABLE VI. Deduction of atomic Hartree–Fock (ROHF) energy CBS limits for nonequivalent orbitals from the analogous limits for equivalent orbitals.

	Equivalent orbitals			Nonequivalent orbitals	
Atom	cc-pVQZ[a] (hartree)	HF limit[b] (hartree)	Difference (millihartree)	cc-pVQZ[a] (hartree)	HF limit[c] (hartree)
C (^3P)	−37.688 23	−37.688 62	−0.39	−37.688 30	−37.688 69
N (^4S)	−54.400 18	−54.400 94	−0.76	−54.400 18	−54.400 94
O (^3P)	−74.807 98	−74.809 40	−1.43	−74.810 84	−74.812 27
F (^2P)	−99.406 98	−99.409 35	−2.37	−99.408 95	−99.411 32

[a]ROHF energies calculated with cc-pVQZ basis sets, for equivalent and nonequivalent orbitals given in the EMSL basis set library describing information (Ref. 98).
[b]Best estimates for ROHF-CBS limits in the literature (Ref. 98–100) for equivalent orbitals.
[c]Estimates for ROHF-CBS limit for nonequivalent orbitals, obtained by adding the preceding two columns.

TABLE VII. Errors of various CBS-extrapolation procedures for the neon atom (in millihartree).

Extrapolation formula	Energy error[a]
Total energies extrapolated using $X=2,3,4$	
(1) $\mathrm{Exp}(-\alpha X)$	5.2
(2) $(X)^{-3}$	7.1
(3) $(X+0.5)^{-3}$	−6.7
(4) $[(X+0.5)^{-3}$ and $(X+0.5)^{-5}]$	−12.9
(5) $(X+0.5)^{-\alpha}$, $\alpha=$optimized	−16.8
Total energies extrapolated using $X=3,4$	
(6) $(X+0.5)^{-3}$	−10.8
(7) $(X)^{-3}$	−4.2
(8) $(X-0.1)^{-3}$	−2.9
(9) $(X-0.2)^{-3}$	−1.6
(10) $(X-0.3)^{-3}$	−0.3
(11) $(X+0.5)^{-4}$	2.1
Hartree–Fock and correlation energies extrapolated separately using $X=2,3,4$	
(12) $\mathrm{Exp}(-\alpha X)$ and $[(X+0.5)^{-3}$ and $(X+0.5)^{-5}]$	−7.7
Hartree–Fock energy extrapolated using $X=2,3,4$ correlation energies extrapolated using $X=3,4$	
(13) $\mathrm{Exp}(-\alpha X)$ and $(X+0.5)^{-3}$	−4.7
(14) $\mathrm{Exp}(-\alpha X)$ and $(X)^{-3}$	0.0
(15) HF-limit[b] and $(X)^{-3}$	0.6
Target energy[c]	−128 869. 6

[a]The value in entries 1–15 are the deviations from the target value listed in the last line.
[b]Taken from Ref. 99.
[c]Nonrelativistic valence-only-correlated energy deduced from Chakravorty and Davidson (Ref. 101) and Klopper (Ref. 17), as discussed in the text.

In order to examine the claim that the method of separate extrapolations embodied in Eqs. (14)–(17) is a sounder approach, we tested a number of different extrapolations procedures on the neon atom, for which all pertaining data are known very accurately. For the $X=2,3,4$ cc-pVXZ bases, the Hartree–Fock energies are given in Ref. 98 and the correlation energies are given in Ref. 49. The Hartree–Fock-CBS limit is very accurately given in Refs. 99 and 100. Chakravorty, Davidson, and co-workers[101–103] have determined the total nonrelativistic energy of neon to be −128.9383 hartree, and Klopper[17] has determined the correlations involving the core to be −68.65 millihartree. Subtraction of the latter from the former yields the very accurate value of −128.8696 hartree for the nonrelativistic valence-only-correlated energy of neon, which is the target of our calculations.

The results of extrapolations by 15 different formulas are listed in Table VII. The abbreviations for the formulas given in the first column manifestly refer to Eqs. (16)–(19). It is evident that the results in entries 14 and 15, which correspond to the procedures advocated in Eqs. (16) and (17) are indeed superior to all others. It might appear that the extrapolation of the total energy in entry 10 is also good. Use of this formula yields however an error of −3.75 millihartree for the Hartree–Fock-CBS limit and an error of 3.45 millihartree for the correlation CBS limit, so that the total value of −0.3 millihartree is the result of a cancellation between large

errors, which cannot necessarily be relied upon in general. By contrast, in entry 15, the HF energy is error-free and the correlation error is only 0.6 millihartree. It follows that, in entry 14, there is only a cancellation between −0.6 millihartree in the HF energy and +0.6 millihartree in the correlation energy.

We have made comparisons similar to Table VII for the molecules and atoms that are the objects of the present investigation. They are exhibited in the Appendix and confirm the aforementioned conclusions. Nonetheless, we shall occasionally also consider the results of extrapolations of the type given in entries 10 and 11 of Table VII for the total energy. They will be denoted as follows:

$$\text{CBS-2} = \text{Total energy extrapolated using}$$
$$(X+0.5)^{-4} \text{ with } X=3,4, \qquad (20)$$

$$\text{CBS-3} = \text{Total energy extrapolated using}$$
$$(X-0.3)^{-3} \text{ with } X=3,4. \qquad (21)$$

V. COMPLETE BASIS LIMITS FOR THE FULL-VALENCE CI ENERGIES OF C, N, O, F AND C_2, N_2, O_2, F_2

A. Analysis of the molecular valence-correlation energies

We begin by analyzing the CBS limits of the correlation energies in terms of contributions from excitation levels in order to gain a quantitative insight in the way in which the various excitation levels participate in the total valence correlation.

The relevant results for the four molecules are summarized in Table VIII. For each molecule, the various rows list the contributions from the various excitation levels and the correlation totals. Columns 2–4 give the FCI energies for cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, the values for the quadruple-ζ bases being identical to those in Tables I–IV. The last column lists the CBS limits obtained via the extrapolation method specified in Eqs. (16) and (17) for the correlation energy.

For the C_2 molecule, two sets of results are listed in Table VIII, in accordance with the discussion in Sec. III A. In the first set, the excitations are generated from the dominant single reference determinant, as was done in Table I. In the second set, the excitations are generated from the seven-determinant zeroth-order reference space identified in Sec. III A. The correlation energy *totals* obtained along the two avenues are manifestly the same, as they must be. The slight differences between them are within the uncertainties predicted in Table I and could be readily reduced if desirable. The two avenues differ significantly in the magnitudes of the individual contributions of the higher excitation, i.e., for $x \geqslant 4$. These are much smaller for the calculations based on the seven-determinant reference function and, in fact, more similar to those in the other molecules. In this respect, this choice of reference function is preferable. The corresponding

TABLE VIII. Analysis of the valence-correlation energy contributions in C_2, N_2, O_2, F_2 for the cc-pVXZ basis sets ($X=2,3,4$) and the complete basis set (in millihartree).

Contribution	VDZ	VTZ	VQZ	CBS[a]
	C_2 [single-determinant zeroth-order reference]			
$\Delta E_{HF}(1,2)$[b]	273.87	306.97	317.99	326.03
$\Delta E(3)$	21.41	24.80	25.48	25.98
$\Delta E(4)$	39.06	43.34	44.84	45.93
$\Delta E(5,6)$	7.15	8.23	8.54	8.77
$\Delta E(7,8)$	0.16	0.19	0.20	0.21
Total	341.65	383.53	397.02	406.86
	C_2 [seven-determinant zeroth-order reference]			
$\Delta E_{HF}(MCREF)$[c]	80.32	79.29	79.14	79.03
$\Delta E_{MCREF}(1,2)$[d]	231.76	267.55	279.16	287.63
$\Delta E(3)$	18.48	23.12	24.20	24.99
$\Delta E(4)$	10.01	12.20	12.92	13.45
$\Delta E(5,6)$	1.07	1.44	1.54	1.61
$\Delta E(7,8)$	0.01	0.01	0.01	0.01
Total	341.65	383.61	396.97	406.72
	N_2 [single-determinant zeroth-order reference]			
$\Delta E_{HF}(1,2)$[b]	287.45	344.98	364.76	379.19
$\Delta E(3)$	10.86	16.01	16.95	17.64
$\Delta E(4)$	22.35	27.70	29.65	31.07
$\Delta E(5,6)$	2.14	3.07	3.22	3.33
$\Delta E(7,8)$	0.04	0.06	0.07	0.08
Total	322.84	391.83	414.65	431.30
	O_2 [two-determinant zeroth-order reference]			
$\Delta E_{HF}(MCREF)$[c]	37.51	36.44	36.39	36.35
$\Delta E_{MCREF}(1,2)$[d]	317.85	403.85	432.96	454.20
$\Delta E(3)$	14.90	22.91	25.30	27.04
$\Delta E(4)$	8.78	13.41	15.29	16.66
$\Delta E(5,6)$	0.75	1.35	1.58	1.75
$\Delta E(7,8)$	0.01	0.02	0.02	0.02
Total	379.80	477.98	511.54	536.03
	F_2 [single-determinant zeroth-order reference]			
$\Delta E_{HF}(1,2)$[b]	376.31	488.40	528.27	557.36
$\Delta E(3)$	7.95	14.84	16.70	18.06
$\Delta E(4)$	27.74	38.91	43.29	46.49
$\Delta E(5,6)$	1.65	3.15	3.53	3.81
$\Delta E(7,8)$	0.03	0.04	0.05	0.06
Total	413.68	545.34	591.84	625.77

[a]See Eqs. (16) and (17).
[b]Energy of wave function including single+double excitations minus energy of optimized single-determinant HF energy, as defined in Eq. (13).
[c]Energy of SD-NO-based multiconfigurational reference function minus energy of optimized single determinant.
[d]Energy of wave function including single+double excitations minus energy of SD-NO-based multiconfigurational reference function.

calculations are no more difficult than those for the single-determinant reference function.

For the three cases with single-determinant reference functions (the first C_2 set, N_2, F_2), the contributions $\Delta E_{HF}(1,2)$ listed for the single+double excitations represent the differences from the Hartree–Fock energies, i.e., the optimized single-determinant energies [see Eq. (13)], as was done in Tables I–IV, so that the totals represent the conventional correlation energies. For the two cases with a multideterminant reference function (the second C_2 set and O_2), the contribution listed first, viz. $\Delta E_{HF}(MCREF)$, is the difference between the energy of the multiconfigurational reference function (MCREF) and the optimized Hartree–Fock energy of the dominant single determinant. The contribution listed next, viz. $\Delta E_{MCREF}(1,2)$, is the difference between the wave function including all single and double excitations with respect to the reference function and the energy of the reference function.

The data in Table VIII furthermore show the following.

(A) In confirmation of the statement at the end of Sec. II A 1, the convergence in terms of successive excitation levels is rapid.

(i) The excitations $x=1+2$ contribute hundreds of milli-hartree to the correlation energy.

(ii) The excitations $x=3+4$ contribute tens of millihartree to the correlation energy.

(iii) The excitations $x=5+6$ contribute a few millihartree to the correlation energy.

(iv) The excitations $x=7+8$ contribute hundredths of millihartree to the correlation energy, provided the multiconfigurtional reference for C_2 is used.

(B) The contributions for $x=3$ and for $x=4$ are comparable in magnitude and both are always important. The contributions of the quadruples are larger than those of the triples when the reference function is a singlet single determinant, but the converse is true for the other two cases. *It must therefore be concluded that any type of CI procedure omitting triple excitations while including quadruple excitations is unsound.*

(C) The singles+doubles contributions approach the CBS limit more slowly than those from the higher excitations.

(D) The correlation energy contributions from $x=2$ increases with the number of valence electrons in the system, whereas that is not so for the contributions from the higher excitations. This is consistent with recent observations by the present authors of a near linear increase of the correlation energy with the number of valence electrons.[104]

We also observe that, in all cases, the same CBS total is obtained regardless of whether one directly extrapolates the totals or whether one extrapolates the contributions of each excitation level separately and then adds these up.

As regards the comparison to previous work, we note that the correlation energy results of N_2 and F_2 for the triple-ζ as well as the quadruple-ζ bases are close to those from CCSD(T) calculations, namely, -390.4 millihartree and -544.1 millihartree, respectively.[105] On the other hand, our CBS correlation energies for these two molecules are considerably larger than those mentioned in Ref. 104, viz., -421.4 millihartree and -609.5 millihartree, which were based on CCSD(T) extrapolations listed in Ref. 27. This may be because the latter were obtained by an exponential rather than a X^{-3} CBS extrapolation (see Sec. IV).

B. Total atomic and molecular energies

For the atoms C, N, O, F, the full CI energies of the ground states were obtained as follows. For carbon and nitrogen, we calculated the FCI energies directly for the VDZ, VTZ, and VQZ basis sets. In the case of oxygen, we took the FCI/ROHF values for the VDZ and VQZ basis sets from the Environmental and Molecular Sciences Laboratory (EMSL) basis set library information.[98] Since the oxygen value for the VTZ basis is not reported in the EMSL library, we calculated its FCI/ROHF energy directly. For fluorine, the energy values for all three basis sets ($X=2,3,4$) were taken from the EMSL basis set Library. These energies have been obtained from CCSDT/unrestricted Hartree–Fock (UHF) calculations. We found all of them to be within 0.1 millihartree of the FCI energies that we determined with the CEEIS method. For example, the fluorine CEEIS-FCI energy for the

VQZ basis is -99.65048 hartree, whereas the EMSL library information lists -99.65045 hartree. The atomic correlation energies were calculated as differences between the FCI energies and the Hartree–Fock energies.

The final results of our calculations for the molecules C_2, N_2, O_2, F_2 as well as for the constituent atoms C, N, O, F are collected in Table IX. It exhibits the Hartree–Fock, valence-correlation, and total energies for the cc-pVDZ, cc-pVTZ, cc-pVQZ basis sets in the columns 2, 3, and 4. The fifth and sixth columns of Table IX list the CBS limits, obtained with the extrapolation methods CBS-1A of Eq. (16) and CBS-1B of Eq. (17). The molecular correlation energies are identical with the total correlation energies we had analyzed in Table VIII.

Most of the accurate literature values for the HF-CBS limits are slightly higher than our (VDZ-VTZ-VQZ-based) HF-CBS estimates: by 0.55 millihartree for C, by 0.54 millihartree for N, by 0.66 millihartree for O, by 0.69 millihartree for F, by 1.02 millihartree for C_2, by 0.08 millihartree for F_2. On the other hand, our estimate is higher by 0.08 millihartree for N_2 and by 0.82 millihartree for O_2.

VI. RELATION BETWEEN EXPERIMENTAL DATA AND CALCULATED ENERGY VALUES

A. Experimental values

The experimental information to which our theoretical results have to be related are the atomic energies $E_{ex}(atom)$ and the binding energies $E_{ex}(bond)$ of the corresponding homonuclear diatomic molecules. The former are obtained as the sums of the atomic ionization energies given in the tables of Moore[106] and of Kelly.[107] For the binding energies, we used the optimized values recently established by Ruscic *et al.* in the *Active Thermochemical Data Project*.[108,109] From these experimental data, one obtains the experimental molecular energies

$$E_{ex}(mol) = 2E_{ex}(atom) + E_{ex}(bond), \qquad (22)$$

where all quantities are taken to be negative. For each system, the values of these three energies for the various systems are listed in Table X in the four rows labeled "experimental."

These energies contain however a number of small additional effects, which have to be accounted for in the intended comparison with our computations.

B. Zero-point vibrations

First, the experimental binding energies are measured with respect to the lowest molecular vibrational level. The *electronic* binding energy is therefore

$$E_{el}(bond) = E_{ex}(bond) - E_{zpvb}(bond). \qquad (23)$$

We obtained the zero-point-vibrational energies $E_{zpvb}(bond)$ from the tables of Huber and Herzberg,[82] which are also quoted by Ruscic *et al.*[108,109] The values for the four atoms and their diatomic molecules are listed in Table X in the four rows labeled "vibration-rotation."

TABLE IX. Summary of energies calculated for C, N, O, F and C_2, N_2, O_2, F_2 (in hartree).

Energy type	VDZ	VTZ	VQZ	CBS-1A[a]	CBS-1B[b,c]
		C_2 molecule ($^1\Sigma_g^+$)			
Hartree–Fock	−75.386 90	−75.401 45	−75.405 77	−75.407 59	−75.406 57
Valence correlation	−0.341 65	−0.383 53	−0.397 02	−0.406 86	−0.406 86
Total	−75.728 55	−75.784 97	−75.802 80	−75.814 45	−75.813 43
		C atom (^{3}P)			
Hartree–Fock	−37.682 42	−37.686 71	−37.688 30	−37.689 24	−37.688 69
Valence correlation	−0.078 36	−0.094 57	−0.098 76	−0.101 82	−0.101 82
Total	−37.760 78	−37.781 28	−37.787 05	−37.791 06	−37.790 51
		N_2 molecule ($^1\Sigma_g^+$)			
Hartree–Fock	−108.954 13	−108.983 47	−108.991 08	−108.993 75	−108.993 83
Valence correlation	−0.322 84	−0.391 83	−0.414 65	−0.431 3	−0.431 3
Total	−109.276 98	−109.375 30	−109.405 73	−109.425 05	−109.425 13
		N atom (^{4}S)			
Hartree–Fock	−54.388 41	−54.397 36	−54.400 18	−54.401 48	−54.400 94
Valence correlation	−0.090 28	−0.117 64	−0.124 96	−0.130 3	−0.130 3
Total	−54.478 70	−54.515 00	−54.525 14	−54.531 78	−54.531 24
		O_2 molecule ($^3\Sigma_g^-$)			
Hartree–Fock	−149.608 08	−149.652 57	−149.663 99	−149.667 93	−149.668 75
Valence correlation	−0.379 80	−0.477 98	−0.511 54	−0.536 03	−0.536 03
Total	−149.987 87	−150.130 55	−150.175 53	−150.203 96	−150.204 78
		O atom (^{3}P)			
Hartree–Fock	−74.787 51	−74.805 64	−74.810 84	−74.812 93	−74.812 27
Valence correlation	−0.122 55	−0.168 59	−0.182 97	−0.193 46	−0.193 46
Total	−74.910 06	−74.974 24	−74.993 81	−75.006 39	−75.005 73
		F_2 molecule ($^1\Sigma_g^+$)			
Hartree–Fock	−198.685 67	−198.752 04	−198.768 27	−198.773 52	−198.773 44
Valence correlation	−0.413 68	−0.545 34	−0.591 84	−0.625 77	−0.625 77
Total	−199.099 35	−199.297 38	−199.360 11	−199.399 29	−199.399 21
		F atom (^{2}P)			
Hartree–Fock	−99.371 86	−99.400 93	−99.408 95	−99.412 01	−99.411 32
Valence correlation	−0.155 79	−0.219 61	−0.241 50	−0.257 47	−0.257 47
Total	−99.527 65	−99.620 54	−99.650 45	−99.669 48	−99.668 79

[a]See Eq. (16).
[b]See Eq. (17).
[c]The exact ROHF-CBS limits are taken from Refs. 98–100 and adjusted to correspond to nonequivalent orbitals as discussed in Sec. IV B, Table VI.

C. Relativistic effects

Next, the atomic as well as the molecular energies in Eqs. (22) contain relativistic effects, whereas our calculations do not. These energy contributions are commonly expressed as the sum of spin-orbit coupling energies and scalar-relativistic energies. For the systems at hand, only the atoms F, O, and C contain spin-orbit couplings since, in N and in the four molecules, either the spin or the orbital angular momentum vanishes. We took these three nonzero spin-orbit-coupling energies from the work of Feller and Sordo[29] and they are listed in Table X in the four rows labeled "spin-orbit coupling."

Feller and Sordo[29] also gave the scalar-relativistic contributions to the energy differences $E(\text{bond})=[E(\text{mol}) -2E(\text{at})]$, and we used these values for the binding energies. From them, we deduced the scalar-relativistic energies for the separate atoms and molecules as follows. For atoms, ex-

cellent theoretical nonrelativistic total energies have been given by Chakravorty, Davidson et al.[101–103] and, by subtracting these from the above-mentioned experimental atom energies (obtained from the atomic ionization tables[106,107]), we deduced the atomic relativistic energies. Further subtraction of the spin-orbit coupling energies, where nonzero, yielded then the atomic scalar-relativistic energies. Adding to them the aforementioned scalar-relativistic energy differences of Feller and Sordo,[29] we then found the scalar-relativistic energies of the molecules. All scalar-relativistic contributions are listed in Table X in the four rows labeled "scalar relativistic."

D. Electron correlations involving the core

Finally, the energies in Eqs. (22) also contain the correlation effects between the core electrons and between the

TABLE X. Relations between experimental and nonrelativistic valence-correlated energies of the ground states of C, N, O, F and C_2, N_2, O_2, F_2 (in millihartree).

	C_2	C	$2C \rightarrow C_2$
Experimental[a]	−75 935.3	−37 851.8	−231.7±0.8
Vibration-rotation[b]	4.2	0.0	4.2
Scalar relativistic[c]	−13.0	−6.65	0.3
Spin-orbit coupling[c]	0.0	−0.15	0.3
Core correlations[d]	−112.4	−55.0	−2.4
Nonrelativistic valence-correlated[e]	−75 814.1	−37 790.0	−234.1
	N_2	N	$2N \rightarrow N_2$
Experimental[a]	−109 578.5	−54 610.0	−358.5±(<0.1)
Vibration-rotation[b]	5.4	0.0	5.4
Scalar relativistic[c]	−41.2	−20.7	0.2
Spin-orbit coupling[d]	0.0	0.0	0.0
Core correlations[d]	−119.0	−58.8	−1.4
Nonrelativistic valence-correlated[e]	−109 423.7	−54 530.5	−362.7
	O_2	O	$2O \rightarrow O_2$
Experimental[a]	−150 400.2	−75 106.1	−188.0±(<0.1)
Vibration-rotation[b]	3.6	0.0	3.6
Scalar relativistic[c]	−76.4	−38.35	0.3
Spin-orbit coupling[c]	0.0	−0.35	0.7
Core correlations[d]	−124.9	−62.1	−0.7
Nonrelativistic valence-correlated[e]	−150 202.5	−75 005.3	−191.9
	F_2	F	$2F \rightarrow F_2$
Experimental[a]	−199 670.1	−99 805.6	−58.9±0.2
Vibration-rotation[b]	2.1	0.0	2.1
Scalar relativistic[c]	−141.8	−70.9	0.0
Spin-orbit coupling[c]	0.0	−0.6	1.2
Core correlations[d]	−130.8	−65.4	0.0
Nonrelativistic valence-correlated[e]	−199 399.6	−99 668.7	−62.2

[a]The molecular energy is that in the lowest vibrational level. See Secs. VI A and VI B.
[b]See Sec. VI B.
[c]See Sec. VI C.
[d]See Sec. VI D.
[e]See Sec. VI E.

core and the valence electrons, which are omitted in our calculations listed in Table IX. Fortunately, these additional correlation energy corrections have also been determined by previous authors. They are summarized in Table XI.

For the atoms, Noga *et al.*[18] as well as Gdanitz[19,20] have made calculations of very high accuracy, which agree quite closely with each other. Gdanitz' values,[20] which are obtained with the r_{12}-MR-ACPF method (r_{12} added to a multireference averaged-coupled-pair-functional[110]), appear to be slightly more accurate. We chose however the values of Noga *et al.*,[18] which are obtained using the CCSD(T)-R12 method, because the available molecular values are also

TABLE XI. Correlation energy contributions involving the cores (millihartree).

	C, C_2	N, N_2	O, O_2	F, F_2
Values used in the present study				
Atom[a]	−55.04	−58.78	−62.14	−65.44
Molecule	−112.37[b]	−118.98[c]	−124.92[b]	−130.75[c]
Binding	−2.29	−1.42	−0.64	0.13
Other literature values for the binding energy				
Peterson *et al.*[d] (best estimate)	−2.39	−1.43	−0.48	0.16
Boese *et al.*[e] (best estimate)	⋯	−1.26	−0.37	0.16

[a]Values obtained by Noga *et al.* (Ref. 18) at the CCSD(T)-R12 level of theory.
[b]Deduced by the present authors, as discussed in Sec. VI D, from the values given by Noga *et al.* (Ref. 18) and Klopper (Ref. 17) for N_2, F_2, C, N, O, and F, using CCSD(T)-R12 calculations (see Sec. IV B 2 for more details).
[c]Molecular values obtained by Klopper (Ref. 17) using the CCSD(T)-R12 level of theory.
[d]See Ref. 56.
[e]See Ref. 44.

TABLE XII. Errors (in millihartree) of the atomic, molecular, and binding energies for the CEEIS-FCI calculations and the corresponding CBS limits with respect to the nonrelativistic valence-corrected energies derived from experiment in Table X.

System	CEEIS-FCI calculations			CBS extrapolations			
	VDZ	VTZ	VQZ	1A[a]	1B[b]	2[c]	3[d]
C	29.2	8.7	3.0	−1.1	**−0.6**	−0.4	−0.7
C_2	85.6	29.1	11.3	−0.4	**0.6**	1.0	−0.1
$2C \rightarrow C_2$	27.2	11.7	5.4	1.8	**1.8**	1.8	1.3
N	51.8	15.5	5.4	−1.3	**−0.7**	−0.5	−1.1
N_2	146.7	48.4	18.0	−1.4	**−1.4**	0.4	−1.4
$2N \rightarrow N_2$	43.1	17.4	7.3	1.2	**0.0**	1.4	0.8
O	95.3	31.1	11.5	−1.1	**−0.5**	0.2	−1.0
O_2	214.6	72.0	27.0	−1.5	**−2.3**	1.0	−1.6
$2O \rightarrow O_2$	24.1	9.9	4.0	0.7	**−1.3**	0.6	0.4
F	141.1	48.2	18.3	−0.8	**−0.1**	1.0	−0.8
F_2	300.3	102.2	39.5	0.3	**0.4**	3.3	−0.4
$2F \rightarrow F_2$	18.2	5.9	3.0	1.9	**0.6**	1.3	1.2

[a]CBS-1A extrapolation: see Eq. (16).
[b]CBS-1B extrapolation: see Eq. (17).
[c]CBS-2 extrapolation: see Eq. (20)
[d]CBS-3 extrapolation: see Eq. (21)

computed by this approach. These atomic values are listed in the first row of Table XI.

For the molecules N_2 and F_2, Klopper[17] as well as Noga *et al.*[18] have determined very accurate values, the former using the CCSD(T)-R12B method, the latter with the CCSD[T]-R12 method, in both cases using very large ($spdfgh$) basis sets. Their values agree very closely. Since calculations of similar accuracy are not available for the molecules C_2 and O_2, we estimated the correlation involving the core here as follows. Assuming that the environment surrounding the $1s$ core orbitals changes little when the atoms combine to form a molecule, we conjectured a linear relation between the free atoms and the corresponding homonuclear diatomic molecules for the correlation energy *changes* when going from one atom to the next. Thus, we interpolated the core correlation energies for C_2 and O_2 with the formula

$$E_{cc}(C_2 \text{ or } O_2) = E_{cc}(N_2) + [E_{cc}(C \text{ or } O) - E_{cc}(N)]$$
$$\times [E_{cc}(F_2) - E_{cc}(N_2)]/[E_{cc}(F) - E_{cc}(N)],$$

where $E_{cc}(X)$ denotes the correlation energy involving the core of system X. The core correlation energies of the molecules are listed in the second row of Table XI. Subtraction of the first row, multiplied by 2, from the second row yields the core correlation contributions to the binding energies in the third row of Table XI.

The second section of Table XI contains core correlation values for the binding energies that were obtained earlier by Dunning and co-workers[56] and by Boese *et al.*[44] For N_2 and F_2, they exhibit satisfactory agreement with the values of the third row. For C_2 and O_2, the equally good agreement with the third row implies that our interpolated values are reasonable.

The core correlation energy values of the first section of Table XI are also entered in Table X in the four rows labeled "core correlation."

E. The nonrelativistic valence-correlated energy

The "total" energies calculated in Sec. III and listed in Table IX are the total electronic energies exclusive of the correlations involving the core and exclusive of the relativistic effect. We call it the *nonrelativistic valence-correlated energy* $E(nr, vcrl)$. According to the preceding discussion, each of the three *experimental* energies that occur in Eq. (22) can then be expressed as follows:

$$E_{ex} = E(nr, vcrl) + E(\text{core corrl}) + E(\text{spin-orbit})$$
$$+ E(\text{scalar corrl}) + E(\text{zero-point vibr}), \quad (24)$$

if the value zero is assigned to appropriate contributions. Conversely, experiment-based values for the $E(nr, vcrl)$ can be deduced from Eq. (24) by subtracting the four corrections on the right-hand side from E_{ex}. These values are listed in Table X in the four rows labeled "nonrelativistic valence correlated" and they are thus the values with which our theoretical results ought to be compared.

VII. COMPARISON OF CEEIS-FCI-CBS ENERGIES WITH EXPERIMENT

A. CEEIS-FCI-CBS predictions for atoms, molecules, and binding energies

How close do our calculated nonrelativistic valence-correlated energies $E(nr, vcrl)$ come to those deduced in Table X from experiment? An overview of the relevant errors is given in Table XII. The columns list the CEEIS-FCI en-

ergy errors for the three kinds of basis sets as well as for the CBS limits obtained with the four CBS extrapolations formulated in Sec. IV above by Eqs. (16), (17), (20), and (21). The binding energies are obtained by subtracting the extrapolated reactant and product values.

It is apparent that, for the calculated $X=2,3,4$ FCI energies, the errors in the individual systems are considerably larger than the errors in the binding energies, implying that some cancellation of errors is taking place in forming the differences. Nonetheless, even for the largest basis sets (cc-pVQZ), chemical accuracy cannot be achieved in any of these systems without extrapolation, even for the binding energies. The CBS extrapolations lead to substantial improvement in the predictions and there remain only slight differences between the magnitudes of the errors of the individual systems and those of the binding energies.

There are only three errors in the table that fall slightly outside the chemical accuracy criterion of 1 kcal/mol ≈ 1.6 millihartree. The first is the binding energy of C_2 (1.8 millihartree). As regards this system, we note that Ruscic[108] give an uncertainty of 0.8 millihartree for their best-estimated experimental value (see Table X, line 1), and that the two most recently reported experimental values[108,111] for this binding energy differ in fact by 0.5 millihartree. Thus, we may still claim "chemical accuracy within the experimental error bars." The second error in excess of 1 millihartree is the binding energy of F_2 (1.9 millihartree) for method 1A. But, for the better method 1B it is only 0.6 millihartree. The third error larger than 1.6 millihartree is the energy of the oxygen molecule (−2.3 millihartree) for method 1B. Since this molecule has a triplet ground state, it is possible that, here, our neglect of the X^{-5} term in the CBS extrapolation of Eq. (15) causes a larger error than in the other molecules, which have singlet ground states (see Ref. 17). Also, the possibility of a slight error in the corrections applied in Table X for O_2 cannot be entirely excluded.

Overall, the method CBS-1B, defined by Eq. (17), appears to be the best of the four extrapolation choices, as in fact it should be, and it is therefore printed in bold face. Moreover, it allows for separate treatments of the Hartree–Fock and the correlation parts. The only exception is the O_2 molecule for the reason discussed above. It may also be noted that the errors of all calculated VXZ energies decrease by a factor of about 3 in going from one VXZ basis to the corresponding V$(X+1)$Z basis. One might therefore surmise a further decrease by a factor of 3 in the errors of the CBS limits when quintuple-ζ basis sets are taken into account in the FCI calculations, which would bring all of them below 1 millihartree. In this case, it would also be possible to use the CBS extrapolation formula (15), including X^{-5} as well as X^{-3} terms.

It should be appreciated that the explicit full CI calculations for the quadruple-ζ bases would have required the capability of handling 3.6×10^{12}, 1.6×10^{15}, 1.7×10^{17}, and 3.7×10^{19} determinants for C_2, N_2, O_2, and F_2, respectively, computational tasks that lie beyond the reach of current direct full CI programs by a wide margin. The CEEIS method of determining full CI energies has therefore been essential in achieving the accuracy documented in Table XII.

B. Comparison with other methods

In Table XIII we compare our CBS limits with the best recent calculations by other sophisticated methods. For each system, the first entry lists the nonrelativistic valence-correlated energy deduced in Table X from experiment. The next four rows list the deviations from these experiment-deduced target values for our four CBS extrapolations from Table XII. The remaining rows list the analogous deviations for the following investigations.

(1) CCSD(T)/CBS and internally contracted multireference configuration (ICMRCI)+Q/CBS calculations by Peterson, Wilson, Woon, and Dunning,[56]

(2) CCSD(T)-R12 and CCSD[T]-R12 calculations by Klopper[17] and by Noga, Valiron, and Klopper.[18]

(3) R12-MR-ACPF calculations by Gdanitz.[20,21]

It is apparent that only the R12-based methods approach the target energies uniformly as closely as the CEEIS-FCI-CBS method. So far however, complete R12-based results are only available for N_2 and F_2 viz., those by Klopper and Noga *et al.* The error of 2.6 millihartree obtained by CCSD(T)-R12B for F_2 is surprisingly large. In the case of Gdanitz' R12-MR-ACPF method, all atomic energies calculated in Ref. 20 are excellent, but the atomic and molecular energies obtained in Ref. 21 for N_2 are both in error by 5 millihartree, so that the excellent binding energy appears to result from the cancellation of quite large errors (5 millihartree). The methods that do not include R12 terms, viz. the coupled-cluster as well as the multi-reference-CI methods, yield larger errors.

In Table XIV we compare the binding energy errors predicted by the CEEIS-FCI-CBS approach with those obtained by a number of commonly used methods that include no R12 terms. Not listed are any of the less accurate methods involving only double excitations (such as MP2 and CCSD).

The first four entries list the binding energy errors of the present work found in Table XI. The fifth entry is another extrapolation of our cc-pVXZ data using the total energies, which is elaborated in more detail as entry No. 3 in Table XV to be discussed below in the Appendix. Although it yields good binding energies, Table XV shows that it does quite poorly for the individual systems.

Entries 6 and 7 list variational ICMRCI calculations. In the case of entry 7, they are complemented by the multireference analog of the Davidson correction Q.[112] Entries 8, 9, 10 are coupled-cluster calculations including triple excitations. The extrapolation procedures used in entries 6, 7, 8 differ from those used in entries 9, 10 as indicated in the table. In all of them the total energies are extrapolated. The basis set ranges used in the extrapolation procedures are given by the X values in the second column. It is apparent from these X ranges that, *in all of these calculations (entries 6 to 10), the basis sets are considerably larger than the quadruple-ζ basis sets used in the present work (entries 1–5): They are up to quintuple-ζ bases in entries 6,7, up to sextuple-ζ bases in entry 8, and up to augmented septuple-ζ bases in entries 9, 10.*

Notwithstanding this use of larger basis sets, the methods in entries 6–10 perform worse than the CEEIS-FCI

TABLE XIII. Errors of accurate theoretical methods for calculating the nonrelativistic valence-correlated energies of C_2, N_2, O_2, F_2 (in millihartree).

	C_2	C	$2C \rightarrow C_2$
Deduced from experiment[a]	**−75 814.1**	**−37 790.0**	**−234.1**
CEEIS-FCI CBS-1A[b]	−0.4	−1.1	1.8[1.3][c]
CEEIS-FCI CBS-1B[d]	0.6	−0.6	1.8[1.3][c]
CEEIS-FCI CBS-2[e]	1.0	−0.4	1.8[1.3][c]
CEEIS-FCI CBS-3[f]	−0.1	−0.7	1.3[0.8][c]
CCSD(T)+CBS[g]	5.5	1.4	2.7[2.2][c]
ICMRCI+Q+CBS[h]	5.1	0.3	4.5[4.0][c]
R12-MR-ACPF[i]	⋯	0.0	⋯
	N_2	**N**	**$2N \rightarrow N_2$**
Deduced from experiment[a]	**−109 423.7**	**−54 530.5**	**−362.7**
CEEIS-FCI CBS-1A[b]	−1.4	−1.3	1.2
CEEIS-FCI CBS-1B[d]	−1.4	−0.7	0.0
CEEIS-FCI CBS-2[e]	0.4	−0.5	1.4
CEEIS-FCI CBS-3[f]	−1.4	−1.1	0.8
CCSD(T)+CBS[g]	5.0	1.9	1.2
ICMRCI+Q+CBS[h]	6.2	2.1	2.0
R12-MR-ACPF[i]	⋯	0.2	⋯
R12-MR-ACPF[j]	5.0	2.5	0.0
CCSD(T)-R12B[k]	2.2	⋯	⋯
CCSD[T]-R12[l]	1.3	0.7	0.1
	O_2	**O**	**$2O \rightarrow O_2$**
Deduced from experiment[a]	**−150 202.5**	**−75 005.3**	**−191.9**
CEEIS-FCI CBS-1A[b]	−1.5	−1.1	0.7
CEEIS-FCI CBS-1B[d]	−2.3	−0.5	−1.3
CEEIS-FCI CBS-2[e]	1.0	0.2	0.6
CEEIS-FCI CBS-3[f]	−1.6	−1.0	0.4
CCSD(T)+CBS[g]	7.5	2.8	1.9
ICMRCI+Q+CBS[h]	11.8	4.9	2.0
R12-MR-ACPF[i]	⋯	0.7	⋯
	F_2	**F**	**$2F \rightarrow F_2$**
Deduced from experiment[a]	**−199 399.6**	**−99 668.7**	**−62.2**
CEEIS-FCI+CBS-1A[b]	0.3	−0.8	1.9
CEEIS-FCI+CBS-1B[d]	0.4	−0.1	0.6
CEEIS-FCI+CBS-2[e]	3.3	1.0	1.3
CEEIS-FCI CBS-3[f]	−0.4	−0.8	1.2
CCSD(T)+CBS[g]	8.6	3.5	1.6
ICMRCI+Q+CBS[h]	17.6	7.2	3.2
R12-MR-ACPF[i]	⋯	0.8	⋯
CCSD(T)-R12B[k]	2.6	⋯	⋯
CCSD[T]-R12[l]	1.7	0.8	0.1

[a]Total nonrelativistic valence-correlated energy from Table X. For the theoretical entries, the differences [(predicted value) minus (experimentally deduced target value)] are listed.
[b]CBS-1A extrapolation defined by Eq. (16).
[c]The error in the square bracket corresponds to the comparison with the experimental binding energy value reported by Urdahl *et al.* (Ref. 111).
[d]CBS-1B extrapolation defined by Eq. (17).
[e]CBS-2 extrapolation defined by Eq. (20).
[f]CBS-3 extrapolation defined by Eq. (21).
[g]CCSD(T)+CBS estimate by Dunning and co-workers (Ref. 56).
[h]ICMRCI+Q+CBS estimate by Dunning and co-workers (Ref. 56).
[i]R12-ACPF: The results for atoms are taken from Gdanitz (Ref. 20).
[j]R12-MR-ACPF: The values for the N_2 molecule and for the binding energy are taken from Gdanitz in Ref. 21. We have deduced the value for the N atom by subtraction.
[k]CCSD(T)-R12B value of Klopper (Ref. 17).
[l]CCSD[T]-R12 values of Noga *et al.* (Ref. 18) obtained with very large basis set (*spdfgh*) for molecules. For atoms the data corresponds to CCSD(T)-R12 level of theory (Ref. 18).

method in rows 1–5, which uses only quadruple-ζ bases. The reason must be that certain relevant configurations, which are taken into account in the latter, are missing in the former. The most rigorous CCSDT method yields the worst results.

In recent years, the quantum Monte Carlo (QMC) approach[113–118] has received attention. Some results reflecting the performance of these methods are therefore included in Table XIV. The results of fixed-node diffusion quantum Monte Carlo (FN-DQMC) calculations by Lüchow and Fink,[115] listed in entry 11, yield errors of about 9 millihartree for the binding energy. The Ornstein–Uhlenbeck-type diffusion quantum Monte Carlo calculations by Lu,[116] listed as entry 12, yield binding energies within chemical accuracy, but the paper does not give any information regarding the energies of the atoms and molecules.

Tables XIII and XIV suggest that the CEEIS-FCI-CBS approach compares favorably with other high-accuracy *ab initio* methods in recovering the energies of C, N, O, F atoms and C_2, N_2, O_2, F_2 molecules and their binding energies.

VIII. CONCLUSIONS

Full CI energies of the molecules C_2, N_2, O_2, F_2, and of their constituent atoms were closely approximated, within the context of Dunning's correlation-consistent double-, triple- and quadruple-ζ basis sets, by the method of correlation energy extrapolation by intrinsic scaling (CEEIS).[49,50] These accurate extrapolations to the optimal energies in very large full CI spaces are obtained from *sequences* of CI calculations of *much smaller* dimensions, and increasing the latter will yield increasingly more precise extrapolations. Here, we have pushed the method to approximate the variational full CI energies within about 0.3 millihartree, an accuracy usually not achieved by coupled-cluster methods. Also, in contrast to most coupled cluster methods, the CEEIS method was found to work for reference wave functions of the multiconfiguration type equally well as of the single-determinant type.

The CEEIS-FCI method also provided an accurate elucidating account of the relative contributions to the correlation energy that are due to the different levels of excitation with respect to the zeroth-order reference wave function.

The FCI energies were then extrapolated to their CBS limits. For N_2 and F_2, the results agree within 1 millihartree with the energies obtained by wave functions including r_{12} terms. For C_2 and O_2, such wave functions are not yet available and the present results appear to be the best existent to date. The binding energies obtained by the present work agree with the corresponding experimental values within the chemical accuracy criterion of 1 kcal/mol.

It appears justified to expect the CEEIS-FCI-CBS approach to yield accurate energies, for individual systems as well as reaction energies, with a computational effort that is sufficiently smaller than that of standard full CI methods, so that these energies become accessible in cases where that has not heretofore been possible (e.g., for F_2 with 10^{19} determinants in the full quadruple-ζ CI space).

TABLE XIV. Absolute values of errors (in millihartree) of various theoretical methods in calculating the binding energies of C_2, N_2, O_2, F_2.

	X range	C_2	N_2	O_2	F_2
CEEIS–FCI method–cc-pVXZ basis–CBS extrapolations as indicated					
(1) CBS-1A[a]	2–4	1.8	1.2	0.7	1.9
(2) CBS-1B[b]	**2–4**	**1.8**	**0.0**	**1.3**	**0.6**
(3) CBS-2[c]	3–4	1.8	1.4	0.6	1.3
(4) CBS-3[d]	3–4	1.3	0.8	0.4	1.2
(5) CBS-4[e]	2–4	1.6	0.8	0.4	0.4
cc-pCVXZ Basis–Exponential CBS extrapolation [Eq. (18)][f]					
(6) IC-MRCI	2–5	2.1	0.5	4.9	7.0
(7) IC-MRCI+Q	2–5	4.5	1.9	1.9	3.0
(8) CCSD(T)	2–6	2.7	1.1	1.8	1.4
aug-cc-pVXZ Basis–Mixed exponential/Gaussian CBS extrapolation[g]					
(9) CCSD(T)	5–7	2.9	0.8	1.3	0.6
(10) CCSDT	5–7	6.1	1.8	1.9	1.1
Quantum Monte Carlo method					
(11) FN-DQMC[h]	⋯	8.6(±1.6)	8.8(±1.6)	⋯	⋯
(12) OUDQMC[i]	⋯	⋯	1.3(±0.5)	⋯	0.0(±0.5)

[a]See Eq. (16).
[b]See Eq. (17).
[c]See Eq. (20).
[d]See Eq. (21).
[e]CBS extrapolation of total energies by Eq. (19) with $b=0.5$, $\beta=3$, $C=0$ using $X=2, 3, 4/LMSQ$.
[f]Peterson *et al.* (Ref. 56).
[g]Feller and Sordo (Ref. 29).
[h]Fixed-node diffusion quantum Monte Carlo method by Lüchow and Fink (Ref. 115).
[i]Ornstein–Uhlenbeck diffusion quantum Monte Carlo method by Lu (Ref. 116).

TABLE XV. Energy errors[a] (millihartree) of various FCI-CBS-extrapolations applied to $X=2,3,4$ for C, N, O, F and C_2, N_2, O_2, and F_2.

Formula	C_2	C	$2C \rightarrow C_2$	N_2	N	$2N \rightarrow N_2$	O_2	O	$2O \rightarrow O_2$	F_2	F	$2F \rightarrow F_2$
Total energies extrapolated using $X=2,3,4$												
(1) $\exp(-\alpha X)$	3.0	0.7	1.6	4.3	1.4	1.4	6.3	2.9	0.5	10.4	4.1	2.3
(2) $(X)^{-3}$	2.4	−0.5	3.3	2.3	−0.7	3.8	4.5	1.2	2.1	8.4	3.8	0.8
(3) $(X+0.5)^{-3}$	−3.8	−2.7	1.6	−8.4	−4.6	0.8	−11.2	−5.8	0.4	−13.4	−6.5	−0.5
(4) $[(X+0.5)^{-3}$ and $(X+0.5)^{-5}]$	−5.0	−1.9	−1.2	−9.4	−3.1	−3.1	−14.0	−6.0	−2.0	−17.7	−9.3	0.9
(5) $(X+0.5)^{-\alpha}$, $\alpha=$optimized	−5.7	−1.6	−2.5	−10.1	−2.5	−5.0	−15.7	−6.0	−3.8	−20.2	−11.1	2.1
Total energies extrapolated using $X=3,4$												
(6) $(X+0.5)^{-3}$	−4.6	−2.2	−0.2	−9.1	−3.6	−1.8	−13.0	−5.9	−1.2	−16.3	−8.3	0.4
(7) $(X)^{-3}$	−1.8	−1.3	0.8	−4.2	−2.0	−0.2	−5.9	−2.8	−0.3	−6.3	−3.6	0.8
(8) $(X-0.1)^{-3}$	−1.2	−1.1	1.0	−3.3	−1.7	0.1	−4.4	−2.2	−0.1	−4.3	−2.6	0.9
(9) $(X-0.2)^{-3}$	−0.6	−0.9	1.2	−2.3	−1.4	0.5	−3.0	−1.6	0.1	−2.3	−1.7	1.0
(10) $(X-0.3)^{-3}$	−0.1	−0.7	1.4	−1.4	−1.1	0.8	−1.6	−1.0	0.3	−0.4	−0.8	1.1
(11) $(X+0.5)^{-4}$	1.0	−0.4	1.7	0.4	−0.5	1.4	1.0	0.2	0.6	3.3	1.0	1.3
Hartree–Fock and correlation energies extrapolated separately using $X=2,3,4$												
(12) $\exp(-\alpha X)$ and $[(X+0.5)^{-3}$ and $(X+0.5)^{-5}]$	−3.0	−1.3	−0.4	−6.1	−1.9	−2.3	−8.9	−3.6	−1.7	−10.9	−5.7	0.6
Hartree–Fock energy extrapolated using $X=2,3,4$; correlation energies extrapolated using $X=3,4$												
(13) $\exp(-\alpha X)$ and $(X+0.5)^{-3}$	−2.6	−1.7	0.9	−5.0	−2.4	−0.1	−6.8	−3.4	−0.1	−7.1	−4.3	1.4
(14) $\exp(-\alpha X)$ and $(X)^{-3}$	−0.4	−1.0	1.7	−1.4	−1.3	1.2	−1.5	−1.1	0.7	0.3	−0.8	1.8
(15) HF-limit and $(X)^{-3}$	0.6	−0.6	1.8	−1.4	−0.7	0.0	−2.3	−0.5	−1.3	0.4	−0.1	0.6

[a]Listed are the deviations from the nonrelativistic valence-correlated target energy values in Table XIII.

Various extensions of the CEEIS method are of interest. The inclusion of quintuple-ζ bases can be expected to lower the CBS error reliably below 0.5 millihartree and it will also permit an assessment of the effectiveness of the (-5) term in the CBS extrapolation of the correlation energy. Next, the CEEIS method will presumably prove useful for calculating the correlations involving the core. Recent calculations have furthermore shown that the CEEIS method is capable of yielding accurate potential energy curves.[119] Finally, the use of appropriately localized orbitals[120] is likely to facilitate applications to larger molecules.[121–135]

ACKNOWLEDGMENTS

APPENDIX: COMPARISON OF CBS EXTRAPOLATIONS FOR THE MOLECULES

In Table XV, we examine how the 15 extrapolation schemes, which had been considered for neon in Table VII of Sec. IV D, perform for the carbon, nitrogen, oxygen, and fluorine atoms and molecules. The table is organized similarly to Table VII. The comparison of the results in the various entries is seen to confirm the same general conclusions that had been reached in Sec. IV D. An exception is the formula of entry 11, which seems to perform better in these systems than it did for neon, and which is the reason for including it as Eq. (20) in Sec. IV D.

[1] E. Schrödinger, Ann. Phys. **79**, 361 (1926); Phys. Rev. **28**, 1049 (1926).

[2] E. A. Hylleraas, Z. Phys. **54**, 347 (1929); **65**, 209 (1930).

[3] S. F. Boys, Proc. R. Soc. London, Ser. A **309**, 195 (1969).

[4] S. F. Boys and N. C. Handy, Proc. R. Soc. London, Ser. A **310**, 43 (1969); **310**, 63 (1969); **311**, 309 (1969).

[5] N. C. Handy, J. Chem. Phys. **51**, 3205 (1969); Mol. Phys. **21**, 817 (1971); **26**, 169 (1973); J. Chem. Phys. **58**, 279 (1973).

[6] S. Ten-no, Chem. Phys. Lett. **330**, 169 (2000); O. Hino, Y. Tanimura, and S. Ten-no, J. Chem. Phys. **115**, 7865 (2001).

[7] R. López-Boada, E. V. Ludeña, V. Karasiev, and R. Colle, Int. J. Quantum Chem. **69**, 439 (1998).

[8] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **109**, 8232 (1998).

[9] N. Umezawa and S. Tsuneyuki, J. Chem. Phys. **119**, 10015 (2003).

[10] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **78**, 1420 (1983); K. B. Wenzel, J. G. Zabolitzky, K. Szalewicz, B. Jeziorski, and H. J. Monkhorst, ibid. **85**, 3964 (1986).

[11] W. Cencek and J. Rychlewski, J. Chem. Phys. **98**, 1252 (1993); **102**, 2533 (1995); J. Komasa and J. Rychlewski, Mol. Phys. **91**, 909 (1997); R. Bukowski, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. **104**, 3306 (1996); **110**, 4165 (1999); T. Korona, H. L. Williams, R. Bukowski, B. Jeziorski, and K. Szalewicz, ibid. **106**, 5109 (1997).

[12] B. J. Persson and P. R. Taylor, J. Chem. Phys. **105**, 5915 (1996); Theor. Chem. Acc. **97**, 240 (1997).

[13] W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985).

[14] W. Klopper and W. Kutzelnigg, Chem. Phys. Lett. **134**, 17 (1987); W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).

[15] J. Noga, W. Kutzelnigg, and W. Klopper, Chem. Phys. Lett. **199**, 497 (1992); J. Noga and W. Kutzelnigg, J. Chem. Phys. **101**, 7738 (1994).

[16] H. Müller, W. Kutzelnigg, and J. Noga, Mol. Phys. **92**, 535 (1997).

[17] W. Klopper, Mol. Phys. **99**, 481 (2001).

[18] J. Noga, P. Valiron, and W. Klopper, J. Chem. Phys. **115**, 2022 (2001).

[19] R. J. Gdanitz, Chem. Phys. Lett. **210**, 253 (1993).

[20] R. J. Gdanitz, J. Chem. Phys. **109**, 9795 (1998).

[21] R. J. Gdanitz, Chem. Phys. Lett. **283**, 253 (1998).

[22] B. O. Roos, Chem. Phys. Lett. **15**, 152 (1972); P. J. Knowles and N. C. Handy, ibid. **111**, 315 (1984); H. J. Werner and P. J. Knowles, J. Chem. Phys. **94**, 1264 (1991); J. Olsen, P. Jørgensen, and J. Simons, Chem. Phys. Lett. **169**, 463 (1990); J. Olsen, B. O. Roos, P. Jørgensen, and H. J. A. Jensen, J. Chem. Phys. **89**, 2185 (1988); R. J. Harrison, ibid. **94**, 5021 (1991); A. Povill, J. Rubio, and F. Illas, Theor. Chim. Acta **82**, 229 (1992); P. Saxe, D. J. Fox, H. F. Schaefer III, and N. C. Handy, J. Chem. Phys. **77**, 5584 (1982); C. D. Sherrill and H. F. Schaefer III, J. Phys. Chem. **100**, 6069 (1996); J. Ivanic and K. Ruedenberg, Theor. Chem. Acc. **106**, 339 (2001).

[23] J. Ivanic, J. Chem. Phys. **119**, 9364 (2003); **119**, 9377 (2003).

[24] F. Coester, Nucl. Phys. **7**, 421 (1958); F. Coester and H. Kümmel, ibid. **17**, 477 (1960); J. Čížek, J. Chem. Phys. **45**, 4256 (1966); J. Paldus, J. Čížek, and I. Shavitt, Phys. Rev. A **5**, 50 (1974); R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981); J. Phys. Chem. **93**, 1697 (1989); T. D. Crawford and H. F. Schaefer III, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (Wiley, New York, 2000), Vol. 14, p. 33; W. Klopper, J. Noga, H. Koch, and T. Helgaker, Theor. Chem. Acc. **97**, 164 (1997); T. Helgaker, T. A. Ruden, P. Jorgensen, J. Olsen, and W. Klopper, J. Phys. Org. Chem. **17**, 913 (2004).

[25] S. R. White, Phys. Rev. Lett. **69**, 2863 (1992); Phys. Rev. B **48**, 10345 (1993); S. R. White and R. L. Martin, J. Chem. Phys. **110**, 4127 (1999); A. O. Mitrushenkov, R. Linguerri, P. Palmieri, and G. Fano, ibid. **119**, 4148 (2003); G. K.-L. Chan and M. Head-Gordon, ibid. **118**, 8551 (2003); G. K.-L. Chan, M. Kállay, and J. Gauss, ibid. **121**, 6110 (2004); Ö. Legeza, J. Röder, and B. A. Hess, Mol. Phys. **101**, 2019 (2003).

[26] M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, J. Chem. Phys. **114**, 8282 (2001); M. Nakata, M. Ehara, and H. Nakatsuji, ibid. **116**, 5432 (2002); D. A. Mazziotti, ibid. **121**, 10957 (2004); Phys. Rev. Lett. **93**, 213001 (2004); T. Juhász and D. A. Mazziotti, J. Chem. Phys. **121**, 1201 (2004).

[27] D. Feller and K. A. Peterson, J. Chem. Phys. **108**, 154 (1998).

[28] D. Feller and J. A. Sordo, J. Chem. Phys. **112**, 5604 (2000); D. Feller and K. A. Peterson, ibid. **110**, 8384 (1999); D. Feller, D. A. Dixon, and J. S. Francisco, J. Phys. Chem. A **107**, 1604 (2003); D. Feller and D. A. Dixon, ibid. **107**, 9641 (2003).

[29] D. Feller and J. A. Sordo, J. Chem. Phys. **113**, 485 (2000).

[30] J. M. L. Martin and P. R. Taylor, J. Phys. Chem. A **102**, 2995 (1998).

[31] J. M. L. Martin, Chem. Phys. Lett. **310**, 271 (1999).

[32] A. D. Pradhan, H. Partridge, and C. W. Bauschlicher, Jr., J. Chem. Phys. **101**, 3857 (1994); C. W. Bauschlicher, Jr. and A. Ricca, J. Phys. Chem. A **103**, 4313 (1999).

[33] T. Yan, W. L. Hase, and C. Doubleday, J. Chem. Phys. **120**, 9253 (2004).

[34] A. G. Császár, W. D. Allen, and H. F. Schaefer III, J. Chem. Phys. **108**, 9751 (1998).

[35] G. Tarczay, A. G. Császár, W. Klopper, V. Szalay, W. D. Allen, and H. F. Schaefer III, J. Chem. Phys. **110**, 11971 (1999).

[36] G. Tarczay, A. G. Császár, M. L. Leininger, and W. Klopper, Chem. Phys. Lett. **322**, 119 (2000).

[37] A. G. Császár and M. L. Leininger, J. Chem. Phys. **114**, 5491 (2001).

[38] M. S. Schuurman, S. R. Muir, W. D. Allen, and H. F. Schaefer III, J. Chem. Phys. **120**, 11586 (2004); S. Hirata, T. Yanai, W. A. de Jong, T. Nakajima, and K. Hirao, ibid. **120**, 3297 (2004); D. W. Schwenke, ibid. **122**, 014107 (2005).

[39] J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, J. Chem. Phys. **90**, 5622 (1989); L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, ibid. **93**, 2537 (1990); L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, ibid. **94**, 7221 (1991); L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, ibid. **109**, 7764 (1998); L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, ibid. **110**, 4703 (1999).

[40] J. A. Pople, Rev. Mod. Phys. **71**, 1267 (1999).

[41] J. A. Montgomery, Jr., J. W. Ochterski, and G. A. Petersson, J. Chem. Phys. **101**, 5900 (1994).

[42] J. W. Ochterski, G. A. Petersson, and J. A. Montgomery, Jr., J. Chem. Phys. **104**, 2598 (1996).

[43] J. M. L. Martin and G. De Oliveira, J. Chem. Phys. **111**, 1843 (1999).

[44] A. D. Boese, M. Oren, O. Atasoylu, J. M. L. Martin, M. Kállay, and J. Gauss, J. Chem. Phys. **120**, 4129 (2004).

[45] C. D. Sherrill and H. F. Schaefer III, Adv. Quantum Chem. **34**, 143 (1999); I. Shavitt, Mol. Phys. **94**, 3 (1998).

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

[47] R. J. Cave, S. S. Xantheas, and D. Feller, Theor. Chim. Acta **83**, 31 (1992); D. Feller, J. Chem. Phys. **111**, 4373 (1999).

[48] P. Y. Ayala, G. E. Scuseria, and A. Savin, Chem. Phys. Lett. **307**, 227 (1999).

[49] L. Bytautas and K. Ruedenberg, J. Chem. Phys. **121**, 10905 (2004).

[50] L. Bytautas and K. Ruedenberg, J. Chem. Phys. **121**, 10919 (2004).

[51] L. Bytautas and K. Ruedenberg, J. Chem. Phys. **121**, 10852 (2004).

[52] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

[53] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **100**, 2975 (1994).

[54] A. K. Wilson, T. van Mourik, and T. H. Dunning, Jr., J. Mol. Struct.: THEOCHEM **388**, 339 (1996).

[55] M. W. Schmidt, M. T. B. Lam, S. T. Elbert, and K. Ruedenberg, Theor. Chim. Acta **68**, 69 (1985).

[56] K. A. Peterson, A. K. Wilson, D. E. Woon, and T. H. Dunning, Jr., Theor. Chem. Acc. **97**, 251 (1997).

[57] D. Feller, J. Chem. Phys. **96**, 6104 (1992); **98**, 7059 (1993).

[58] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **99**, 1914 (1993).

[59] K. A. Peterson, R. A. Kendall, and T. H. Dunning, Jr., J. Chem. Phys. **99**, 1930 (1993).

[60] K. A. Peterson, R. A. Kendall, and T. H. Dunning, Jr., J. Chem. Phys. **99**, 9790 (1993).

[61] D. E. Woon, J. Chem. Phys. **100**, 2838 (1994).

[62] A. K. Wilson and T. H. Dunning, Jr., J. Chem. Phys. **106**, 8718 (1997).

[63] G. A. Petersson and M. J. Frisch, J. Phys. Chem. A **104**, 2183 (2000).

[64] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, Chem. Phys. Lett. **286**, 243 (1998).

[65] W. Klopper, K. L. Bak, P. Jørgensen, J. Olsen, and T. Helgaker, J. Phys. B **32**, R103 (1999).

[66] D. G. Truhlar, Chem. Phys. Lett. **294**, 45 (1998).

[67] P. L. Fast, M. L. Sánchez, and D. G. Truhlar, J. Chem. Phys. **111**, 2921 (1999).

[68] K. L. Bak, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, J. Chem. Phys. **112**, 9229 (2000).

[69] J. M. L. Martin, Chem. Phys. Lett. **259**, 669 (1996).

[70] J. S. Lee and S. Y. Park, J. Chem. Phys. **112**, 10746 (2000).

[71] S. B. Huh and J. S. Lee, J. Chem. Phys. **118**, 3035 (2003).

[72] J. S. Lee, Phys. Rev. A **68**, 043201 (2003).

[73] A. J. C. Varandas, J. Chem. Phys. **113**, 8880 (2000).

[74] R. J. Gdanitz, J. Chem. Phys. **113**, 5145 (2000).

[75] W. Klopper, J. Chem. Phys. **115**, 761 (2001).

[76] E. F. Valeev, W. D. Allen, R. Hernandez, C. D. Sherrill, and H. F. Schaefer III, J. Chem. Phys. **118**, 8594 (2003).

[77] K. Kahn and T. C. Bruice, Theor. Chem. Acc. **111**, 18 (2004).

[78] W. Klopper and W. Kutzelnigg, J. Mol. Struct. THEOCHEM **135**, 339 (1986); W. Kutzelnigg, Int. J. Quantum Chem. **51**, 447 (1994); F. Jensen, Theor. Chem. Acc. **104**, 484 (2000).

[79] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955); Adv. Phys. **5**, 1 (1956).

[80] P. O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956); E. R. Davidson, Rev. Mod. Phys. **44**, 451 (1972); I. Shavitt, B. J. Rosenberg, and S. Palakit, Int. J. Quantum Chem., Symp. **10**, 33 (1976).

[81] M. W. Schmidt, K. K. Baldridge, J. A. Boatz *et al.*, J. Comput. Chem. **14**, 1347 (1993).

[82] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure: Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[83] M. Douay, R. Nietmann, and P. F. Bernath, J. Mol. Spectrosc. **131**, 250 (1988).

[84] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[85] J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987).

[86] K. Raghavahari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).

[87] G. E. Scuseria, C. L. Janssen, and H. F. Schaefer III, J. Chem. Phys. **89**, 7382 (1988).

[88] G. E. Scuseria and H. F. Schaefer III, J. Chem. Phys. **90**, 3700 (1989).

[89] G. E. Scuseria and T. J. Lee, J. Chem. Phys. **93**, 5851 (1990).

[90] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **83**, 4041 (1985); P. Piecuch and J. Paldus, Theor. Chim. Acta **78**, 65 (1990).

[91] P. Piecuch, S. A. Kucharski, K. Kowalski, and M. Musiał, Comput. Phys. Commun. **149**, 71 (2002).

[92] M. J. McGuire and P. Piecuch (private communication).

[93] K. L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker, and J. F. Stanton, J. Chem. Phys. **114**, 6548 (2001).

[94] S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **97**, 4282 (1992); **108**, 9221 (1998); S. Hirata and R. J. Bartlett, Chem. Phys. Lett. **321**, 216 (2000); S. A. Kucharski, M. Kolaski, and R. J. Bartlett, J. Chem. Phys. **114**, 692 (2001); M. Musiał, S. A. Kucharski, and R. J. Bartlett, *ibid.* **116**, 4382 (2002).

[95] M. Kállay and P. R. Surján, J. Chem. Phys. **113**, 1359 (2000); **115**, 2945 (2001); J. Olsen, *ibid.* **113**, 7140 (2000).

[96] C. Schwartz, Phys. Rev. **126**, 1015 (1962).

[97] W. Kutzelnigg and J. D. Morgan III, J. Chem. Phys. **96**, 4484 (1992).

[98] Supporting information of the *Extensible Computational Chemistry Environment Basis Set Database*, developed by D. Feller at the Environmental and Molecular Sciences Laboratory, Pacific Northwest Laboratory, US-DOE, Richland, WA, USA, (www.emsl.pnl.gov/forms/basisform.html)

[99] T. Koga, S. Watanbe, K. Kanayama, R. Yasuda, and A. J. Thakkar, J. Chem. Phys. **103**, 3000 (1995).

[100] F. Jensen, J. Chem. Phys. **116**, 7372 (2002).

[101] S. J. Chakravorty and E. R. Davidson, J. Phys. Chem. **100**, 6167 (1996).

[102] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. Froese Fischer, Phys. Rev. A **47**, 3649 (1993).

[103] E. R. Davidson, S. A. Hagstrom, S. J. Chakravorty, V. M. Umar, and C. Froese Fischer, Phys. Rev. A **44**, 7071 (1991).

[104] L. Bytautas and K. Ruedenberg, Mol. Phys. **100**, 757 (2002).

[105] K. Rościszewski, Int. J. Quantum Chem. **58**, 471 (1996).

[106] C. E. Moore, *Tables of Spectra of Hydrogen, Carbon, Nitrogen and Oxygen Atoms and Ions* (CRC, Boca Raton, FL, 1993).

[107] R. L. Kelly, J. Phys. Chem. Ref. Data **16**, 114 (1987); [ionization potentials for F atom].

[108] B. Ruscic (private communication).

[109] B. Ruscic, R. E. Pinzon, M. L. Morton *et al.*, J. Phys. Chem. A **108**, 9979 (2004).

[110] R. J. Gdanitz and R. Ahlrichs, Chem. Phys. Lett. **143**, 413 (1988).

[111] R. S. Urdahl, Y. Bao, and W. M. Jackson, Chem. Phys. Lett. **178**, 425 (1991).

[112] S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974); E. R. Davidson and D. W. Silver, Chem. Phys. Lett. **52**, 403 (1977); C. E. Dykstra and E. R. Davidson, Int. J. Quantum Chem. **78**, 226 (2000); S. C. Racine and E. R. Davidson, J. Phys. Chem. **97**, 6367 (1993).

[113] D. M. Ceperly and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); P. J. Reynolds, D. M. Ceperly, B. J. Alder, and W. A. Lester, Jr., J. Chem. Phys. **77**, 5593 (1982); J. B. Anderson, Int. Rev. Phys. Chem. **14**, 85 (1995); Rev. Comput. Chem. **13**, 133 (1999).

[114] C. Filippi and C. J. Umrigar, J. Chem. Phys. **105**, 213 (1996).

[115] A. Lüchow and R. F. Fink, J. Chem. Phys. **113**, 8457 (2000).

[116] S.-I. Lu, J. Chem. Phys. **118**, 6152 (2003).

[117] S. Datta, S. A. Alexander, and R. L. Coldwell, J. Chem. Phys. **120**, 3642 (2004).

[118] M. Casula, C. Attaccalite, and S. Sorella, J. Chem. Phys. **121**, 7110 (2004).

[119] L. Bytautas and K. Ruedenberg (unpublished).

[120] J. E. Lennard-Jones and J. A. Pople, Proc. R. Soc. London **A202**, 166 (1950); J. M. Foster and S. F. Boys, Rev. Mod. Phys. **32**, 300 (1960); C. Edmiston and K. Ruedenberg, *ibid.* **35**, 457 (1963); S. F. Boys, *Quantum Theory of Atoms, Molecules and the Solid State*, edited by P. O. Löwdin (Academic, New York, 1966), p. 253; W. England, L. S. Salmon, and K. Ruedenberg, Fortschr. Chem. Forsch. **23**, 31 (1971); W. von Niessen, J. Chem. Phys. **56**, 4290 (1972); D. A. Kleier, T. A. Halgren, J. H. Hall, Jr., and W. N. Lipscomb, *ibid.* **61**, 3905 (1974); J. Pipek and P. G. Mezey, *ibid.* **90**, 4916 (1989); R. C. Raffenetti, K. Ruedenberg, C. L. Janssen, and H. F. Schaefer, Theor. Chim. Acta **86**, 149 (1993); H. Feng, J. Bian, L. Li, and W. Yang, J. Chem. Phys. **120**, 9458 (2004); J. E. Subotnik, Y. Shao, W. Liang, and M. Head-Gordon, *ibid.* **121**, 9220 (2004).

[121] P. Pulay, Chem. Phys. Lett. **100**, 151 (1983); S. Saebø and P. Pulay, Annu. Rev. Phys. Chem. **44**, 213 (1993); S. Saebø and P. Pulay, J. Chem. Phys. **115**, 3975 (2001).

[122] M. Häser and J. E. Almlöf, J. Chem. Phys. **96**, 489 (1992).

[123] P. E. Maslen and M. Head-Gordon, Chem. Phys. Lett. **283**, 102 (1998); M. S. Lee, P. E. Maslen, and M. Head-Gordon, J. Chem. Phys. **112**, 3592

(2000).

[124] M. Head-Gordon, J. Phys. Chem. **100**, 13213 (1996).

[125] G. E. Scuseria and P. Y. Ayala, J. Chem. Phys. **111**, 8330 (1999); P. Constans, P. Y. Ayala, and G. E. Scuseria, *ibid.* **113**, 10451 (2000).

[126] M. Schütz and H. J. Werner, J. Chem. Phys. **114**, 661 (2001); M. Schütz, *ibid.* **116**, 8772 (2002); T. Korona and H. J. Werner, *ibid.* **118**, 3006 (2003).

[127] H. J. Werner, F. R. Manby, and P. J. Knowles, J. Chem. Phys. **118**, 8149 (2003).

[128] R. A. Friesner, R. B. Murphy, M. D. Beachy, M. N. Ringnalda, W. T. Pollard, B. D. Dunietz, and Y. Cao, J. Phys. Chem. A **103**, 1913 (1999).

[129] B. D. Dunietz and R. A. Friesner, J. Chem. Phys. **115**, 11052 (2001).

[130] D. Walter, A. Venkatnathan, and E. A. Carter, J. Chem. Phys. **118**, 8127 (2003).

[131] D. Maynau, S. Evangelisti, N. Guihéry, C. J. Calzado, and J.-P. Malrieu, J. Chem. Phys. **116**, 10060 (2002).

[132] T. D. Crawford and R. A. King, Chem. Phys. Lett. **366**, 611 (2002).

[133] N. Flocke and R. J. Bartlett, Chem. Phys. Lett. **367**, 80 (2003); J. Chem. Phys. **118**, 5326 (2003).

[134] L. Bytautas, J. Ivanic, and K. Ruedenberg, J. Chem. Phys. **119**, 8217 (2003).

[135] W. C. Lu, C. Z. Wang, M. W. Schmidt, L. Bytautas, K. M. Ho, and K. Ruedenberg, J. Chem. Phys. **120**, 2638 (2004).