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Accurate Ab Initio Potential Energy Curve of F₂. I. Nonrelativistic Full Valence Configuration Interaction Energies Using the Correlation Energy Extrapolation by Intrinsic Scaling Method

Laimutis Bytautas
Iowa State University

Takeshi Nagata
Iowa State University

Mark S. Gordon
Iowa State University, mgordon@iastate.edu

Klaus Ruedenberg
Iowa State University, klausrg@iastate.edu

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Abstract

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Keywords

Dissociation, Coupled cluster, Excitation energies, Dissociation energies, Wave functions

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Comments

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Accurate *ab initio* potential energy curve of F₂. I. Nonrelativistic full valence configuration interaction energies using the correlation energy extrapolation by intrinsic scaling method

Laimutis Bytautas, Takeshi Nagata, Mark S. Gordon, and Klaus Ruedenberg^{a)}

Department of Chemistry and Ames Laboratory U.S. DOE, Iowa State University, Ames, Iowa 50011, USA

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The recently introduced method of *correlation energy extrapolation by intrinsic scaling* (CEEIS) is used to calculate the nonrelativistic electron correlations in the valence shell of the F₂ molecule at 13 internuclear distances along the ground state potential energy curve from 1.14 Å to 8 Å, the equilibrium distance being 1.412 Å. Using Dunning's correlation-consistent double-, triple-, and quadruple-zeta basis sets, the full configuration interaction energies are determined, with an accuracy of about 0.3 mhartree, by successively generating up to octuple excitations with respect to multiconfigurational reference functions that strongly change along the reaction path. The energies of the reference functions and those of the correlation energies with respect to these reference functions are then extrapolated to their complete basis set limits. The applicability of the CEEIS method to strongly multiconfigurational reference functions is documented in detail. © 2007 American Institute of Physics. [DOI: 10.1063/1.2800017]

I. INTRODUCTION

The basic aim of the present series of investigations is the *ab initio* determination of molecular electronic energies along reaction paths. Since the most detailed experimental information regarding energies along the *entire* reaction paths is available in diatomic molecules by virtue of their vibrational spectra, they furnish exacting tests for methods attempting to describe potential energy surfaces. It has indeed proven difficult to obtain accurate diatomic dissociation curves *ab initio* and no such curve has as yet been reported for any 18-electron system such as the fluorine molecule, which is the object of the present study. In this first paper, we establish its nonrelativistic potential energy curve taking into account only electron correlations in the valence shell. In the subsequent paper, we will add the correlations involving core electrons as well as the relativistic effects, including spin-orbit coupling. In the final paper, the resulting potential energy curve is used to calculate the rotational and vibrational energy levels, which are then compared with the experimental spectrum.

Accurate quantum mechanical quantifications of electronic energy variations on potential energy surfaces are relevant in many contexts.¹ Thermal and photochemical reaction rates, vibrational and rotational spectra, kinetic isotope effects (see, e.g., Refs. 2–11), to name but a few important properties, depend on accurate descriptions of surface features, such as transition states, reaction paths, conical intersections, etc.^{12–23} In many instances, such accurate descriptions require the use of many-electron *ab initio* wavefunctions, and our discussion is limited to these. In this context, the *full configuration interaction* (FCI) method^{24,25}

has as yet remained the benchmark approach because of its variational attributes.^{26–29} However, while considerable strides have been made in CI methodology,^{30–38} its excessively long configurational expansions still present the challenge of discovering the most efficiently converging reordering of its terms.

An elegant alternative approach is the single-configuration-reference coupled-cluster method,^{39–41} which has proven extremely successful near-equilibrium geometries when a single determinant dominates the zeroth-order function. Other single-configuration reference methods are the renormalized coupled-cluster methods of Kowalski and Piecuch,⁴² and Piecuch *et al.*,⁴³ the spin-flip methodology of Krylov⁴⁴ and Krylov and Sherrill,⁴⁵ and the coupled electron pair approximation of Nooijen and Le Roy.⁴⁶

The challenge of quantitatively accurate energy calculations *on potential energy surfaces* arises, however, from the fact that, away from equilibrium geometries, even *zeroth-order* descriptions typically call for *multiconfigurational* wavefunctions. This is the reason why bond formation and bond breaking present demanding tests for quantum chemical methods.^{47–50} Considerable effort has gone into adapting single-configuration-reference methods to these situations and some of the aforementioned versions have been created for this purpose.^{42–46} As yet, these methods remain, however, challenged by the presence of strongly multiconfigurational zeroth-order terms. Recent discussions of the coupled-cluster methods in this context have been given by Bartlett and Musiał.^{51,52}

A different tack, which is particularly geared toward work on reaction paths, consists of first determining a multiconfigurational zeroth-order wavefunction, typically by MCSCF optimization,^{53–55} and then to recover the dynamical correlation energy⁵⁶ by a configurational perturbation theory.

^{a)}Electronic mail: ruedenberg@iastate.edu

A variety of such multireference perturbation methods have been developed, e.g., variational methods,⁵⁷ MRPT2,^{58,59} CASPT2,⁶⁰ CASPT3,⁶¹ GMP2,⁶² and CIPT2,⁶³ and found useful for discussing bond formation and dissociation. For larger systems, the determination of zeroth-order wavefunctions large enough to describe the dominant electronic structure changes adequately, but small enough to perform the MCSCF and perturbation calculations efficiently is a challenge.^{64,65} The incorporation of multiconfigurational reference functions into the coupled-cluster formalism is the object of current research.^{66–71} Section IV will deal in more detail with some recent coupled-cluster results.

Different attempts to avoid the length of configurational expansions are the density matrix renormalization group method,^{72–75} the variational density matrix method,^{76,77} and the iterative configuration interaction method.⁷⁸

In order to make contact with physical reality, all orbital-configuration-based wavefunctions and/or energies must be extrapolated to the “complete basis set (CBS) limit.”^{79–88} Hylleraas⁸⁹ was the first to show that this problem can be greatly alleviated by the explicit inclusion of the interelectronic distance in the wavefunctions for He and H₂. More recently, a number of authors have succeeded in adapting this approach to the general case of many-electron systems,^{90–97} notwithstanding nontrivial algorithmic complexities. These methods yield indeed very accurate energies, but studies of potential energy surfaces are as yet rare.⁹⁷

In a series of recent papers,^{98–102} we have introduced another strategy for accurately approximating full CI energies, the *correlation energy extrapolation by intrinsic scaling* (CEEIS). It can be used with single- as well as multiconfigurational zeroth-order reference functions; it systematically approximates the full CI limit while monitoring the closeness of this approximation along the way; it uses standard computational CI machinery and its efficiency is increased by the parallelization of these codes.^{103,104} Application of this method using Dunning’s correlation-consistent basis sets,¹⁰⁵ in conjunction with CBS extrapolations yielded¹⁰¹ the binding energies of the diatomic molecules, C₂, N₂, O₂, and F₂, within the “chemical accuracy”¹⁰⁶ of 1.6 mhartree, comparing well with the recent experimentally based benchmark estimates of O’Neill and Gill.¹⁰⁷

In the present investigation, we demonstrate that the CEEIS method can also be successfully applied along a reaction path where the zeroth-order reference function is multiconfigurational and undergoes strong changes. Specifically, we calculate the potential energy curve for the dissociation of the F₂ molecule into two F atoms. Its rovibrational ground state spectrum has been accurately determined by experiment,^{108,109} which allows the critical assessment of the theoretical results in all regions of the dissociation curve. While there exist numerous investigations of the near-equilibrium properties^{110–118} and some theoretical studies of the dissociation curve,^{66,68,69,71,119–129} the latter has proven to be a difficult case due to the weakness of its chemical bond.¹³⁰ As yet, no attempt has been made to obtain the full potential energy curve with an accuracy that would warrant calculating the full vibration rotation spectrum. The present

approach generates a potential energy curve for F₂ that yields its spectrum in close agreement with experiment, as will be shown in the third paper of this series.

II. THE CEEIS METHOD

Since the CEEIS method has been described in detail in previous papers,^{98–102} we highlight here only the very basics. In Ref. 101, the method was generalized to multiconfigurational reference functions and this generalized form is used in the present study of the F₂ dissociation. While the method is applicable to all electrons, it is used here only to recover the valence shell correlations.

A. Expansion in terms of excitations

The CEEIS method presupposes a “zeroth-order configuration space” that is generated from a set of M_R reference valence orbitals, which are called “occupied.” This reference space need not be limited to a single Hartree-Fock-type determinant but can be multiconfigurational. The reference orbitals are considered equal or close to those that would result from the MCSCF optimization in this zeroth-order configuration space. The full configurational reference space that is generated by the occupied molecular orbitals is then supplemented by adding M *additionally* available valence orbitals, called “virtual” or “correlating,” so that the total number of valence, i.e., noncore orbitals, becomes $M_R + M$. The substitution of 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.

Let $E(x)$ denote the CI energy obtained by using *all* configurations containing up to x excited electrons in the virtual orbital space so that $E(0)$ is the reference energy of the zeroth-order wavefunction, $E(1)$ is the S-CI energy, $E(2)$ is the SD-CI energy, and so on. The full configuration space energy is then $E(f)$, where f is the smaller of $2M$ and N . The total energy improvement over the zeroth-order energy in the full space, ΔE , can then be expressed as the sum of *excitation contributions* $\Delta E(x)$,

$$\begin{aligned}\Delta E &= [E(f) - E(0)] \\ &= \Delta E(1) + \Delta E(2) + \Delta E(3) + \dots + \Delta E(f),\end{aligned}\quad (1)$$

with the increments

$$\Delta E(x) = E(x) - E(x-1), \quad x = 1, 2, \dots, f. \quad (2)$$

B. Choice of orbitals

While the individual excitation contributions $\Delta E(x)$ are independent of the choice of the configuration-generating correlating orbitals *when all M correlating orbitals are used, the convergence of the expansion of each excitation contribution $\Delta E(x)$ in terms of determinants* does depend on the choice of these orbitals. An optimal choice and ordering of the configuration-generating orbitals is therefore important.

In the absence of the natural orbitals¹³¹ (NOs) of the full CI solution, an effective practical alternative is to use the NOs of a full SD-CI calculation,³⁴ ordered by occupation numbers. The present analysis is therefore based on wavefunctions and energies generated using these SD-NOs for all orbitals except the 1s core orbitals. The M_R strongly occupied SD-NOs are used as the *reference* orbitals, while the M weakly occupied SD-NOs are used as *correlating* orbitals. To be sure, this orbital choice causes the zeroth-order energy $E(0)$ to be slightly above what is obtained when SCF or MCSCF orbitals are taken as reference orbitals, but the energy differences between the two choices vanish for higher than triple excitations.

C. Extrapolation of excitation contributions by intrinsic scaling

In the CEEIS approach, we consider, for each excitation level, *partial* excitation contributions $\Delta E(x|m)$. They are obtained in exactly the same way as the increments of Eq. (2), *except that, instead of using all M ordered correlating orbitals, one uses only the first m of them.* The CEEIS method is then based on an analysis of the convergence of the partial contributions to the full contributions at each excitation level,

$$\Delta E(x) = \Delta E(x|M) = \lim_{m \rightarrow M} \Delta E(x|m) \quad \text{for } m \rightarrow M. \quad (3)$$

Specifically, the CEEIS method exploits certain similarities we have identified in the way the partial contributions to the excitation levels x and $(x-2)$, i.e., $\Delta E(x|m)$ and $\Delta E(x-2|m)$ considered as functions of m , converge toward 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,

$$\Delta E(x|m) = a_x \Delta E(x-2|m) + c_x \quad (4)$$

($x = \text{fixed}, m = \text{variable}$),

are found to hold for $x=4,5,6$ and higher x values. The validity of these relationships has been confirmed by detailed examination in a number of systems.⁹⁸⁻¹⁰²

This relationship [Eq. (4)] is used in the CEEIS procedure to obtain the *desired full* value $\Delta E(x)=\Delta E(x|M)$ for a given excitation level x from the *known full* value $\Delta E(x-2|M)$ of the lower excitation level $(x-2)$ by

- (i) calculating a number of contribution pairs $\{\Delta E(x|m), \Delta E(x-2|m)\}$ for a set of *low* m values, defined by $m_0 \leq m \leq m_1 < M$, called the “fitting range” $\{m_0, m_1\}$,
- (ii) determining the coefficients a_x and c_x by least-squares fitting to the data in this range, and
- (iii) extrapolating the straight line of Eq. (4) to the full value $m=M$, thereby deducing the value of $\Delta E(x|M)$ from that of $\Delta E(x-2|M)$.

Through this sequential procedure, the $\Delta E(x) = \Delta E(x|M)$ for $x > 3$ are deduced from $\Delta E(2)$, $\Delta E(3)$, and a number of $\Delta E(x|m)$ values for $x > 3$ that require much shorter CI expansions than the direct calculation of $\Delta E(x)$ would. We note parenthetically that, in practice, the values

TABLE I. Energy convergence toward CBS values of optimized Hartree-Fock and FORS[14/8] wavefunctions along the dissociation path of the F₂ molecule. Energies in hartree.

Zeta basis ^a	HF	FORS	HF	FORS
	$R=1.14 \text{ \AA}$		$R=1.2 \text{ \AA}$	
2	-198.628 64	-198.669 32	-198.662 39	-198.710 38
3	-198.702 81	-198.742 64	-198.735 53	-198.782 53
4	-198.720 47	-198.760 27	-198.752 66	-198.799 62
5	-198.725 44	-198.765 20	-198.757 49	-198.804 42
6	-198.726 12	-198.765 86	-198.758 14	-198.805 03
CBS	-198.726 23	-198.765 96	-198.758 24	-198.805 12
	$R=1.3 \text{ \AA}$		$R=1.36 \text{ \AA}$	
2	-198.686 70	-198.748 67	-198.688 80	-198.760 17
3	-198.757 12	-198.818 01	-198.757 12	-198.827 46
4	-198.773 65	-198.834 50	-198.773 45	-198.843 76
5	-198.778 29	-198.839 11	-198.777 99	-198.848 29
6	-198.778 88	-198.839 67	-198.778 56	-198.848 82
CBS	-198.778 97	-198.839 75	-198.778 64	-198.848 90
	$R=1.411 \text{ 93 \AA}$		$R=1.5 \text{ \AA}$	
2	-198.685 67	-198.765 74	-198.673 28	-198.769 19
3	-198.752 04	-198.831 19	-198.736 40	-198.831 68
4	-198.768 27	-198.847 41	-198.752 56	-198.847 84
5	-198.772 74	-198.851 87	-198.756 92	-198.852 21
6	-198.773 29	-198.852 38	-198.757 44	-198.852 70
CBS	-198.773 37	-198.852 45	-198.757 51	-198.852 76
	$R=1.6 \text{ \AA}$		$R=1.8 \text{ \AA}$	
2	-198.652 65	-198.767 93	-198.603 26	-198.759 94
3	-198.712 56	-198.827 63	-198.659 44	-198.816 65
4	-198.728 73	-198.843 79	-198.675 64	-198.832 76
5	-198.733 01	-198.848 11	-198.679 92	-198.837 09
6	-198.733 50	-198.848 57	-198.680 35	-198.837 52
CBS	-198.733 56	-198.848 63	-198.680 40	-198.837 57
	$R=2.0 \text{ \AA}$		$R=2.2 \text{ \AA}$	
2	-198.554 12	-198.752 46	-198.510 75	-198.747 81
3	-198.610 00	-198.808 86	-198.568 33	-198.804 79
4	-198.626 16	-198.824 80	-198.584 58	-198.820 60
5	-198.630 57	-198.829 18	-198.589 15	-198.825 00
6	-198.630 99	-198.829 60	-198.589 60	-198.825 42
CBS	-198.631 04	-198.829 64	-198.589 65	-198.825 46
	$R=2.4 \text{ \AA}$		$R=2.8 \text{ \AA}$	
2	-198.474 61	-198.745 45	-198.422 25	-198.743 91
3	-198.534 44	-198.802 89	-198.485 55	-198.801 78
4	-198.551 04	-198.818 71	-198.503 35	-198.817 72
5	-198.555 79	-198.823 12	-198.508 55	-198.822 12
6	-198.556 30	-198.823 54	-198.509 19	-198.822 54
CBS	-198.556 36	-198.823 58	-198.509 28	-198.822 58
	$R=8.0 \text{ \AA}$			
2	-198.324 75	-198.743 72		
3	-198.385 33	-198.801 87		
4	-198.402 70	-198.817 90		
5	-198.408 16	-198.822 34		
6	-198.408 82	-198.822 76		
CBS	-198.408 91	-198.822 80		

^aThe value $X=2$ implies the cc-pVDZ basis set, the value $X=3$ implies the cc-pVTZ basis set, etc.

$\Delta E(1,2|m) = \Delta E(1|m) + \Delta E(2|m)$ are used in lieu of the $\Delta E(2|m)$ since the $\Delta E(1|m)$ are very small by virtue of the Brillouin theorem. Some modifications of this extrapolation scheme were given in Refs. 98 and 101.

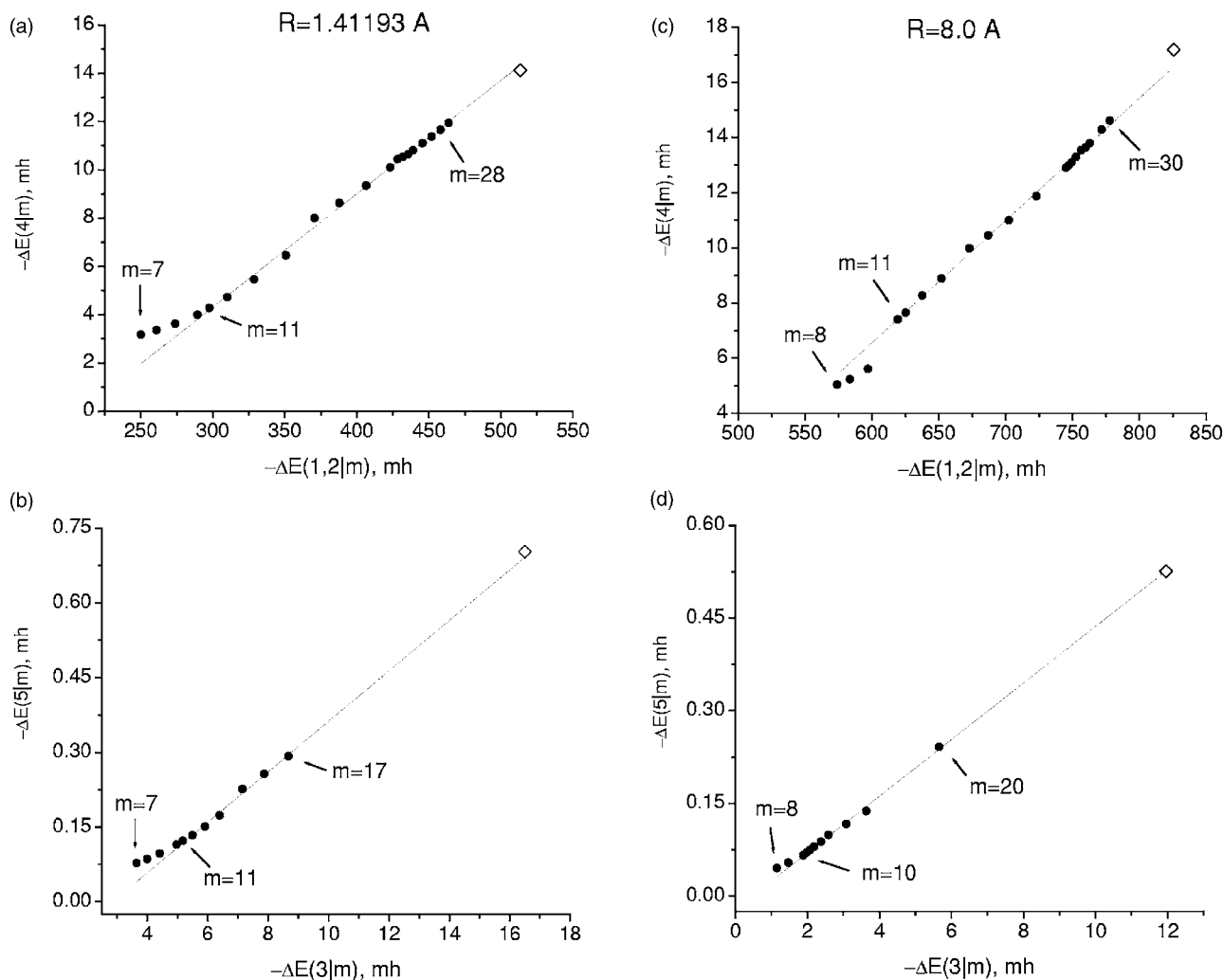


FIG. 1. Illustration of CEEIS extrapolations for up to quintuple excitations with respect to the FORS[14/8] reference function at 1.411 93 Å [panels (a) and (b)] and at 8 Å [panels (c) and (d)] employing the cc-pVTZ basis set. The $-\Delta E(4|m)$ values are plotted vs the $-\Delta E(1,2|m)$ values in panels (a) and (c); the $-\Delta E(5|m)$ values vs the $-\Delta E(3|m)$ values in panels (b) and (d). Solid points: calculated for the indicated m values. Solid lines: LMSQ fits based on the fitting ranges {11,28}, {11,17}, {11,30}, and {10,20} for panels (a), (b), (c), and (d), respectively. The open diamonds represent the best estimates in all panels.

D. Quality assessment

An important feature of the CEEIS method is that, in contrast to the situation in the coupled-cluster methods, a good estimate can be calculated for the deviation of the extrapolated energy from the exact full CI energy. On this basis, the extrapolation can then be improved if necessary (contingent, of course, upon the capabilities of the available computational equipment). The error assessment algorithm is described in Refs. 98 and 101.

III. ZERO-ORDER REFERENCE FUNCTIONS ALONG THE DISSOCIATION CURVE

A. Choice of zeroth-order functions

Along the dissociating reaction path of F_2 , the zeroth-order reference function changes multiconfigurationaly. The determinants of the zeroth-order reference function are constructed from the eight optimal or near-optimal molecular orbitals that span the full valence space, viz.,

$$2\sigma_g, 2\sigma_u, 3\sigma_g, 3\sigma_u, 1\pi x_u, 1\pi y_u, 1\pi x_g, 1\pi y_g. \quad (5)$$

We have examined the CEEIS performance for three types of reference functions:

- (i) the optimal 12-determinant full valence MCSCF wavefunctions of 14 valence electrons in 8 valence orbitals, i.e., the full optimized reaction space (FORS[14/8]) function;⁵⁴
- (ii) the two-determinant reduced FORS function (RFORS[2/2]) corresponding to the two occupation sets

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi x_u^2 1\pi y_u^2 1\pi x_g^2 1\pi y_g^2, \quad (6)$$

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_u^2 1\pi x_u^2 1\pi y_u^2 1\pi x_g^2 1\pi y_g^2. \quad (7)$$

- (iii) A single-determinant Hartree-Fock (HF) wavefunction corresponding to occupation set (6).

We shall document that choices (i) and (ii) yield practically identical CEEIS full CI results at all geometries, with

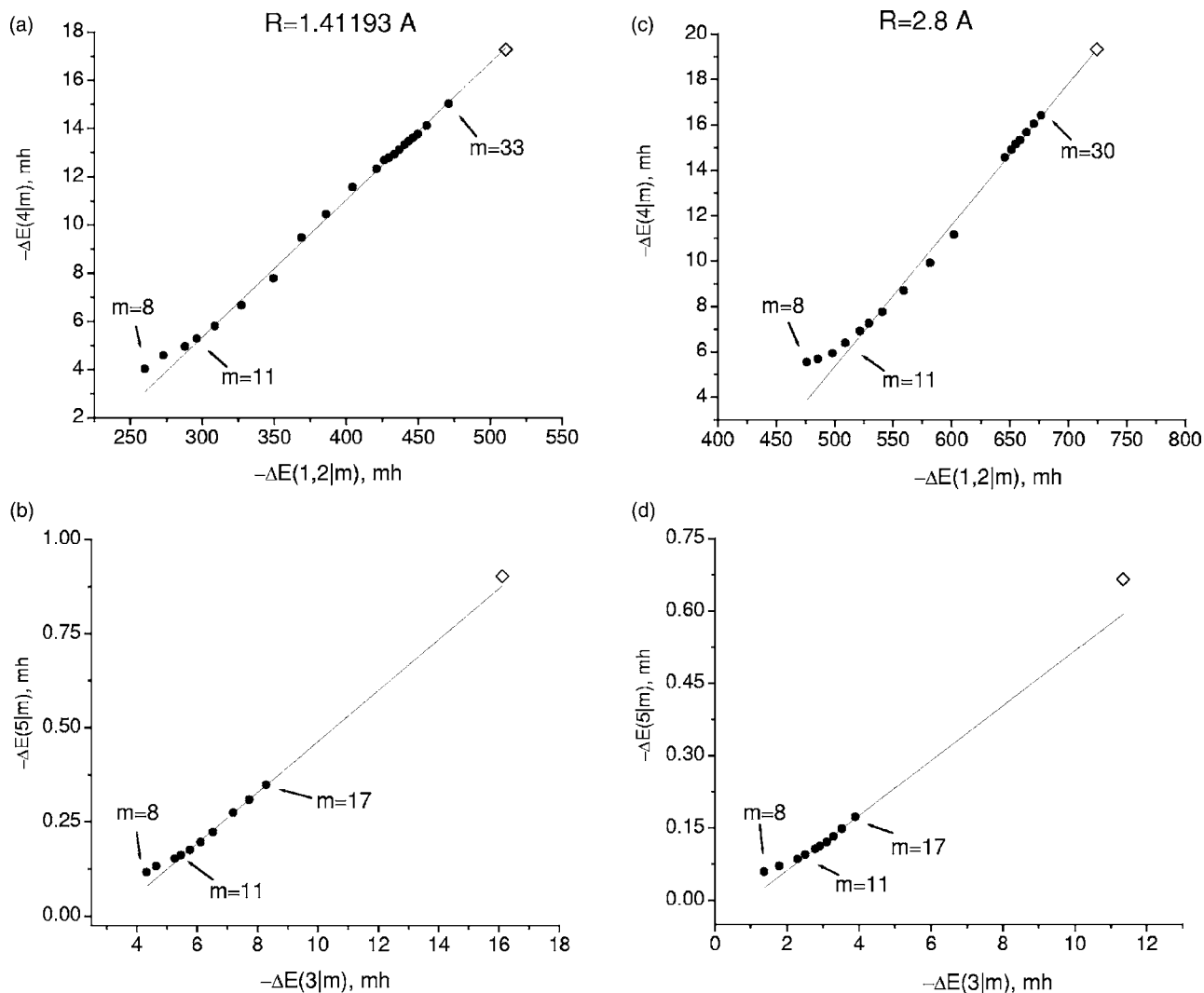


FIG. 2. Illustration of CEEIS extrapolations for up to quintuple excitations with respect to the RFORS[2/2] reference function at 1.41193 Å [panels (a) and (b)] and at 2.8 Å [panels (c) and (d)] employing the cc-pVTZ basis set. The $-\Delta E(4|m)$ values are plotted vs the $-\Delta E(1,2|m)$ values in panels (a) and (c); the $-\Delta E(5|m)$ values vs the $-\Delta E(3|m)$ values in panels (b) and (d). Solid points: calculated for the indicated m values. Solid lines: LMSQ fits based on the fitting ranges $\{11,33\}$, $\{11,17\}$, $\{11,30\}$, and $\{11,17\}$ for panels (a), (b), (c), and (d), respectively. The open diamonds represent the best estimates in all panels.

choice (ii) requiring less computational effort, and that choice (iii) entails a much slower convergence to the FCI value away from equilibrium geometries.

We use the nomenclature of Ref. 54: CASSCF (complete active space) as a generic term, FORS=CASSCF in a full valence space, and RFORS=CASSCF in part of the full valence space.

B. Complete basis set limit of the reference function

Chemically accurate determinations of electronic energies by the CI approach require extrapolation of the full CI energy to the CBS limit. Thorough studies of this problem^{79,86,87} have shown that the HF energies and the dynamic correlation energies approach the CBS limit differently and that they should therefore be extrapolated separately. The convergence also depends somewhat on the kind of basis sets used. The present calculations are performed using sequences of the correlation-consistent cc-pVXZ basis sets of Dunning.¹⁰⁵

Theoretical considerations have shown that, for these X -tuple-zeta bases, Hartree-Fock energies approach their HF-CBS limit according to an exponential law,^{86,87} and it is generally believed⁹ that this also holds for multiconfigurational zeroth-order functions of the type discussed in the preceding subsection. Thus, we have

$$E(X) = E(\text{CBS}) + a_0 \exp(-\alpha X) \quad \text{for HF, FORS, RFORS.} \quad (8)$$

The data presented in Table I document that this assumption is, in fact, justified in the present case and it also provides the CBS energy limits of the reference functions that we will need later on in this investigation. Listed are energy values for the 13 internuclear distances from 1.14 to 8.0 Å, which will be considered throughout this investigation. For each distance, two columns are given, one for the HF energies and the other for the optimized FORS [14/8] energies. The rows correspond to different X values from $X=2$ (double zeta) to $X=6$ (sextuple zeta) and the CBS limit, as indicated at the beginning of each row, to the left of the energy col-

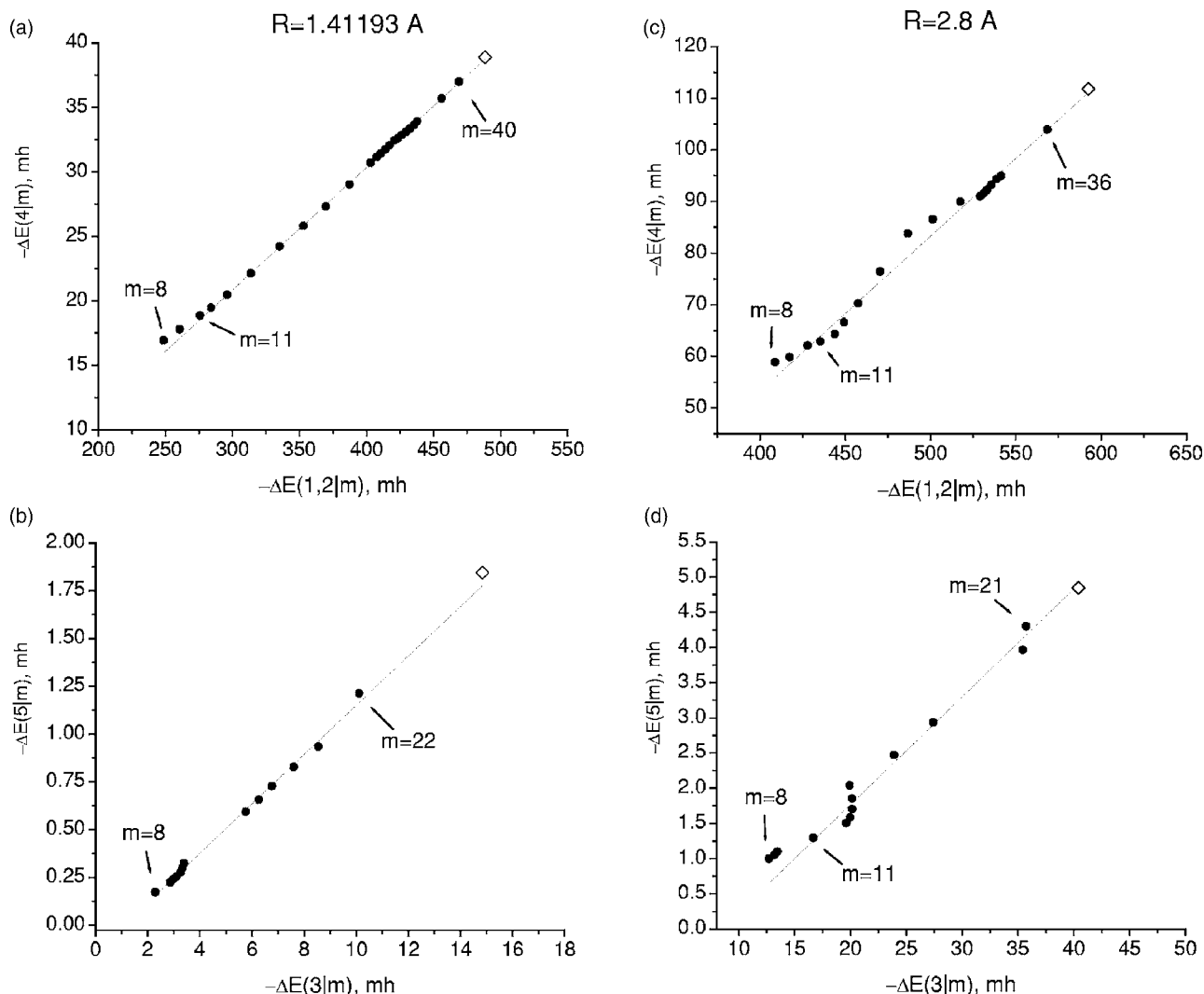


FIG. 3. Illustration of CEEIS extrapolations for up to quintuple excitations with respect to the single-determinant reference function at 1.411 93 Å [panels (a) and (b)] and at 2.8 Å [panels (c) and (d)] employing the cc-pVTZ basis set. The $-\Delta E(4|m)$ values are plotted vs $-\Delta E(1,2|m)$ values in panels (a) and (c); the $-\Delta E(5|m)$ values vs the $-\Delta E(3|m)$ values in panels (b) and (d). Solid points: calculated for the indicated m values. Solid lines: LMSQ fits based on the fitting ranges $\{11,40\}$, $\{8,22\}$, $\{11,36\}$, and $\{11,21\}$ for panels (a), (b), (c), and (d), respectively. The open diamonds represent the best estimates in all panels.

umns. The table entries show that, at all distances, the sextuple energies differ from the CBS limit by less than 0.2 mhartree for the HF energies as well as the FORS energies.

The determination of the three unknowns $E(\text{CBS})$, a_0 , and α in Eq. (8) requires at least three energy points. We have used the values for $X=4,5,6$ to obtain these CBS limits. The calculations were performed with the MOLPRO package.¹³²

IV. CEEIS EXTRAPOLATIONS FOR DIFFERENT ZERO-ORDER REFERENCE FUNCTIONS

Proceeding now to the dynamic correlations, a major objective of the present investigation is to show that the CEEIS also works well along a reaction path, where the zeroth-order reference function is multiconfigurational and undergoes strong changes. We shall therefore settle this question first. We are using Dunning's correlation-consistent cc-pVXZ bases¹⁰⁵ with $X=2,3,4$ to calculate the dynamic correlations and hence document the extrapolations for

triple-zeta as well as quadruple-zeta bases. The total number of correlating functions is $M=51$ for the former and $M=101$ for the latter basis set.

The calculations were executed using the GAMESS program suite,^{133,134} notably the occupation-restricted multiple-active-space CI (ORMAS-CI) code of Ivanic.³⁷ The CEEIS code is part of the latest version of the GAMESS program suite.

A comment is necessary with regard to the generation of excitations by the ORMAS code when the reference function consists of only the two configurations [Refs. 6 and 7] in Sec. III A. In this case, any excitation group (SD, SDT, SDTQ, etc.) includes the excitations of this type from the orbital set $\{2\sigma_g, 2\sigma_u, 1\pi x_u, 1\pi y_u, 1\pi x_g, 1\pi y_g\}$ to the orbital set $\{3\sigma_g, 3\sigma_u$ plus all virtual orbitals} as well as the excitations from the orbital set $\{3\sigma_g, 3\sigma_u\}$ to the virtual orbital set.

We also call attention to the difference between x and X . Whereas $x=2,3,4,\dots$ denote excitation levels of correlating configurations, $X=2,3,4$ denote double-, triple-, and quadruple-zeta basis sets.

TABLE II. Quality assessment of the extrapolations of valence-only correlation energy contributions (boldface type indicates the best values) at the excitation levels $x=4,5,6$ in the CI wavefunctions for three reference function choices. Basis set=cc-pVTZ. Internuclear distance=1.411 93 Å. Energy in millihartree.

Fitting range		Energy contributions		Estim. abs. error	
m_0	m_1	$-\Delta E(x m_1)$	$-\Delta E(x 51)$	$\delta(\text{RMSQ})$	$\delta(\text{max})$
Ψ_0 =single determinant					
Excitation $x=4$, extrapolation to $\Delta E(4 51)$					
11	21	31.75	38.74	0.18	0.31
11	40	36.99	38.76	0.09	0.18
14	29	33.91	38.79	0.15	0.24
26	40	36.99	38.90	0.03	0.05
Excitation $x=5$, extrapolation to $\Delta E(5 51)$					
8	22	1.21	1.78	0.04	0.10
15	22	1.21	1.85	0.06	0.11
Excitation $x=6$, extrapolation to $\Delta E(6 51)$					
8	17	0.93	1.29	0.02	0.02
10	17	0.93	1.30	0.01	0.02
Ψ_0 =RFORS[2/2]					
Excitation $x=4$, extrapolation to $\Delta E(4 51)$					
11	21	12.94	17.56	0.39	0.83
11	33	15.03	17.35	0.23	0.55
14	33	15.03	17.32	0.25	0.68
25	33	15.03	17.29	0.06	0.09
Excitation $x=5$, extrapolation to $\Delta E(5 51)$					
11	17	0.35	0.88	0.02	0.04
13	17	0.35	0.90	0.01	0.02
Excitation $x=6$, extrapolation to $\Delta E(6 51)$					
8	13	0.10	0.28	0.002	0.004
Ψ_0 =FORS[14/8]					
Excitation $x=4$, extrapolation to $\Delta E(4 51)$					
11	21	10.64	14.46	0.35	0.78
11	28	11.65	14.35	0.25	0.64
14	28	11.65	14.25	0.28	0.69
21	28	11.65	14.13	0.03	0.05
21	30	11.94	14.20	0.05	0.09
24	30	11.94	14.22	0.09	0.12
Excitation $x=5$, extrapolation to $\Delta E(5 51)$					
11	17	0.29	0.69	0.03	0.05
13	17	0.29	0.70	0.03	0.06
Excitation $x=6$, extrapolation to $\Delta E(6 51)$					
7	12	0.06	0.22	0.004	0.007

A. CEEIS extrapolations for triple-zeta basis sets

Figures 1–3 illustrate the quality of CEEIS extrapolations for several cases. Figures 1–3 exhibit typical results corresponding to the reference functions FORS[14/8], RFORS[2/2], and HF-SCF, respectively. In each figure, the upper two panels [(a) and (c)] display plots of the quadruple contributions $\Delta E(4|m)$ versus the corresponding single + double contributions $\Delta E(1,2|m)$, whereas the lower two panels [(b) and (d)] display plots of the quintuple contributions $\Delta E(5|m)$ versus the corresponding triple contributions $\Delta E(3|m)$. In each figure, the two panels at the left [(a) and (b)] display these correlations for the equilibrium distance

$R=1.411\ 93\ \text{\AA}$, whereas the panels at the right [(c) and (d)] display them for a greatly stretched distance, viz., $R=8\ \text{\AA}$ in Fig. 1 and $R=2.8\ \text{\AA}$ in Figs. 2 and 3.

Consider plot (a) in Fig. 1. The solid points are calculated data for the m values $m=7,8,9,\dots,27,28,30$. The solid line is the least-mean-squares (LMSQ) fit for the fitting range choice {11–28}. The open diamond is the extrapolated value using the LMSQ fit of only the high-value range {21–30}. Since the number of correlating orbitals is $M=51$ for the cc-pVTZ bases, extrapolation means here that the LMSQ fit is used to calculate $\Delta E(4|51)$ from $\Delta E(1,2|51)$. In the analogous plot (b) of Fig. 1, the quintuple data have only been pushed up to $m=20$, the straight line represents the

TABLE III. Quality assessment of the extrapolations of valence-only correlation energy contributions (boldface type indicates the best values) at the excitation levels $x=4,5,6$ in the CI wavefunctions with FORS[14/8] reference functions. Basis set=cc-pVTZ. Internuclear distance=8.0 Å. Energy in millihartree.

Fitting range		Energy contributions		Estim. abs. error	
m_0	m_1	$-\Delta E(x m_1)$	$-\Delta E(x 51)$	$\delta(\text{RMSQ})$	$\delta(\text{max})$
Excitation $x=4$, extrapolation to $\Delta E(4 51)$					
11	21	13.11	16.39	0.16	0.43
11	30	14.61	16.56	0.14	0.29
19	30	14.61	17.10	0.09	0.19
24	30	14.61	17.19	0.06	0.11
Excitation $x=5$, extrapolation to $\Delta E(5 51)$					
8	17	0.14	0.46	0.02	0.03
10	17	0.14	0.48	0.01	0.03
10	20	0.24	0.53	0.01	0.03
Excitation $x=6$, extrapolation to $\Delta E(6 51)$					
8	12	0.16	0.44	0.009	0.014

LMSQ fit for the range {11–17}, and the open diamond is the result of the extrapolation using the LMSQ fit from the high-value range {13–17}. Analogous notation and interpretations apply to all other plots. In panel (c) of Fig. 1, the straight line is the LMSQ fit for the range {11,30} and the extrapolation uses the range {24,30}. In panel (d) of Fig. 1, the straight line is the LMSQ fit for the range {10,20} and this range is also used for the extrapolation results. Since the quadruple-

excitation contribution $\Delta E(4|51)$ is about 15 mhartree [panels (a) and (c)] and the quintuple-excitation contribution $\Delta E(5|51)$ is about 0.5–0.8 mhartree [panels (b) and (d)], it is apparent that extrapolation cannot introduce a significant error in the quintuple and higher excitations, but it has to be done carefully for the quadruple excitations.

While Fig. 1 displays extrapolations for the full FORS[14/8] reference functions, Fig. 2 exhibits entirely

TABLE IV. Valence-only correlation energy contributions $\Delta E(x)$ for excitations $x=1-8$, based on three zeroth-order wavefunctions. Basis set=cc-pVTZ. Energy in millihartree.

Excitation	Zeroth-order reference function		
	FORS[14/8]	RFORS[2/2]	Single determinant
$R=1.411\ 93\ \text{Å}$			
$E(\text{HF})$	-198 752.04	-198 752.04	-198 752.04
$E(0)^a$	-198 829.22	-198 824.73	-198 752.04
$\Delta E(\text{FORS})^b$	-77.18	-72.69	...
$\Delta E(1,2)$	-436.33	-438.12	-488.40
$\Delta E(3)$	-16.49	-16.11	-14.84
$\Delta E(4)$	-14.22(± 0.05)	-17.29(± 0.04)	-38.90(± 0.05)
$\Delta E(5)$	-0.70(± 0.06)	-0.90(± 0.02)	-1.85(± 0.11)
$\Delta E(6)$	-0.22(± 0.01)	-0.28(± 0.004)	-1.30(± 0.02)
$\Delta E(7,8)$	-0.01	-0.01	-0.04
$E(\text{total})$	-199 297.20(± 0.12)	-199 297.45(± 0.06)	-199 297.37(± 0.18)
$R=2.8\ \text{Å}$			
$E(\text{HF})$	-198 485.55	-198 485.55	-198 485.55
$E(0)^a$	-198 794.06	-198 793.78	-198 485.55
$\Delta E(\text{FORS})^b$	-308.51	-308.23	...
$\Delta E(1,2)$	-416.44	-415.90	-592.36
$\Delta E(3)$	-12.85	-11.34	-40.40
$\Delta E(4)$	-17.19(± 0.12)	-19.35(± 0.06)	-111.83(± 0.45)
$\Delta E(5)$	-0.54(± 0.01)	-0.67(± 0.01)	-4.85(± 0.24)
$\Delta E(6)$	-0.35(± 0.01)	-0.37(± 0.01)	-4.39(± 0.14)
$\Delta E(7)$	-0.01	-0.01	-0.16
$\Delta E(8)$	-0.01	-0.00	-0.06
$E(\text{total})$	-199 241.44(± 0.14)	-199 241.42(± 0.08)	-199 239.60(± 0.83)

^a $E(0)$ =energy of reference function, see text before Eq. (1).

^b $\Delta E(\text{FORS})=E(0)-E(\text{HF})$.

TABLE V. Contributions (boldface type indicates the best values) of the various excitation levels to the full valence correlation energy based on the two-determinant RFORS[2/2] reference function. Basis set =cc-pVQZ. Internuclear distance=1.411 93 Å. Energy in millihartree.

Fitting range		Energy contributions		Estim. abs. error	
m_0	m_1	$-\Delta E(x m_1)$	$-\Delta E(x 101)$	$\delta(\text{RMSQ})$	$\delta(\text{max})$
Excitation $x=4$, extrapolation to $\Delta E(4 101)$					
14	25	14.13	20.12	0.50	1.07
14	33	15.72	19.98	0.33	0.83
25	33	15.72	20.13	0.06	0.08
Excitation $x=5$, extrapolation to $\Delta E(5 101)$					
8	20	0.47	0.98	0.04	0.07
14	20	0.47	1.04	0.02	0.03
Excitation $x=6$, extrapolation to $\Delta E(6 101)$					
9	13	0.10	0.33	0.003	0.005
Excitation $x=7$, extrapolation to $\Delta E(7 101)$					
8	11	0.002	0.015
Excitation $x=8$, extrapolation to $\Delta E(8 101)$					
8	10	0.001	0.003
$\Delta E_{\text{HF}}(1,2 101)$		551.80		Calculated exactly, Eq. (9)	
$\Delta E(3 101)$		18.69		Calculated exactly	
$\Delta E(4-8 101)$		21.52±0.12		Extrapolated, see above	
Total valence correlation energy		592.01±0.12		Eq. (1)	

analogous results for the two-determinant RFORS[2/2] reference functions. It is apparent that, for both zeroth-order functions, the LMSQ fittings show only a small scattering so that the CEEIS extrapolation procedure works well not only at the equilibrium distance but also very far from equilibrium, even near complete dissociation. This observation is consistent with the recent study of optimal active space choices by Sears and Sherrill,¹³⁵ who showed that appropriate minimal reference spaces, while less costly, typically perform on a par with much larger reference spaces.

The situation is, however, quite different in Fig. 3, which displays the analogous results when the *single determinant* of the strongly occupied NOs is used as the reference function for the excitations. While the linearity of the data for the equilibrium geometry [panels (a) and (b)] is of similar quality as that found in Figs. 1 and 2, this is not the case at twice the equilibrium distance [panels (c) and (d)]. Here, the calculated data display large fluctuations around the LMSQ-fitted line, which leads to significantly larger error bars in the CEEIS extrapolations for comparable fitting ranges. This result is consistent with the fact that multiconfigurational wavefunctions are more appropriate for describing dissociations than single-reference wavefunctions.

Some quantitative details regarding the extrapolations that yield the values of the quadruple excitations $\Delta E(4)$, the quintuple excitations $\Delta E(5)$, and the sextuple excitations $\Delta E(6)$ are given in Tables II and III.

Table II exemplifies these extrapolations at the equilibrium distance for all three reference functions, FORS[14/8], RFORS[2/2], and single determinant. The first two columns in this table identify the fitting ranges $\{m_0, m_1\}$. The third column lists the *calculated* value of $\Delta E(x|m_1)$, i.e., from the

largest CI calculation made at this excitation level for this fitting range. The fourth column gives the *extrapolation results* $\Delta E(x|51)=\Delta E(x)$. The last two columns list the estimated uncertainties in the extrapolations, which are calculated from the root-mean-square deviation as well as the maximum deviation of the LMSQ fitting, as discussed in Sec. IV B of Ref. 99.

It is apparent that, for all three reference functions, the extrapolation to the quadruple excitation contributions yield reliable results even for the fitting range $\{m_0, m_1\}=\{11, 21\}$: the extrapolated values for $\Delta E(4|51)$ using this range of data deviate from the bold-printed best results only by 0.16, 0.27, and 0.24 mhartree for the single-determinant, RFORS[2/2], and FORS[14/8] reference functions, respectively. These deviations correlate very well with the corresponding estimated error bars based on the RMSQ deviations, viz., 0.18, 0.39, and 0.35 mhartree, respectively. As had been observed earlier, use of the maximum deviation appears to overestimate the uncertainty in the extrapolations. The extrapolations to the quintuple and sextuple excitation contributions, too, are manifestly very stable.

Table III exhibits the extrapolations for the FORS[14/8] reference function at the internuclear distance of 8.0 Å, i.e., practically at the dissociation limit. Here, the extrapolation using the low- m fitting range of $\{m_0, m_1\}=\{11, 21\}$ yields for the quadruple-excitation contribution $\Delta E(4)=\Delta E(4|51)$ the value of 16.39 mhartree, while extrapolation for the high- m fitting range $\{m_0, m_1\}=\{24, 30\}$ yields the value of 17.19 mhartree with an error bar of less than 0.1 mhartree.

Table IV complements Tables II and III by a comparative listing of all extrapolated excitation contributions up to eight-tuple excitations and their sum, i.e., the total valence

TABLE VI. Contributions (boldface type indicates the best values) of the various excitation levels to the full valence correlation energy based on the two-determinant RFORS[2/2] reference function. Basis set =cc-pVQZ. Internuclear distance=2.8 Å. Energy in millihartree.

Fitting range		Energy contributions		Estim. abs. error	
m_0	m_1	$-\Delta E(x m_1)$	$-\Delta E(x 101)$	$\delta(\text{RMSQ})$	$\delta(\text{max})$
Excitation $x=4$, extrapolation to $\Delta E(4 101)$					
14	25	16.05	22.54	0.55	0.87
25	38	18.42	21.99	0.03	0.04
Excitation $x=5$, extrapolation to $\Delta E(5 101)$					
8	23	0.43	0.86	0.07	0.13
15	23	0.43	0.99	0.02	0.02
Excitation $x=6$, extrapolation to $\Delta E(6 101)$					
9	13	0.14	0.43	0.01	0.01
Excitation $x=7$, extrapolation to $\Delta E(7 101)$					
8	11	0.002	0.015
Excitation $x=8$, extrapolation to $\Delta E(8 101)$					
8	10	0.001	0.005
$\Delta E_{\text{HF}}(1,2 101)$		760.27		Calculated exactly, Eq. (9)	
$\Delta E(3 101)$		14.06		Calculated exactly	
$\Delta E(4-8 101)$		23.43±0.07		Extrapolated, see above	
Total valence correlation energy		797.76±0.07		Eq. (1)	

full CI energy, obtained using all three reference functions. The data are given for the equilibrium distance as well as for twice that distance. In all cases, the best fitting ranges were used in the extrapolation. At the equilibrium distance, excellent agreement is seen to exist among all three reference functions: the differences between the total energies are at most 0.25 mhartree and about of the same order of magnitude as the estimated error bars given in parentheses. At twice the equilibrium distance, the total energies obtained with the FORS[14/8] and the RFORS[2/2] reference functions still differ only by 0.02 mhartree, in good agreement with the estimated errors of 0.14 and 0.08 mhartree. The calculation with the single-determinant reference function yields, however, an error bar of close to 1 mhartree and its total energy, in fact, deviates from the multireference results by about 2 mhartree. It also yields considerably larger contributions at all excitation levels. At larger internuclear distances, the multiconfigurational reference functions are manifestly much more effective than the single-reference function in converging to the full CI results.

B. CEEIS extrapolations for quadruple-zeta basis sets

The preceding results obtained for the triple-zeta basis have shown that, whereas the single-determinant reference function does not work well for larger internuclear distances, the FORS[14/8] and RFORS[2/2] both serve equally well as reference functions along the entire dissociation path. The RFORS[2/2] function has, however, the advantage of generating shorter CI expansions for any given choice of m and excitation level. In the case of the quadruple-zeta bases,

with a total of $M=101$ correlating orbitals, this difference is substantial and we have therefore chosen the two-determinant RFORS[2/2] zeroth-order reference functions for all our calculations with Dunning's cc-pVQZ bases.¹⁰⁵

Tables V and VI document the working of the CEEIS extrapolation procedure in the case of the quadruple-zeta basis, Table V for the equilibrium distance and Table VI for twice the equilibrium distance.

In both tables, the lower section contains the resolution of the total valence correlation energy in terms of the contributions from the single+double excitations, the triple excitations, and the sum of the remaining excitations $\Delta E(4-8|101)$. The upper sections of the tables document the extrapolations that yield the individual excitation contributions $\Delta E(4)=\Delta E(4|101)$, $\Delta E(5)=\Delta E(5|101)$, ..., $\Delta E(8)=\Delta E(8|101)$ that add up to the value of $\Delta E(4-8|101)$ in the upper section.

The columns in the upper section are similar to those used earlier in Tables II and III: the first two columns identify the fitting ranges $\{m_0, m_1\}$. The third column lists the calculated value of $\Delta E(x|m_1)$, i.e., from the largest CI calculation made in this range for this x value. The fourth column lists the extrapolated result for $\Delta E(x)=\Delta E(x|101)$. The last two columns show the extrapolation uncertainties obtained using the root-mean-square deviation as well as the maximum deviation of the LMSQ fit.

We note that, in the first row of these two tables as well as in some subsequent tables, the quantity $\Delta E_{\text{HF}}(1,2)$ denotes the difference between *our* singles+doubles energy and the independently calculated Hartree-Fock energy, viz.,

$$\Delta E_{\text{HF}}(1,2) = E(2) - E_{\text{HF}}. \quad (9)$$

Since our singles+doubles energy $E(2)$ has been calculated by singles+doubles excitations with respect to one of the discussed reference functions (constructed from strongly occupied SD-CI natural orbitals), we have

$$E(2) = \Delta E(1) + \Delta E(2) + E(0) = \Delta E(1,2) + E(0). \quad (10)$$

In this equation, the quantities $E(0)$, $E(2)$, $\Delta E(1)$, and $\Delta E(2)$ are defined in Eqs. (1) and (2). We list $\Delta E_{\text{HF}}(1,2)$ so that the total in the fourth row of Tables V and VI becomes, in fact, the conventionally defined valence correlation energy and can be compared with results given by other researchers.

It is apparent that the quality of the CEEIS extrapolations shown in Tables V and VI is very similar for the two internuclear distances. The energies obtained for $\Delta E(4)$ at a given geometry by different extrapolations are always within a few tenths of a millihartree of each other, indicating the stability of the method. Interestingly, the extrapolation of $\Delta E(4|101)$ in Table VI using the fitting range $\{m_0, m_1\} = \{14, 25\}$ yields a predicted uncertainty of 0.55 mhartree. The magnitude of this estimated error suggests that higher m values are needed to ensure better extrapolation accuracy and this is indeed achieved by utilizing the fitting range $\{25, 38\}$. A high extrapolation quality is also observed for the excitations $x > 4$, although here one deals with much smaller contributions. The contributions of the excitations $x=9$ and higher become clearly negligible. In fact, the combined contributions for $x > 4$ excitations do not exceed 2.0 mhartree for both geometries. This is manifestly due to the use of the multiconfigurational reference function. Overall, the extrapolated full valence CI energies for the cc-pVQZ basis set are estimated to be within error bars of 0.3 mhartree for all internuclear distances considered.

V. FULL VALENCE CI ENERGIES ALONG THE DISSOCIATION PATH OF F₂

In view of results of the preceding section, we have used the CEEIS method based on multiconfigurational reference functions to calculate the full valence CI energies of the dissociation curve of F₂ for the internuclear distances 1.14, 1.2, 1.3, 1.36, 1.411 93, 1.5, 1.6, 1.8, 2.0, 2.2, 2.4, 2.8, and 8.0 Å, where 1.411 93 Å is the experimental equilibrium geometry.

A. Convergence of the excitation expansion for triple-zeta bases along the dissociation path

For the triple-zeta calculations, we chose the FORS[14/8] reference function. The results are presented in Table VII. For each internuclear distance, six rows are shown that list the six energies indicated by the labels in the first column at the left. The first row $E(\text{SDT})$ is the energy of the SDT-CI wavefunction, where the SDT excitations are taken with respect to the FORS[14/8] reference functions. The next five rows are the energy contributions due to the indicated excitation levels x . The sum of the first six rows, shown boldfaced in the seventh row, is the total full valence CI energy.

At all points, the following fitting ranges $\{m_0, m_1\}$ were used for the CEEIS extrapolations. For $\Delta E(4)$, $\{21, 30\}$; for $\Delta E(5)$, $\{12, 17\}$; for $\Delta E(6)$, $\{9, 13\}$; for $\Delta E(7)$, $\{8, 10\}$; for $\Delta E(8)$, $\{8, 10\}$. These choices for the fitting ranges offer the best balance between the accuracy of the extrapolation and the cost of the calculations needed to obtain the data points. The convergence in terms of excitation levels is manifestly of equal quality at all points and higher excitations are clearly negligible.

B. Convergence of the excitation expansion for quadruple-zeta bases along the dissociation path

In view of the conclusions we had drawn in Sec. IV B, we chose the RFORS[2/2] reference function for the quadruple-zeta calculations at the 13 points of the dissociation curve. Table VIII presents the resulting energies in a similar format as the one used in Table VII except in two respects. First, the contributions from the triple excitations, $\Delta E(3)$, with respect to the reference function are not combined with the energies of the single+double wavefunctions, $E(\text{SD})$, but entered separately in the second row. Secondly, we have added an additional column at the end that lists the breakdown by excitations for the binding energy [$E(8 \text{ Å}) - E(R_{\text{eq}})$], where $R_{\text{eq}} = 1.411 93 \text{ Å}$ is the equilibrium distance and $E(8 \text{ Å})$ is de facto the energy of the separated atoms.

Two conclusions can be drawn from this table.

- The magnitudes of the energy contributions of the various excitation levels vary relatively little along the dissociation curve, which confirms the effectiveness of the choice of the reference function.
- Nonetheless, the contributions change sufficiently so that the contributions of the triple and even quadruple excitations are needed to recover the binding energy to 1 kcal/mol (~ 1.6 mhartree).

Since the $E(\text{SD})$ energies represent, in fact, the MRCI-SD energies for the reference function, it follows that in this case the MRCI-SD wavefunction cannot recover the binding energy to this accuracy, which was confirmed by direct calculations. It also follows that any method based on a single determinant reference function must include at least sextuple excitations to attain kcal/mol accuracy.

At all points, the following fitting ranges $\{m_0, m_1\}$ were used for the CEEIS extrapolations. For $\Delta E(4)$, $\{25, 33\}$; for $\Delta E(5)$, $\{14-17\}$ up to $R=2.4 \text{ Å}$ and $\{14, 20\}$ for $R=2.8$ and 8.0 Å ; for $\Delta E(6)$, $\{10-13\}$; for $\Delta E(7)$, $\{8, 11\}$; for $\Delta E(8)$, $\{8, 10\}$. The convergence in terms of excitation levels is manifestly of equal quality at all points and higher excitations are clearly negligible.

C. Sensitivity to the extrapolation of the quadruple excitations

It has been noted several times in the preceding discussions that the contributions of the quadruple excitations are always sufficiently large compared to those of the higher excitations so that the full CI energy depends most strongly on the extrapolation accuracy of the value for $\Delta E(4)$. We

TABLE VII. Convergence to the full valence CI energy in terms of the excitation contributions generated from the FORS[14/8] reference function along the dissociation path. Basis set=cc-pVTZ. Fitting range for the quadruple excitation extrapolation= $\{m_0, m_1\}=\{21, 30\}$. Energy in hartree.

CI level	Internuclear distance		
	$R=1.14 \text{ \AA}$	$R=1.2 \text{ \AA}$	$R=1.3 \text{ \AA}$
$E(\text{SDT})$	-199.198 373	-199.238 065	-199.272 103
$\Delta E(4)$	-0.01407 0	-0.014 023	-0.013 985
$\Delta E(5)$	-0.000 679	-0.000 669	-0.000 691
$\Delta E(6)$	-0.000 241	-0.000 234	-0.000 224
$\Delta E(7)$	-0.000 012	-0.000 011	-0.000 011
$\Delta E(8)$	-0.000 002	-0.000 002	-0.000 002
$E(\text{total})$	-199.213 377	-199.253 004	-199.287 016
	$R=1.36 \text{ \AA}$	$R=1.411 93 \text{ \AA}$	$R=1.5 \text{ \AA}$
$E(\text{SDT})$	-199.280 015	-199.282 049	-199.279 062
$\Delta E(4)$	-0.014 076	-0.014 192	-0.014 335
$\Delta E(5)$	-0.000 720	-0.000 700	-0.000 641
$\Delta E(6)$	-0.000 219	-0.000 217	-0.000 330
$\Delta E(7)$	-0.000 010	-0.000 009	-0.000 008
$\Delta E(8)$	-0.000 002	-0.000 002	-0.000 002
$E(\text{total})$	-199.295 042	-199.297 169	-199.294 378
	$R=1.6 \text{ \AA}$	$R=1.8 \text{ \AA}$	$R=2.0 \text{ \AA}$
$E(\text{SDT})$	-199.270 590	-199.251 103	-199.237 194
$\Delta E(4)$	-0.014 575	-0.015 593	-0.016 251
$\Delta E(5)$	-0.000 637	-0.000 600	-0.000 571
$\Delta E(6)$	-0.000 332	-0.000 345	-0.000 313
$\Delta E(7)$	-0.000 008	-0.000 008	-0.000 009
$\Delta E(8)$	-0.000 003	-0.000 003	-0.000 004
$E(\text{total})$	-199.286 145	-199.267 652	-199.254 342
	$R=2.2 \text{ \AA}$	$R=2.4 \text{ \AA}$	$R=2.8 \text{ \AA}$
$E(\text{SDT})$	-199.229 575	-199.225 838	-199.223 344
$\Delta E(4)$	-0.016 624	-0.016 876	-0.017 016
$\Delta E(5)$	-0.000 554	-0.000 554	-0.000 543
$\Delta E(6)$	-0.000 320	-0.000 323	-0.000 336
$\Delta E(7)$	-0.000 010	-0.000 008	-0.000 008
$\Delta E(8)$	-0.000 005	-0.000 004	-0.000 005
$E(\text{total})$	-199.247 088	-199.243 595	-199.241 252
	$R=8.0 \text{ \AA}$		
$E(\text{SDT})$	-199.222 767		
$\Delta E(4)$	-0.017 097		
$\Delta E(5)$	-0.000 528		
$\Delta E(6)$	-0.000 437		
$\Delta E(7)$	-0.000 009		
$\Delta E(8)$	-0.000 005		
$E(\text{total})$	-199.240 843		

have therefore examined the sensitivity of $\Delta E(4)$ with respect to the fitting range that is used for its extrapolation. (The contributions from the higher excitations were not changed.)

In this context, we have also considered whether one might obtain different values for $\Delta E(4)$ if one were to replace the scaling equation [Eq. (4)] in Sec. II C by the more general scaling relation

$$\Delta E(4|m) = a_x \Delta E(2|m) + b_x \Delta E(3|m) + c_x, \quad (11)$$

which also involves the triple excitations in extrapolating to $\Delta E(4/M)$.

TABLE VIII. Convergence to the full valence CI energy in terms of the excitation contributions generated from the RFORS[2/2] reference function along the dissociation path. Basis set=cc-pVQZ. Fitting range for the quadruple excitation extrapolation= $\{m_0, m_1\}=\{25, 33\}$. Energy in hartree.

CI level	Internuclear distance		
	$R=1.14 \text{ \AA}$	$R=1.2 \text{ \AA}$	$R=1.3 \text{ \AA}$
$E(\text{SD})$	-199.240 482	-199.278 656	-199.310 958
$\Delta E(3)$	-0.017 487	-0.018 010	-0.018 570
$\Delta E(4)$	-0.019 507	-0.019 525	-0.019 847
$\Delta E(5)$	-0.000 900	-0.000 997	-0.001 054
$\Delta E(6)$	-0.000 329	-0.000 327	-0.000 329
$\Delta E(7)$	-0.000 015	-0.000 015	-0.000 015
$\Delta E(8)$	-0.000 003	-0.000 003	-0.000 003
$E(\text{total})$	-199.278 723	-199.317 534	-199.350 776
	$R=1.36 \text{ \AA}$	$R_{\text{eq}}=1.411 93 \text{ \AA}$	$R=1.5 \text{ \AA}$
$E(\text{SD})$	-199.318 297	-199.320 077	-199.317 045
$\Delta E(3)$	-0.018 699	-0.018 689	-0.018 440
$\Delta E(4)$	-0.019 992	-0.020 124	-0.020 359
$\Delta E(5)$	-0.001 082	-0.001 098	-0.001 092
$\Delta E(6)$	-0.000 331	-0.000 333	-0.000 473
$\Delta E(7)$	-0.000 016	-0.000 015	-0.000 016
$\Delta E(8)$	-0.000 003	-0.000 003	-0.000 003
$E(\text{total})$	-199.358 420	-199.360 339	-199.357 427
	$R=1.6 \text{ \AA}$	$R=1.8 \text{ \AA}$	$R=2.0 \text{ \AA}$
$E(\text{SD})$	-199.308 874	-199.290 250	-199.276 831
$\Delta E(3)$	-0.017 890	-0.016 472	-0.015 334
$\Delta E(4)$	-0.020 730	-0.021 194	-0.021 590
$\Delta E(5)$	-0.001 094	-0.001 059	-0.001 009
$\Delta E(6)$	-0.000 436	-0.000 444	-0.000 452
$\Delta E(7)$	-0.000 020	-0.000 018	-0.000 017
$\Delta E(8)$	-0.000 004	-0.000 004	-0.000 004
$E(\text{total})$	-199.349 048	-199.329 441	-199.315 238
	$R=2.2 \text{ \AA}$	$R=2.4 \text{ \AA}$	$R=2.8 \text{ \AA}$
$E(\text{SD})$	-199.269 390	-199.265 798	-199.263 626
$\Delta E(3)$	-0.014 708	-0.014 401	-0.014 062
$\Delta E(4)$	-0.021 845	-0.022 067	-0.021 989
$\Delta E(5)$	-0.000 969	-0.000 941	-0.000 931
$\Delta E(6)$	-0.000 435	-0.000 437	-0.000 425
$\Delta E(7)$	-0.000 016	-0.000 014	-0.000 015
$\Delta E(8)$	-0.000 005	-0.000 006	-0.000 005
$E(\text{total})$	-199.307 368	-199.303 664	-199.301 053
	$R=8.0 \text{ \AA}$		$E(8 \text{ \AA}) - E(R_{\text{eq}})$ (mhartree)
$E(\text{SD})$	-199.264 453		55.624
$\Delta E(3)$	-0.012 842		5.847
$\Delta E(4)$	-0.021 978		-1.854
$\Delta E(5)$	-0.000 825		0.273
$\Delta E(6)$	-0.000 417		-0.084
$\Delta E(7)$	-0.000 014		0.001
$\Delta E(8)$	-0.000 005		-0.002
$E(\text{total})$	-199.300 534		59.805

Table IX exhibits the changes in the values of $\Delta E(4)$, and hence of the full CI energies, at the 13 internuclear distances (shown in the first column) when the extrapolation of $\Delta E(4)$ is modified in various ways.

The second column, labeled $D(\text{TZa})$, lists the changes in the triple-zeta energies with respect to those given in Table VII when Eq. (11) is used instead of Eq. (4) for extrapolation in the same fitting range $\{21, 30\}$. Manifestly, nothing is

TABLE IX. Changes in the triple-zeta (TZ) and quadruple-zeta (QZ) values of $\Delta E(4)$ due to changes in the $\Delta E(4)$ extrapolation (in millihartree).

$R(\text{\AA})$	$D(\text{TZa})^a$	$D(\text{TZb})^b$	$D(\text{QZc})^c$
1.14	0.004	-0.012	-0.007
1.2	0.000	0.106	-0.065
1.3	0.049	0.039	-0.027
1.36	0.025	0.024	-0.037
1.411 93	-0.013	-0.023	-0.051
1.5	-0.014	-0.023	-0.072
1.6	-0.034	-0.053	-0.017
1.8	0.006	-0.169	-0.041
2.0	-0.003	-0.159	-0.043
2.2	-0.010	-0.197	-0.002
2.4	-0.031	-0.183	0.000
2.8	-0.022	-0.231	0.000
8.0	-0.004	-0.092	0.001

^a $D(\text{TZa})$ =changes relative to the values in Table VII when Eq. (11) is used instead of Eq. (4) for the fitting range {21,30}.

^b $D(\text{TZb})$ =changes relative to the values in Table VII when the fitting range {24,30} is used instead of {21,30}.

^c $D(\text{QZc})$ =changes relative to the values in Table VIII when the fitting range {25,33} is replaced by {26,33}.

gained by including the triple excitations in the extrapolation of the quadruple excitations according to Eq. (11), the largest deviation in $\Delta E(4)$ being 0.03 mhartree for 2.4 Å.

The third column, labeled $D(\text{TZb})$, lists the changes in the triple-zeta energies with respect to those given in Table VII when Eq. (4) is retained for the extrapolation, but the fitting range is changed from {21,30} to {24,30}. This is a more instructive case since an inspection of the data points exhibited in Fig. 4 reveals that the values for $m=23, 24, 25$ exhibit a small but noticeable scatter from the straight line. As a consequence, the shortening of the extrapolation range from eight to five data points skews the slope sufficiently to introduce changes of up to 0.23 mhartree in the extrapolated value, in particular, for the larger distances. Such an unbalancing effect due to the scatter of individual points is minimized by including enough data points in the extrapolation

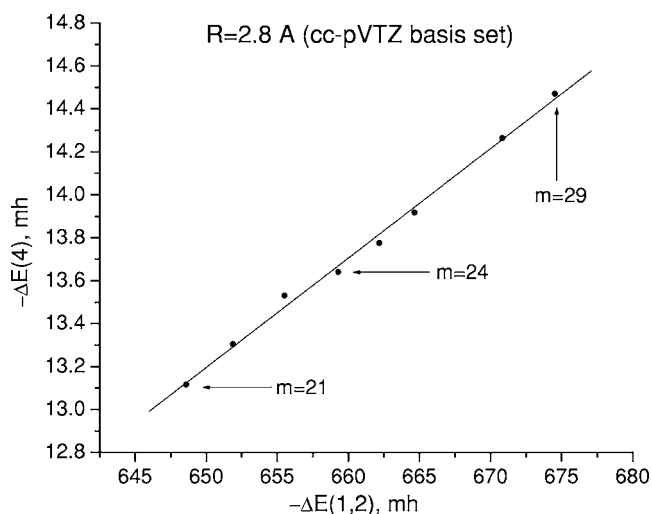


FIG. 4. Illustration of CEEIS extrapolations for quadruple excitations with respect to the FORS[14/8] reference function at the internuclear distance of 2.8 Å (cc-pVTZ basis set).

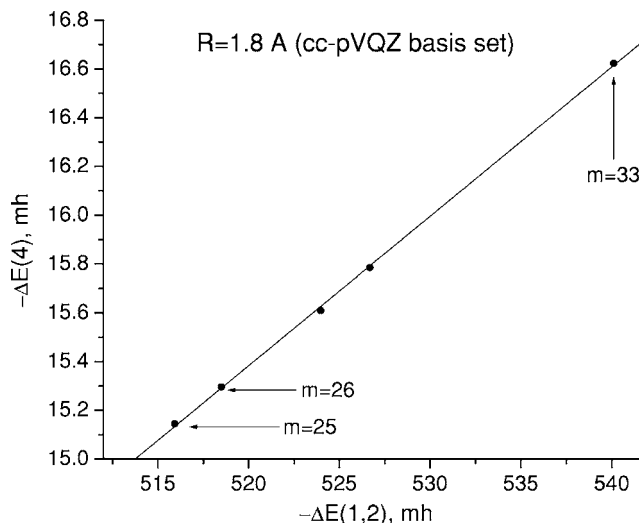


FIG. 5. Illustration of CEEIS extrapolations for quadruple excitations with respect to the RFORS[2/2] reference function at the internuclear distance of 1.8 Å (cc-pVQZ basis set).

range. Hence, the range {21–30} is the best for determining $\Delta E(4)$ from the present data for the cc-pVTZ basis set. Although the change of 0.23 mhartree is still small compared to chemical accuracy, it will be interesting to examine how it affects the calculation of the rovibrational spectrum in the third paper.

The fourth column, labeled $D(\text{QZc})$, lists the changes in the quadruple-zeta energies with respect to those listed in Table VIII when the fitting range is changed from {25,33} to {26,33}. An inspection of the quadruple-zeta data points exhibited in Fig. 5 shows that all five points from $m=25$ to 33 show minimal scatter from a straight line and, consequently, the shortening of the extrapolation range has very little effect on the extrapolated value.

VI. CBS LIMIT ALONG THE DISSOCIATION PATH OF F₂

A. CBS extrapolation procedure

As was mentioned in Sec. III B, in-depth studies^{79,86,87} have shown that HF energies and dynamic correlation energies approach the CBS limit differently and must therefore be extrapolated separately. For Dunning's correlation-consistent cc-pVXZ basis sets, HF energies approach their CBS limits exponentially^{86,87} according to formula (8). On the other hand, correlation energies with respect to the HF energies have been shown⁷⁹ to approach their CBS limits according to the inverse power law,

$$\Delta E_{\text{corr}}(X) = \Delta E_{\text{corr}}(\text{CBS}) + a_c X^{-3}. \quad (12)$$

We have found this two-pronged CBS extrapolation to give indeed reliable results for the full CI energies of diatomic molecules at their equilibrium geometries.¹⁰¹

This approach is predicated on the difference

$$\Delta E_{\text{corr}} = E_{\text{full CI}} - E_{\text{HF}}, \quad (13)$$

representing the dynamic correlations, which implies that the HF single determinant represents an adequate zeroth-order

reference function. By contrast, as we have seen in Secs. IV and V, the appropriate zeroth-order reference functions along the dissociation path are multiconfigurational, so that the difference [Eq. (13)] contains increasing amounts of nondynamic correlation as the dissociation proceeds. It seems therefore reasonable to use in this case the correlation extrapolation [Eq. (12)] for modified dynamic correlation energies defined by

$$\Delta E_{\text{corr}} = E_{\text{full CI}} - E_{\text{FORS}}. \quad (14)$$

This choice is moreover supported by the fact that, as we have already shown in Sec. III B, the multiconfigurational FORS[14/8] reference functions indeed extrapolate to their CBS limits according to the exponential law of Eq. (8) along the entire dissociation path.

We have therefore calculated the CBS limits of the full valence CI energies as

$$E_{\text{full CI}}(\text{CBS}) = E_{\text{FORS}}(\text{CBS}) + \Delta E_{\text{corr}}(\text{CBS}), \quad (15)$$

where $E_{\text{FORS}}(\text{CBS})$ denotes the values given for the FORS[14/8] CBS limits in Table I, and $\Delta E_{\text{corr}}(\text{CBS})$ is obtained by using Eq. (12) with the $\Delta E_{\text{corr}}(X)$ defined as

$$\Delta E_{\text{corr}}(X) = E_{\text{full CI}}(X) - E_{\text{FORS}[14/8]}(X). \quad (16)$$

To determine the two constants $\Delta E_{\text{corr}}(\text{CBS})$ and a_c in Eq. (12), we need $\Delta E_{\text{corr}}(X)$ values for at least two values of X . Since the inclusion of double-zeta energies is well known to degrade CBS extrapolations of the correlation energy (see, e.g., the discussion in Refs. 101 and 102), we use the data for $x=3, 4$ to determine the extrapolated value $\Delta E_{\text{corr}}(\text{CBS})$.

B. CBS limits of the full CI energies along the dissociation path

Table X collects the quantitative data regarding the CBS extrapolation of the full CI energies for all 13 internuclear distances. It lists the zeroth-order FORS[14/8] energies, the correlation energies, and the full valence CI energies for the cc-pVDZ, the cc-pVTZ, and the cc-pVQZ basis sets as well as the extrapolated CBS limits.

In Table X, all FORS energies come from Table I. The full CI energies for the triple- and quadruple-zeta bases come from Tables VII and VIII. The correlation energies for the triple- and quadruple-zeta bases are obtained by subtracting the former from the latter. The CBS correlation energies are extrapolated, as described in Sec. VI A. The full CI CBS limits are the sum of the preceding two rows. Figure 6 displays the potential energy curves corresponding to cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets and the CBS limit.

We note that the full CI CBS energy at 8.0 Å in Table X (−199.337 29 hartree) is very close to the estimate of the exact nonrelativistic valence-only energy of two F atoms (−199.337 32 hartree), which can be deduced by subtracting the core-related correlations of the fluorine atom given by Noga *et al.*⁹⁴ from the nonrelativistic energy of the fluorine atom given by Chakravorty and Davidson.¹³⁶

We can also determine the nonrelativistic valence-only contribution to the binding energy from the full CI CBS en-

ergy curve. The calculation yields −62.35 mhartree, which compares well with the value of -62.56 ± 0.04 derived from the experimental data (see Sec. VII B).

It is relevant to examine the rate of convergence to the CBS limit with increasing basis set size. From the formal difference between the exponential law of Eq. (8) and the inverse third power law of Eq. (12), one would infer that the reference energies, be they HF or FORS, will approach their limits faster with increasing X than the correlation energies. This is borne out by the data in Table X. Even the correlation energies of the quadruple-zeta basis still deviate by about 30 mhartree from their CBS limit. By contrast, the zeroth-order FORS[14/8] energies for the same basis differ by only about 5 mhartree from their limits. The slow rate of convergence of the correlation energy has been noted by many authors.^{137–141} It may be the largest source of uncertainty in the present calculations.

C. Sensitivity to the extrapolation of the quadruple excitations

We finally examine how the slight variations in the extrapolation of $\Delta E(4)$ discussed in Sec. V C affect the CBS limit of the correlation energies and hence the full CI energies. Let EXTR1 denote the combination of triple-zeta and quadruple-zeta extrapolation values from Tables VII and VIII respectively, which was used to obtain Table X. We now consider the effect of changing these values by combining the changes listed in Table IX of Sec. V C as follows:

- EXTR2: triple-zeta extrapolation as in Table X; quadruple-zeta extrapolation as in the fourth column of Table IX.
- EXTR3: triple-zeta extrapolation as in the second column of Table IX; quadruple-zeta extrapolation as in Table X.
- EXTR4: triple-zeta extrapolation as in the second column of Table IX; quadruple-zeta extrapolation taken as the average between that in Table X and that in the fourth column of Table IX.
- EXTR5: triple-zeta extrapolation as in the third column of Table IX; quadruple-zeta extrapolation as in the fourth column of Table IX.

The changes in the CBS limit energies that are caused by these variations in the $\Delta E(4)$ extrapolations are listed in Table XI, where the column headings identify the four cases. In agreement with the discussion in Sec. V C, the changes are extremely slight for the alternatives EXTR2, EXTR3, and EXTR4. In the case of EXTR5, however, there are deviations in excess of 0.1 mhartree at four data points. This is because EXTR5 includes $\Delta E(4)$ values from the triple-zeta basis that resulted from using an unbalanced extrapolation range, as was discussed in Sec. V C. As mentioned there, we carry it along to exhibit its consequences.

Although all fluctuations in Table XI are small compared to chemical accuracy, it is of interest to know how such small

TABLE X. CBS extrapolation of the FORS[14/8] energies, the correlation energies relative to the FORS[14/8] energies, and the full valence CI energies along the dissociation path. Fitting ranges for quadruple excitation extrapolations: {21,30} for VTZ and {25,33} for VQZ. Energy in hartree.

Calculation type	VDZ	VTZ	VQZ	CBS
		$R=1.14 \text{ \AA}$		
FORS	-198.669 32	-198.742 64	-198.760 27	-198.765 96
Correlation (FORS)	-0.337 86	-0.470 74	-0.518 45	-0.553 27
Full valence CI	-199.007 18	-199.213 38	-199.278 72	-199.319 23
		$R=1.2 \text{ \AA}$		
FORS	-198.710 38	-198.782 53	-198.799 62	-198.805 12
Correlation (FORS)	-0.337 74	-0.470 47	-0.517 91	-0.552 53
Full valence CI	-199.048 11	-199.253 00	-199.317 53	-199.357 65
		$R=1.3 \text{ \AA}$		
FORS	-198.748 67	-198.818 01	-198.834 50	-198.839 75
Correlation (FORS)	-0.336 43	-0.469 01	-0.516 27	-0.550 77
Full valence CI	-199.085 10	-199.287 02	-199.350 77	-199.390 52
		$R=1.36 \text{ \AA}$		
FORS	-198.760 17	-198.827 46	-198.843 76	-198.848 90
Correlation (FORS)	-0.335 00	-0.467 58	-0.514 66	-0.549 01
Full valence CI	-199.095 17	-199.295 04	-199.358 42	-199.397 91
		$R=1.41193 \text{ \AA}$		
FORS	-198.765 74	-198.831 19	-198.847 41	-198.852 45
Correlation (FORS)	-0.333 46	-0.465 98	-0.512 93	-0.547 19
Full valence CI	-199.099 20	-199.297 17	-199.360 34	-199.399 64
		$R=1.5 \text{ \AA}$		
FORS	-198.769 19	-198.831 68	-198.847 84	-198.852 76
Correlation (FORS)	-0.330 62	-0.462 70	-0.509 59	-0.543 80
Full valence CI	-199.099 81	-199.294 38	-199.357 43	-199.396 56
		$R=1.6 \text{ \AA}$		
FORS	-198.767 93	-198.827 63	-198.843 79	-198.848 63
Correlation (FORS)	-0.327 17	-0.458 52	-0.505 26	-0.539 37
Full valence CI	-199.095 10	-199.286 15	-199.349 05	-199.388 00
		$R=1.8 \text{ \AA}$		
FORS	-198.759 94	-198.816 65	-198.832 76	-198.837 57
Correlation (FORS)	-0.320 96	-0.451 00	-0.496 68	-0.530 02
Full valence CI	-199.080 90	-199.267 65	-199.329 44	-199.367 59
		$R=2.0 \text{ \AA}$		
FORS	-198.752 46	-198.808 86	-198.824 80	-198.829 64
Correlation (FORS)	-0.316 36	-0.445 48	-0.490 44	-0.523 24
Full valence CI	-199.068 82	-199.254 34	-199.315 24	-199.352 88
		$R=2.2 \text{ \AA}$		
FORS	-198.747 81	-198.804 79	-198.820 60	-198.825 46
Correlation (FORS)	-0.313 85	-0.442 30	-0.486 77	-0.519 22
Full valence CI	-199.061 65	-199.247 09	-199.307 37	-199.344 68
		$R=2.4 \text{ \AA}$		
FORS	-198.745 45	-198.802 89	-198.818 71	-198.823 58
Correlation (FORS)	-0.312 78	-0.440 71	-0.484 95	-0.517 24
Full valence CI	-199.058 23	-199.243 60	-199.303 66	-199.340 82
		$R=2.8 \text{ \AA}$		
FORS	-198.743 91	-198.801 78	-198.817 72	-198.822 58
Correlation (FORS)	-0.311 86	-0.439 47	-0.483 33	-0.515 35
Full valence CI	-199.055 77	-199.241 25	-199.301 05	-199.337 93
		$R=8.0 \text{ \AA}$		
FORS	-198.743 72	-198.801 87	-198.817 90	-198.822 80
Correlation (FORS)	-0.311 73	-0.438 97	-0.482 63	-0.514 49
Full valence CI	-199.055 45	-199.240 84	-199.300 53	-199.337 29

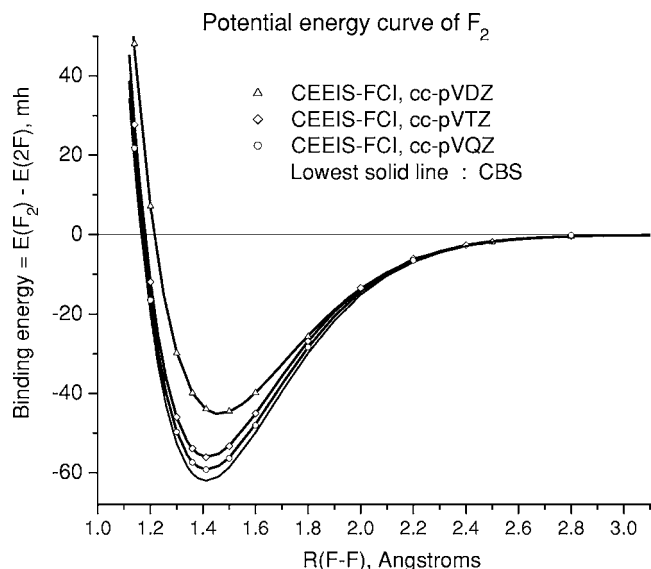


FIG. 6. Potential energy curves $[E(F_2) - 2E(F)]$ from CEEIS-determined full valence-CI calculations for Dunning's correlation-consistent double-, triple-, and quadruple-zeta basis sets and for the complete basis set (CBS) limit.

changes in the potential energy curve affect the vibrational spectrum, which will be calculated in the third paper of this series.

VII. COMPARISON OF COUPLED-CLUSTER ENERGIES WITH CEEIS FULL CI ENERGIES

A. Single-reference coupled-cluster methods

Since the present calculations approximate the full CI energies within about 0.3 mhartree, they provide a benchmark for other high-accuracy calculations of the F_2 dissociation curve.

TABLE XI. Changes in the CBS-extrapolated correlation energies $\Delta E_{\text{corr}}(\text{CBS})$ due to changes in $\Delta E(4)$ extrapolations [listed are the changes with respect to the values in Table X that result when the extrapolations to $\Delta E(4)$ for the TZ and QZ bases are changed, as indicated below with respect to the ones used in Table X] (in millihartree).

$R, \text{\AA}$	EXTR2 $D(\text{TZ}_0/\text{QZc})^a$	EXTR3 $D(\text{TZa}/\text{QZ}_0)^b$	EXTR4 $D(\text{TZa}/\text{QZc}^c)$	EXTR5 $D(\text{TZb}/\text{QZc})^d$
1.14	-0.01	0.00	-0.01	0.00
1.2	-0.11	0.00	-0.06	-0.19
1.3	-0.04	-0.03	-0.06	-0.07
1.36	-0.06	-0.02	-0.05	-0.08
1.411 93	-0.09	0.01	-0.04	-0.08
1.5	-0.13	0.01	-0.05	-0.11
1.6	-0.03	0.02	0.01	0.01
1.8	-0.07	0.00	-0.04	0.06
2.0	-0.07	0.01	-0.03	0.04
2.2	0.00	0.01	0.01	0.14
2.4	0.00	0.02	0.02	0.13
2.8	0.00	0.02	0.02	0.17
8.0	0.00	0.00	0.00	0.07

^aTZ same as in Table X // QZ as for $D(\text{QZc})$ in Table IX.

^bTZ as in $D(\text{TZa})$ of Table IX // QZ same as in Table X.

^cTZ as in $D(\text{TZa})$ of Table IX // QZ=average between that in Table X and that for $D(\text{QZc})$ in Table IX.

^dTZ as in $D(\text{TZb})$ of Table IX // QZ as in $D(\text{QZc})$ in Table IX.

Here, we make a comparison with several coupled-cluster calculations using cc-pVTZ basis sets. Table XII lists the energies obtained at the distances of 1.411 93, 2.2, and 2.8 \AA by the following versions of the coupled-cluster method:

- CCSDT, with fully iterated triple contributions (see Refs. 40 and 41);
- CCSD[T] and CCSD(T), two versions with noniterated triple contributions (see Refs. 40 and 41);
- R-CCSD[T] and R-CCSD(T), renormalized versions of the preceding methods;^{42,43}
- CR-CCSD[T], CR-CCSD(T) completely renormalized versions of the preceding methods;^{42,43}
- CR-CCSD(T)_L, a further improvement of CR-CCSD(T).¹²⁸

The CCSDT calculations were made with the ACES2 code.¹⁴² The other calculations were performed with codes due to Piecuch *et al.*¹³⁴ available in GAMESS. The renormalized and completely renormalized methods are due to Piecuch and co-workers.^{42,43,127,128} The deviations of the coupled-cluster values from the CEEIS full CI results are indicated in parentheses (in mhartree) in the table.

More points regarding these comparisons are exhibited on the plots in Fig. 7, which display the F_2 dissociation curves calculated by these coupled-cluster methods as well as the CEEIS-FCI curve.

The energies calculated with the coupled-cluster methods are seen to differ from the CEEIS full CI results by more than the chemical accuracy¹⁰⁶ value of 1.6 mhartree. The CCSDT method exhibits the smallest errors and, over a large range of internuclear geometries, its results never deviate from the CEEIS-FCI energies by more than 3.7 mhartree. The other CC methods exhibit larger and less consistent deviations. For instance, the CCSD[T] approximation yields an error of only 0.4 mhartree at the equilibrium geometry but an error of -23 mhartree for CCSD[T] at 2.8 \AA . The new¹²⁸ CR-CCSD(T)_L method is a marked improvement over the CCSD(T) method. In very recent articles, Bartlett and Musiał^{51,52} report results for several coupled-cluster methods including up to quadruple excitations and also give a detailed discussion of the general performance of single-reference coupled-cluster methods for bond-breaking processes.

The discussed results appear to confirm the recent conclusion of Nooijen and Le Roy⁴⁶ that, as yet, single-reference CC methods have problems with the potential energy curves, notably that of F_2 .

B. Multireference coupled-cluster (MRCC) methods

To overcome this shortcoming, research efforts are currently on going⁶⁶⁻⁷¹ to develop coupled-cluster expansions based on multiconfigurational reference functions (MRCC methods). A serious difficulty is that, in contrast to the situation in the single-reference CC formalism, the feature of *size-consistency is not intrinsic* to the MR-CC approaches.

Very recently, Evangelista-Allen-Schaefer⁶⁸ (EAS) have

TABLE XII. Comparison of full valence CI energies obtained by various coupled-cluster methods with the values determined by the CEEIS method for the cc-pVTZ basis set. Total energies in hartree. Deviations from CEEIS energies (in the parentheses) in millihartree.

Method	Internuclear distance		
	1.411 93 Å	2.2 Å	2.8 Å
CEEIS-FCI	-199.297 17	-199.247 09	-199.241 25
CCSDT	-199.296 10(1.07)	-199.243 39(3.70)	-199.238 36(2.89)
CCSD[T]	-199.296 81(0.36)	-199.254 21(-7.12)	-199.267 63(-26.38)
CCSD(T)	-199.296 10(1.07)	-199.251 67(-4.58)	-199.264 13(-22.88)
R-CCSD[T] ^a	-199.294 80(2.37)	-199.237 24(9.85)	-199.232 13(9.12)
R-CCSD(T) ^a	-199.294 17(3.00)	-199.235 39(11.70)	-199.229 94(11.31)
CR-CCSD[T] ^a	-199.293 56(3.61)	-199.233 36(13.73)	-199.226 57(14.68)
CR-CCSD(T) ^a	-199.292 96(4.21)	-199.231 67(15.42)	-199.224 67(16.58)
CR-CCSD(T) _L ^b	-199.296 38(0.79)	-199.239 76(7.33)	-199.234 10(7.15)

^aRenormalized and completely renormalized CC approaches (Ref. 134) available in GAMESS package of programs (Ref. 133).

^bCR-CCSD(T)_L data reported in Ref. 128.

discussed various MRCC methods in considerable detail. These authors (EAS) have implemented several “state-specific” MRCC approaches and applied them also to calculate the dissociation energy of F₂.⁶⁸ They find that the multireference coupled-cluster singles and doubles method of Mukherjee⁶⁷ (MkCCSD) appears to have the advantage of becoming near size consistent when the orbitals in the multiconfigurational reference function are chosen to be left-right localized.

The benchmark results of the present work allow an assessment of the dissociation energies of the EAS paper.⁶⁸ Table XIII lists the differences between the dissociation energies listed in Table 1 of the EAS paper and those obtained from the full CI energies for 1.411 93 and 8 Å in Table X of the present paper. Columns 2, 3, 4, and 5 of Table XIII list the deviations for the double-zeta, triple-zeta, quadruple-zeta, and (extrapolated) complete basis sets, respectively.

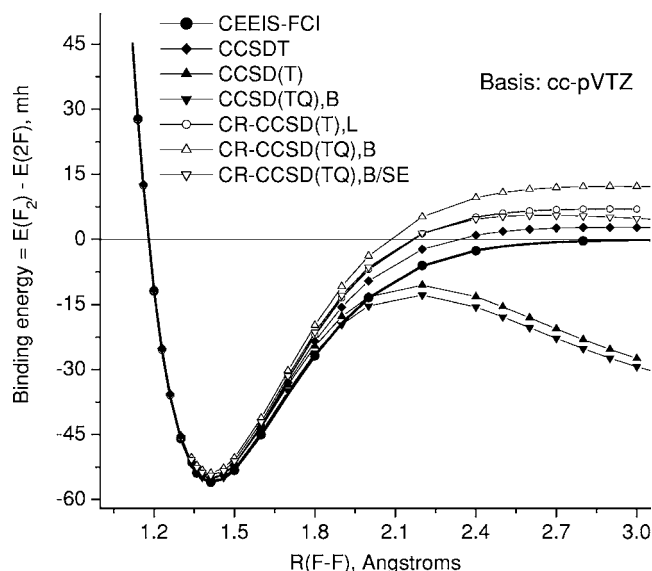


FIG. 7. Comparison of valence-CI potential energy curves of $[E(F_2) - 2E(F)]$ calculated by various coupled-cluster approximations (see text) with the CEEIS-determined full-valence CI curve. All calculations based on cc-pVTZ basis set.

The comparison is slightly inaccurate in as much as our data correspond to the actual equilibrium distance $R = 1.411\ 93\ \text{\AA}$, whereas the EAS data correspond to slightly different distances, namely, $R = 1.455, 1.413, 1.409,$ and $1.406\ \text{\AA}$ for the DZ, TZ, QZ, and CBS basis sets, respectively. For TZ, QZ, and CBS, this discrepancy is presumably very small, however.

The entries in the sixth column represent the proper comparison between the experimental data and the EAS results. Since the latter do not account for electron correlations including the core, spin-orbit coupling, and scalar relativistic effects, this column lists the differences

$$D_e(\text{EAS}) - [D_0 + G_0 + E_{\text{CV}} + E_{\text{SO}} + E_{\text{SR}}] \\ = D_e(\text{EAS}) - 62.558\ \text{mhartree}, \quad (17)$$

where $D_0 = 59.019\ \text{mhartree}$ experimental dissociation energy (from Ref. 143); $G_0 =$ experimental zero-point energy $2.075\ \text{mhartree}$ (from Table X in the third paper of the present series¹⁴⁴); $E_{\text{CV}} + E_{\text{SO}} + E_{\text{SR}} =$ energy contribution due to core-valence correlations + spin-orbital coupling + scalar relativistic corrections = $1.564\ \text{mhartree}$ (from Table IV in the second paper in this series¹⁴⁵).

To omit the terms $(E_{\text{CV}} + E_{\text{SO}} + E_{\text{SR}})$ in the comparison, as EAS do in their paper,⁶⁸ is manifestly not justified.

The consistent deviations of 5–6 mhartree for the natural orbital-based version are presumably attributable to the lack of size consistency. The greatly improved agreement when localized reference orbitals are used then implies a restoration of size consistency. In this context, it should be noted that the actual energies (as opposed to the binding energies) exhibit of course much larger errors with respect to the full CI values. For instance, the comparison of Fig. 1 of EAS with our Table VII shows that the triple-zeta MkCCSD value for the separated atoms lies about 20 mhartree above the actual full CI value.

EAS do not report the dissociation curve for F₂ at the CBS level and hence did not calculate the vibrational spectrum of F₂. Figure 1 in Ref. 68 displays this curve for the triple-zeta basis, calculated with the natural-orbital-based

TABLE XIII. Errors of MkCCSD (see Sec. VII B) dissociation energies of F₂ with respect to the CEEIS full CI benchmarks and to the experiment-deduced value. Energies in millihartree.

Basis of reference function	VDZ ^a	VTZ ^a	VQZ ^a	CBS ^a	EXP ^b
Symmetry-adapted natural orbitals	6.77	6.43	5.85	5.54	5.24
Left-right localized orbitals	1.19	-0.39	-0.69	-1.00	-1.30

^aDeviations of the MkCCSD values from the corresponding CEEIS full CI value of the present study.

^bDeviations of the MkCCSD-CBS values from the experiment-deduced value [see Eq. (17)].

reference function. This implies that the MkCCSD formalism does not break down when generating a dissociation curve for F₂. While, along the dissociation curve of F₂, the localized orbitals would be determined by symmetry for all internuclear distances, in heteroatomic molecules the question of suitable localizations along the reaction path would arise and how the localization choices affect the calculated spectrum.

VIII. CONCLUSIONS

The results of the present investigation demonstrate that the method of CEEIS (Refs. 98–102) also works well in those cases where zeroth-order reference functions are *essentially and strongly* multiconfigurational and that the method is applicable along reaction paths.

Specifically, the full CI energies for Dunning's correlation-consistent double-, triple- and quadruple-zeta bases have been determined within an accuracy of about 0.2–0.3 mhartree along the entire dissociation path of the F₂ molecule. The multiconfigurational FORS[14/8] and reduced RFORS[2/2] functions were used as zeroth-order references. The usefulness of the CEEIS method is highlighted by noting that the achievement of the aforementioned accuracy in the case of the quadruple-zeta basis required CI calculations with at most 1.1×10^8 determinants, whereas the full CI expansion contains, in fact, 3.7×10^{19} determinants.

It is found that, even though only a single bond is broken in the dissociation considered here, nonetheless sextuple excitations with respect to a single-determinant reference functions are required to recover the binding energy with an accuracy of 1 kcal/mol. This explains the difficulties encountered by other approaches such as MRCI-SD and CCSDT in treating this case.

The complete basis set limits of these full valence CI energies along the dissociation curve were obtained by separate extrapolations of the multiconfigurational zeroth-order reference energies (based on quadruple-, quintuple-, and sextuple-zeta bases) and of the correlation energies (based on triple- and quadruple-zeta bases). The binding energy deduced from this CBS potential energy curve –62.35 mhartree, as compared with the nonrelativistic valence-only binding energy estimate of -62.56 ± 0.04 mhartree derived from the experimental data.¹⁴³

The reported potential energy curve does not yet include core-correlation effects or relativity effects (scalar relativistic corrections and spin-orbit coupling). These additional energy terms will be determined and added in the subsequent paper.¹⁴⁵ From the resulting fully *ab initio* potential energy curve of F₂, the vibrational and rotational energy levels will

then be calculated and compared with the experimentally determined spectrum.¹⁰⁹

The accuracy of CEEIS method can be pushed further by taking into account larger CI expansions. This would also call, however, for the use of larger basis sets and the possible accounting of smaller physical corrections such as nonadiabatic effects or spin-spin couplings. Such extensions might be revisited when new approaches to the CI problem, such as nonlinear expansions³⁶ or selection techniques,^{32,38,64,65} are further developed. For larger systems, the use of appropriately localized molecular orbitals^{146–149} should prove helpful.

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