Full Configuration Interaction by Correlation Energy Extrapolation through Intrinsic Scaling (CEEIS)

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Motivation for High Accuracy Quantum Chemistry

Reaction paths and transition state regions
are essential for understanding chemical reactions.

For most reaction paths, experimental information is scarce,
theoretical information is therefore valuable.

To assess the reliability of simpler theoretical approaches,
accurate theoretical benchmarks are needed along reaction paths.

The assessment of accurate theoretical benchmark approaches,
requires accurate experimental data along reaction paths.
They exist only in diatomic molecules from vibrational spectra.

Physical Factors Determining Potential Energy Surfaces

Electronic energy

= correlated nonrelativistic valence energy

with cc-pVXZ bases basis sets, X = 2, 3, 4, …

+ complete basis set extrapolation

For MCSCF reference energy [~exp(−αX)]
for correlation energy [~X^{-3} & X^{-5}]

+ core and core-valence interaction energy

MRCI + correction

+ one and two electron spin-orbit coupling

Spin-orbit coupling interactions (one- and two-electron Pauli-Breit)

+ one-electron scalar relativistic terms

Mass-velocity and Darwin corrections

+ spin-spin coupling terms

Presently not incuded

Challenge

Along reaction paths, valence correlations are calculated with respect to multi-configurational zeroth-order reference functions

Some Basic Quantum Chemical Concepts

- ***Molecular orbitals (MOs)*** are constructed as linear combination of standard ***atomic orbital(AO) basis sets***: double-zeta, triple-zeta, ….. ***cc-pVXZ***
  These have been constructed and gauged so that the resulting energies can be extrapolated to the ***complete basis set (CBS) limit.***
  The possible number of MOs is equal to the number of basis-set AOs.

- ***Configurations = Slater determinants*** = antisymmetrized products of MOs.
  Configuration Interaction = Construction of wavefunctions as linear combinations of configurations. ***Full CI (FCI)*** = wavefunction in terms of *all* configurations that can be constructed for a given AO basis set = the best possible wavefunction in this basis.
  The ***CBS limit of FCI*** wvfctns is expected to be the exact solution of the Schröd. Equ.

- ***Zeroth-order or reference*** configurations capture the dominant part of the exact wavefunction (>80% often >90%). If one determinant: ***SCF***. If several: ***MCSCF***.
  No. of MOs ≤ No. of electrons. MOs must be optimized = ***reference MOs***.
  Reference wavefunctions are said to contain ***no or only static correlation.***

- The difference between the exact wavefunction and the reference wavefunction is said to provide ***dynamic correlation***. It is a superposition of the ***correlating configurations*** which involve the ***correlating or virtual orbitals.***

- ***Chemical accuracy*** ≈ kT at room temperature ≈ ***millihartree (mh)***
  ev = 36.8 mh, kcal/mol = 1.59 mh/molecule, $cm^{-1}\times hc$ = 0.005 mh

Excitation-Ordered Full CI: Wavefunction

Zeroth-order reference Ψ_o **:** SCF or limited MCSCF

Orbitals : Natural orbitals of SD-CI with respect to Φ_o :

Ordered by occupation No: > 0.1: Reference NOs
< 0.1: Correlating NOs

Full CI wavefunction: $\boxed{\Psi = \Psi_0 + \sum_x \Psi_x}$

Ψ_0 **:** One- or multi-determinant reference function in the full reference NO space

$\sum_x \Psi_x$ **:** a finite rapidly convergent series,

$\Psi_x = \sum_k \Psi_{xk}$ over all x-tuply excited determinants Ψ_{xk} with respect to Ψ_0 , i.e. containing x correlating NOs.

This series is very long and very slowly convergent.

Excitation-Ordered Full CI: Energy

Resolution in terms of excitation contributions

$$\mathbf{E}(\Psi) = \mathbf{E}(\Psi_o) + \mathbf{E}_{corr} = \mathbf{E}(\Psi_o) + \sum_x \Delta\mathbf{E}(\mathbf{x})$$ rapidly convergent

$\Delta\mathbf{E}(\mathbf{x}) =$ E(x) – E(x–1) = incremental excitation contribution

$$E(x) = \langle \Psi_0 + \Psi_1 + \Psi_2 + \ldots + \Psi_x | \mathcal{H} | \Psi_0 + \Psi_1 + \Psi_2 + \ldots + \Psi_x \rangle$$

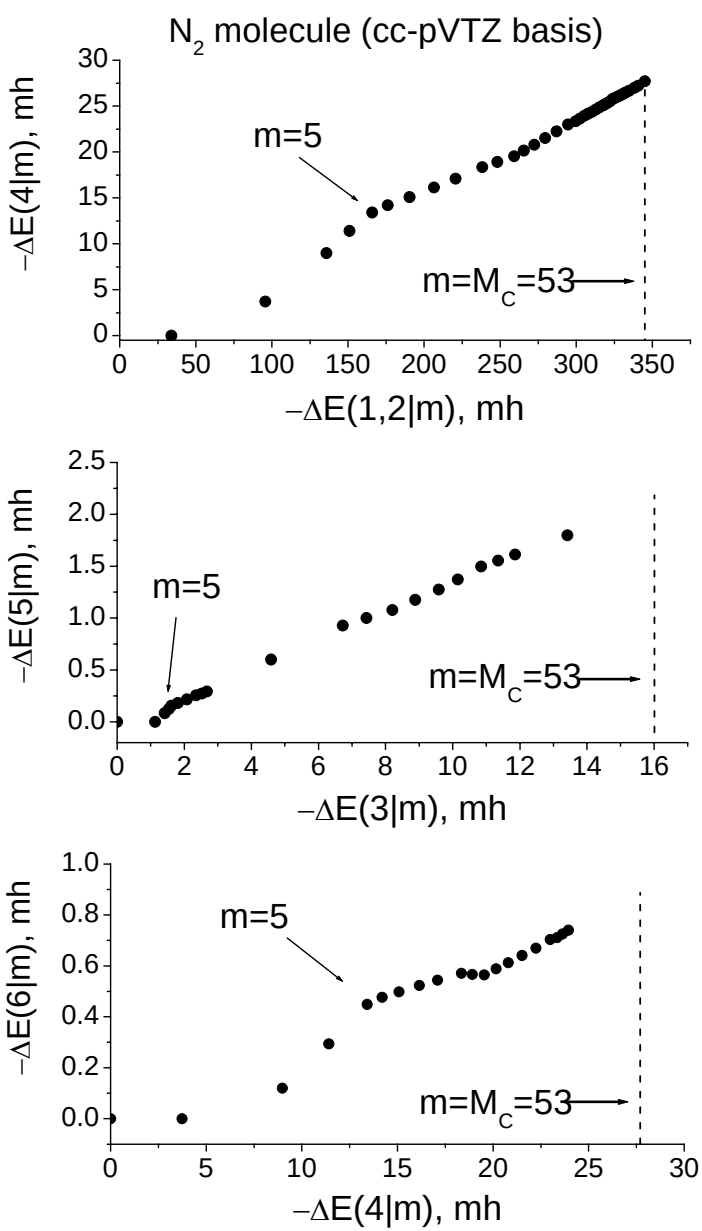
Excitation contributions as orbital limits

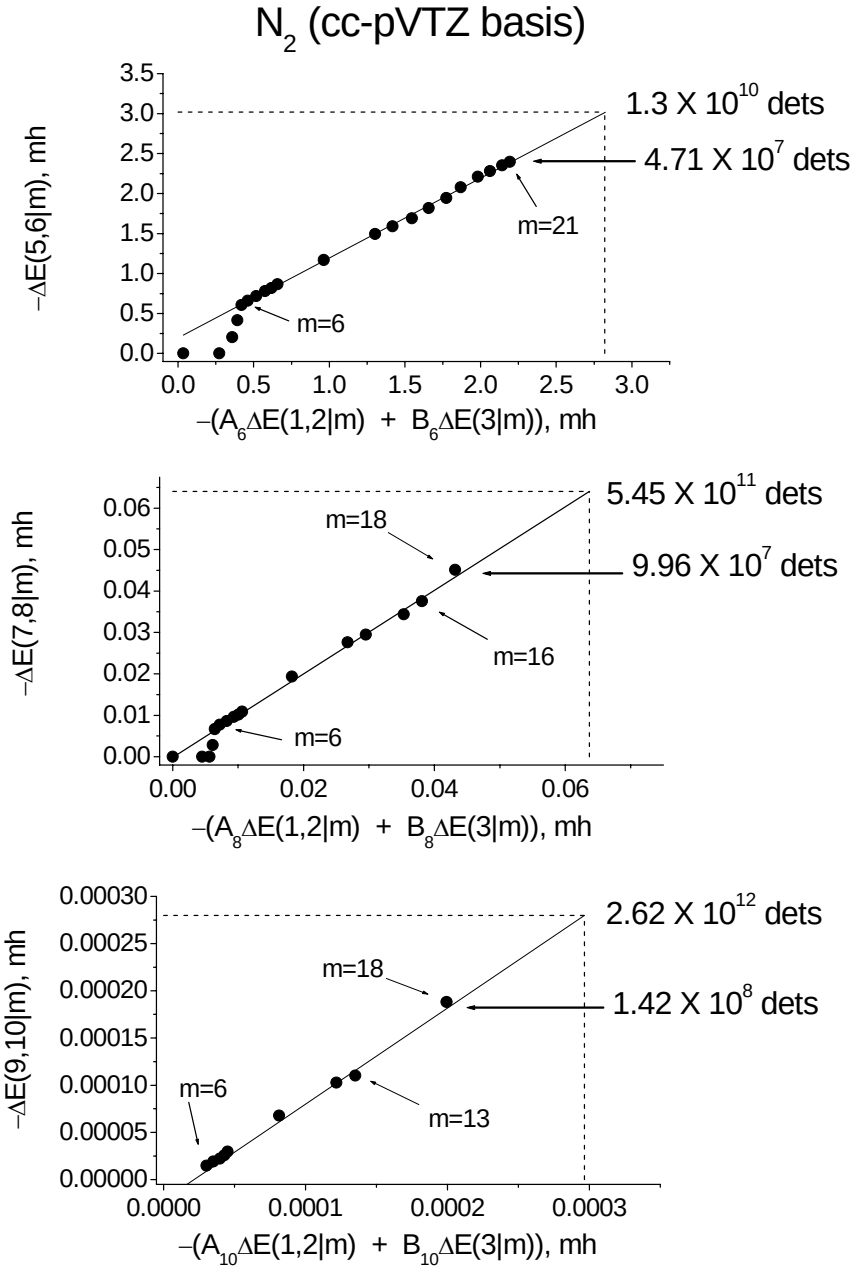
$\Delta\mathbf{E}(\mathbf{x}) = \mathbf{limit}\ \Delta\mathbf{E}(\mathbf{x}|\mathbf{m})$

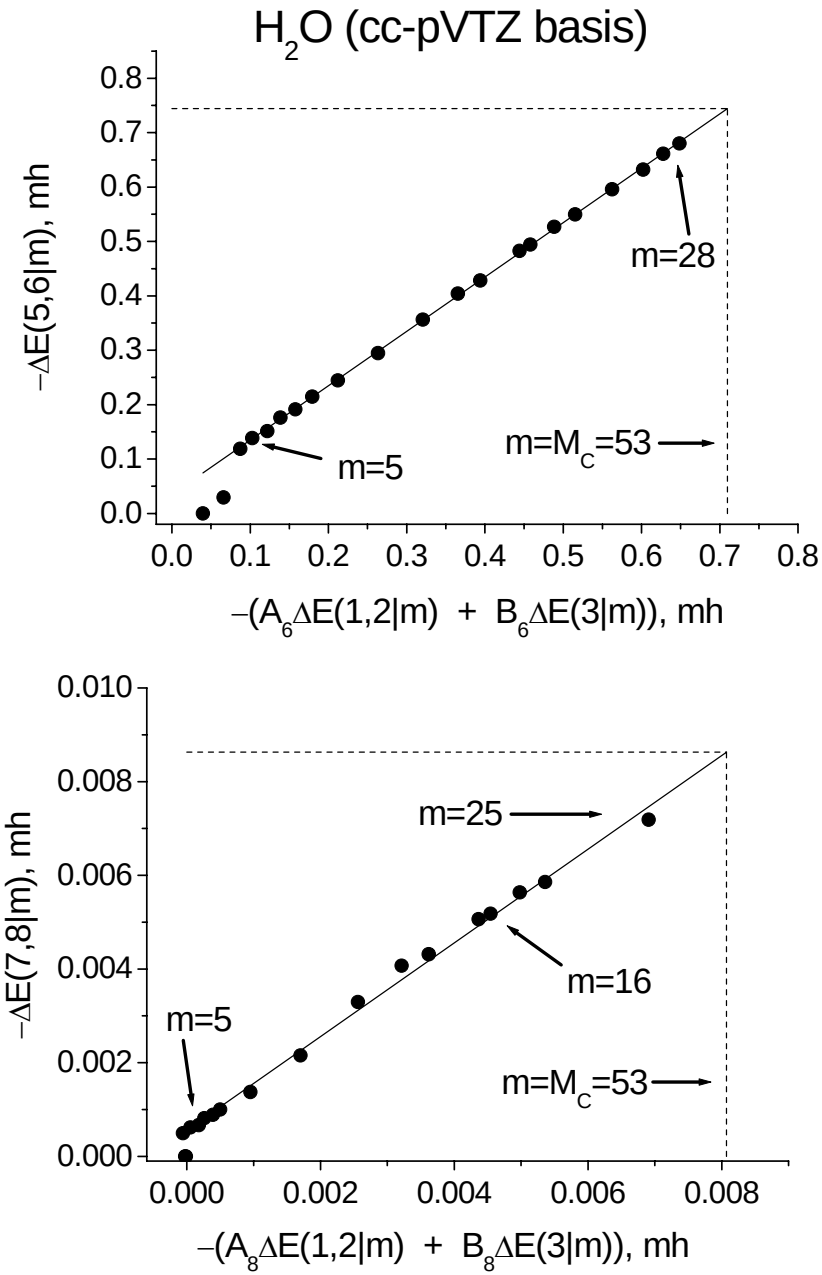
where $\Delta\mathbf{E}(\mathbf{x}|\mathbf{m})$ is analogous to $\Delta\mathbf{E}(\mathbf{x})$ above, EXCEPT that only the first m correlating NOs are used

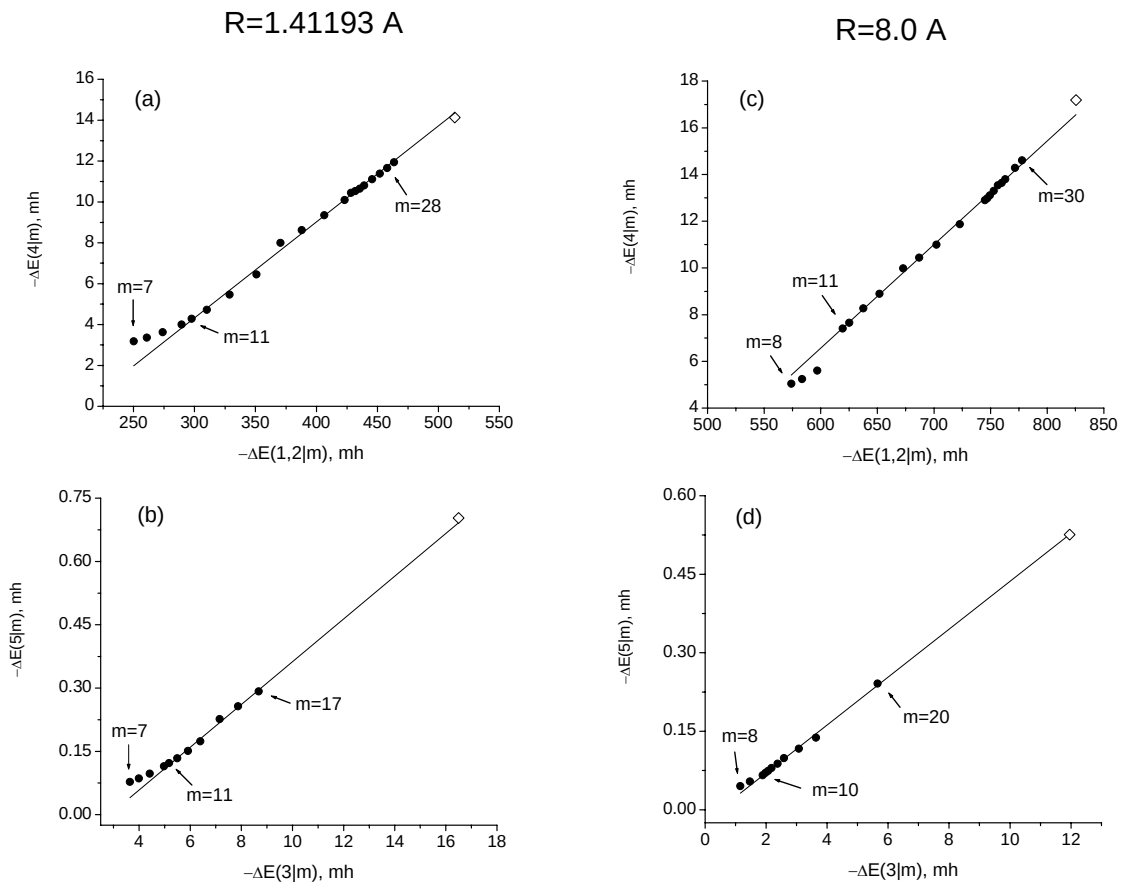
Limit: $m \rightarrow M$ = total No. of correlating NOs

We shall compare the $\Delta E(x|m)$, considered as functions of m, from different excitation levels x.


N2 molecule (cc-pVTZ basis)
m=5
m=MC=53
−ΔE(4|m), mh
−ΔE(1,2|m), mh
m=5
m=MC=53
−ΔE(5|m), mh
−ΔE(3|m), mh
m=5
m=MC=53
−ΔE(6|m), mh
−ΔE(4|m), mh


N2 (cc-pVTZ basis)
1.3 X 10^10 dets
4.71 X 10^7 dets
m=21
m=6
−ΔE(5,6|m), mh
−(A6ΔE(1,2|m) + B6ΔE(3|m)), mh
5.45 X 10^11 dets
9.96 X 10^7 dets
m=18
m=16
m=6
−ΔE(7,8|m), mh
−(A8ΔE(1,2|m) + B8ΔE(3|m)), mh
2.62 X 10^12 dets
1.42 X 10^8 dets
m=18
m=6
m=13
−ΔE(9,10|m), mh
−(A10ΔE(1,2|m) + B10ΔE(3|m)), mh


H2O (cc-pVTZ basis)
−ΔE(5,6|m), mh
−(A6ΔE(1,2|m) + B6ΔE(3|m)), mh
m=28
m=5
m=MC=53
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
−ΔE(7,8|m), mh
−(A8ΔE(1,2|m) + B8ΔE(3|m)), mh
m=25
m=16
m=5
m=MC=53
0.000
0.002
0.004
0.006
0.008
0.010



CEEIS extrapolations up to quintuple excitations w/r to FORS[14/8] reference function of F_2. Solid lines: LMSQ fits to calculated solid points. Open diamonds: best extrapolated estimates.

Correlation energy extrapolation by intrinsic scaling CEEIS

Scaling relations for ΔE(x|m) considered as functions of m for fixed x

$$\boxed{\Delta E(x|m) = a_x\, \Delta E(x-2|m) + c_x} \qquad \text{for } x \geq 4$$

whence also

$$\Delta E(x,x+1|m) = E(x+1|m) - E(x-1|m)$$

$$= A_x\, \Delta E(2|m) + B_x\, \Delta E(3|m) + C_x \qquad \text{for } x \geq 5$$

$$E(\text{all excitations}|m) - E(3|m)] = A\, \Delta E(2|m) + B\, \Delta E(3|m) + C$$

Extrapolation

(i) Obtain coefficients a, b, or A, B, C by LMSQ fitting

***to low values of m* with a *moderate number of determinants*.**

(ii) Obtain the desired values $\Delta E(x) = \Delta E(x|M)$ for $x \geq 4$

from the values $\Delta E(x) = \Delta E(2|M)$ and $\Delta E(x) = \Delta E(3|M)$

Extrapolated contributions of excitation levels >3 to the valence correlation energy of N_2 in the cc-pVTZ basis

Fitting range m_0–m_1	**No. det's in millions for m_1**	NO occ.# in units 10^{-3} for m_1	**$-\Delta E(x\|m)$ in millihartree** $m=m_1$	**$m=53$**
		(SDTQ–SDT)		
13–17	**0.411**	1.7	20.164	**27.887**
13–25	**1.964**	0.4	25.095	**27.663**
Full ,53	**40.6**			**27.702**
		(SDTQ5–SDTQ)		
6–12	**0.500**	4.0	0.928	**2.355**
13–17	**2.979**	1.7	1.373	**2.163**
Full ,53	**945.4**			**2.186**
		(SDTQ56–SDTQ5)		
6–12	**1.526**	4.0	0.565	**0.724**
13–17	**12.938**	1.7	0.704	**0.894**
Full, 53	**1.3×10^4**			**0.888**

Extrapolated contributions of excitation levels >3 to the valence correlation energy of N_2 (cc-pVTZ basis)

Fitting range m_0–m_1	**No. det's in millions for m_1**	NO occ.# in units 10^{-3} for m_1	**$-\Delta E(x\|m)$ in millihartree** $m=m_1$	**$m=53$**
		(SDTQ56–SDTQ)		
5–14	**3.934**	2.0	1.692	**2.927**
5–14	**47.105**	0.5	2.398	**3.020**
Full ,53	**1.4×10^{4}**			**3.074**
		(SDTQ5678–SDTQ56)		
5–12	**4.221**	4.0	0.028	**0.066**
Full ,53	**5.5×10^{5}**			**0.064**
		(FCI–SDTQ78)		
6–13	**9.182**	2.0	1.1×10^{-4}	**2.6×10^{-4}**
Full ,53	**2.6×10^{6}**			**2.8×10^{4}**

Recovery of the valence correlation energy of N_2 in the cc-pVTZ basis by extrapolation (Energies in mh)

Contributions of successive excitations to Valence Correlation Energy

SDT – HFSCF	0.988×10^{6} det's	–360.99
SDTQ56 – SDT	1.304×10^{10} det's	– 30.78
SDTQ5678 – SDTQ56	5.447×10^{11} det's	–0.06
SDTQ5678 – SDT	5.447×10^{11} det's	– 30.84
FCI(M=53) – HFSCF	2.624×10^{12} det's	–391.83

Recovery of (SDTQ5678–SDT) by various extrapolations

----------Fitting ranges---------				Max. No of det's in millions	**Deviation from –30.84 mh**
x=4	x=5	x=6	x=7,8		
m_0,m_1	m_0,m_1	m_0,m_1	m_0,m_1		
13,25	5,12	5,12	–	**1.964**	**0.19**
18,32	5,12	5,12	5,12	**5.323**	**0.05**
18,32	5,21	5,21	5,12	**47.105**	**0.01**

Bond Breaking Energies by CEEIS

	E_{bond}(exp) (mh)	δE^a (mh)	$\Delta_c E^b$ (mh)	$\Delta_r E^c$ (mh)	full CI[d] (dets)	CEEIS[e] (dets)
$C_2 \rightarrow 2C$	235.9 ±0.8	*-1.8*	*2.4*	*-0.6*	4×10^{12}	6×10^{7}
$N_2 \rightarrow 2N$	363.9 ±0.04	*0.00*	*1.4*	*0.2*	2×10^{15}	2×10^{8}
$O_2 \rightarrow 2O$	191.6 ±0.002	*-0.3*	*0.5*	*-1.0*	2×10^{17}	3×10^{7}
$F_2 \rightarrow 2F$	61.0 ±0.2	*-0.2*	*-0.3*	*-1.3*	4×10^{19}	1×10^{8}
$H_2O \rightarrow H_2 + ½O_2$	100.4	*-0.02*	*0.35*	*-0.29*	first bench mark	

[a] Error in the dissocation energy (CEEIS value – experimental value)

[b] Contribution of core and core-valence correlations to disociation energy

[c] Spin orbit coupling + scalar relativistic contribution to dissociation energy

[d] Dimension of full valence CI for quadruple-zeta basis (in # of determinants)

[e] Dimension of largest CI occurring in the CEEIS calculation (in # of determinants)

Breakdown of Binding Energies in O_2 and F_2 (mh)

Energy	O	O_2	$2O \rightarrow O_2$
Nonrelativistic Valence	**–75 005.8**	**–150 204.0**	**–193.2**
Core Correlations	–62.1	–124.9	–0.7
Scalar Relativistic	**–38.35**	**–76.4**	**0.3**
Spin Orbit Coupling	**–0.35**	**0.0**	**0.7**
Theory	**–75 106.6**	**–150 406.1**	**–192.9**
Exp. Dissociation	**–75 106.1**	**–150 400.2**	**–188.0 ±0.002**
Exp. Zero-Point Vibration	*0.0*	*3.6*	*3.6*
Experiment	–75 106.1	–150 403.8	–191.6 ±0.002

Energy	F	F_2	$2F \rightarrow F_2$
Nonrelativistic Valence	**–99 668.8**	**–199 399.2**	**–61.6**
Core Correlations	–65.4	–130.8	0.0
Scalar Relativistic	**–70.9**	**–141.8**	**0.0**
Spin Orbit Coupling	**–0.6**	**0.0**	**1.2**
Theory	**–99 805.7**	**–199 671.8**	**–60.4**
Exp. Dissociation	**–99 805.6**	–199 670.1	**–58.9 ± 0.2**
Exp. Zero-Point Vibration	*0.0*	*2.1*	*2.1*
Experiment	–99 805.6	–199 672.2	–61.0 ± 0.2

Role of Complete Basis Set Extrapolation for Atomic, Molecular and Binding Energy Errors (mh)

	CEEIS-FCI calculations VDZ	VTZ	VQZ	CBS[a] extrapol	Dimensions of CI spaces[b]
2C	58.4	17.4	5.9	-1.2	
C_2	85.6	29.1	11.3	0.6	3.6×10^{12}
$2C\rightarrow C_2$	***27.2***	***11.7***	***5.4***	***1.8***	**6.4×10^{7}**
2N	103.6	31.0	10.7	-1.4	
N_2	146.7	48.4	18.0	-1.4	1.6×10^{15}
$2N\rightarrow N_2$	***43.1***	***17.4***	***7.3***	***0.0***	**2.0×10^{8}**
2O	190.5	62.1	23.0	-1.0	
O_2	214.6	72.0	27.0	-2.3	1.7×10^{17}
$2O\rightarrow O_2$	***24.1***	***9.9***	***4.0***	***-1.3***	**3.2×10^{7}**
2F	282.1	96.3	36.5	-0.2	
F_2	300.3	102.2	39.5	0.4	3.7×10^{19}
$2F\rightarrow F_2$	***18.2***	***5.9***	***3.0***	***0.6***	**1.1×10^{8}**

[a] Extrapolation: HF=exact, Correlation ~ X^{-3} (Relativity correctns included).

[b] Number of determinants in CI spaces of ***molecule for cc-pVQZ basis***:
Black : Full CI space, Blue: Largest space needed in CEEIS method.

Dissociation $F_2(^1\Sigma_g^+) \rightarrow 2\ F(^2P)$

The zeroth-order reference function for an excitation-ordered full CI calculation must be multi-configurational

Reference valence orbitals

$$2\sigma_g,\ 2\sigma_u,\ 3\sigma_g,\ 3\sigma_u,\ 2\pi x_u,\ 2\pi y_u,\ 2\pi x_g,\ 2\pi y_g$$

Reference wavefunction Ψ_o

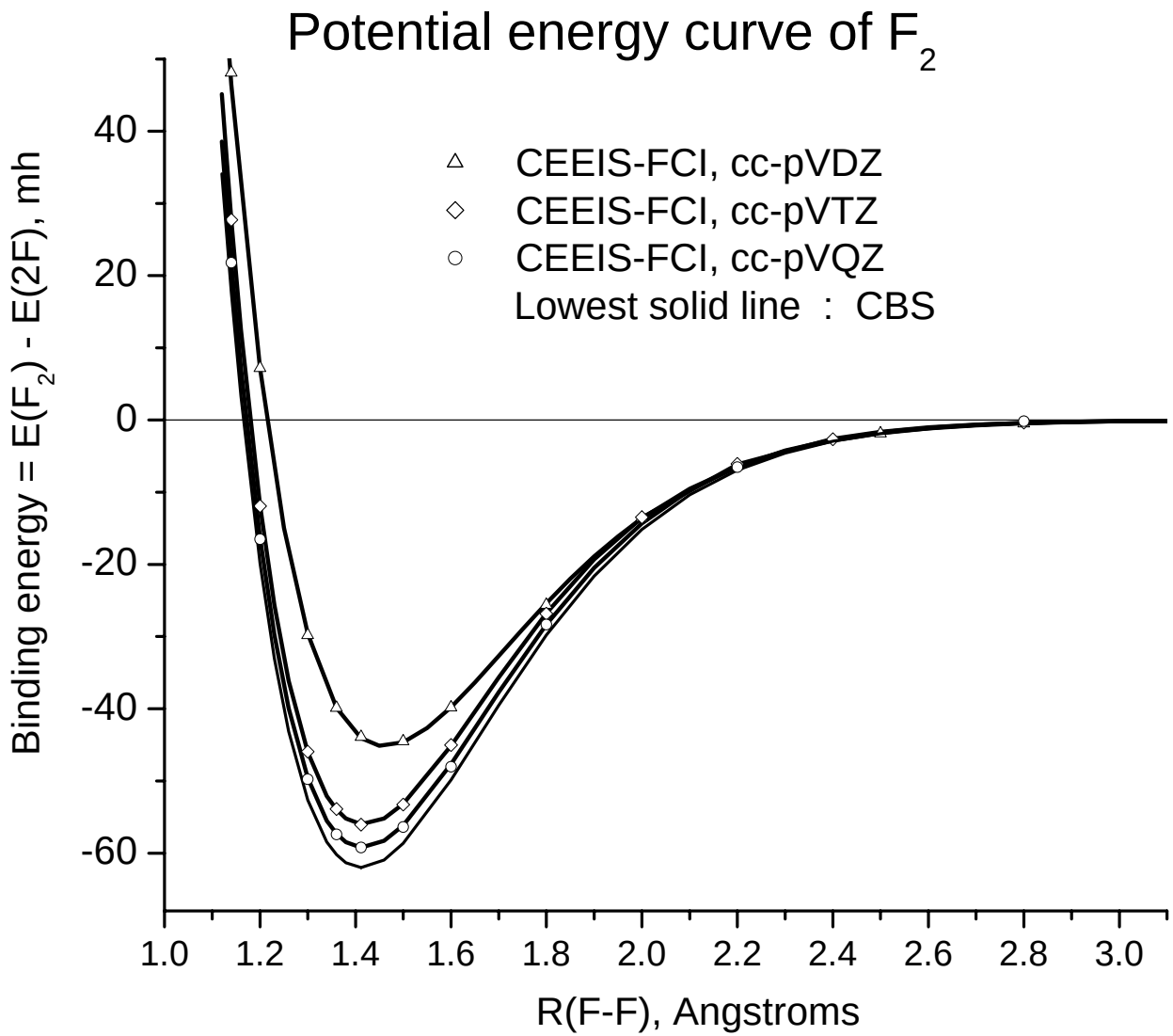
Minimal:

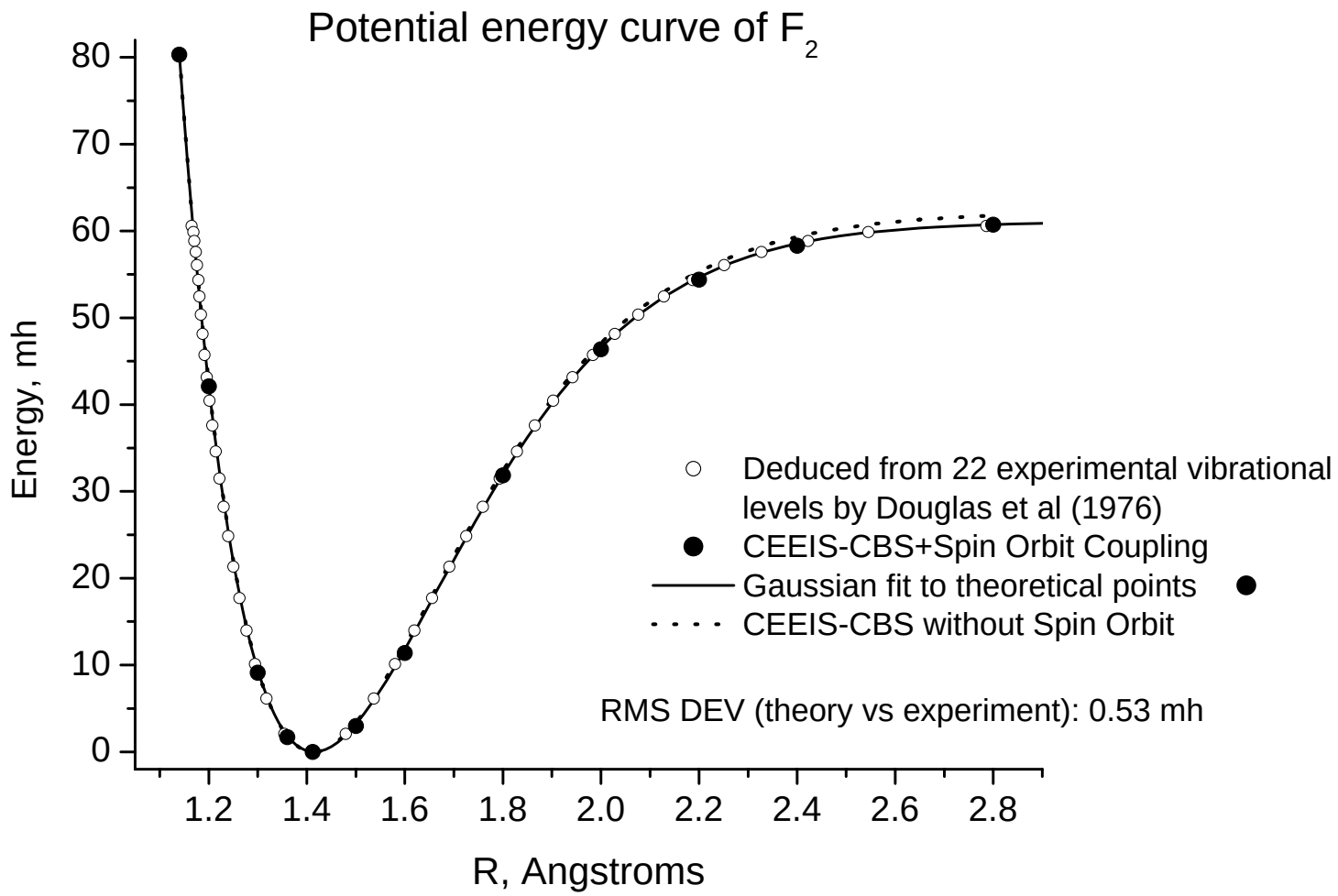
$$a(r)\ \mathcal{A}\{\text{core}^4\ 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 2\pi x_u^2 2\pi y_u^2 2\pi x_g^2 2\pi y_g^2\ (\alpha\beta)^9\}$$
$$+\ b(r)\ \mathcal{A}\{\text{core}^4\ 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_u^2 2\pi x_u^2 2\pi y_u^2 2\pi x_g^2 2\pi y_g^2,\ (\alpha\beta)^9\}$$

upon dissociation [a(r)/b(r)] changes from ≈1 to 0.

Maximal:

Full valence space with 12 determinants


Potential energy curve of F2
CEEIS-FCI, cc-pVDZ
CEEIS-FCI, cc-pVTZ
CEEIS-FCI, cc-pVQZ
Lowest solid line : CBS
Binding energy = E(F2) - E(2F), mh
40
20
0
-20
-40
-60
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
R(F-F), Angstroms


Potential energy curve of F_2
Energy, mh
R, Angstroms
80
70
60
50
40
30
20
10
0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
Deduced from 22 experimental vibrational levels by Douglas et al (1976)
CEEIS-CBS+Spin Orbit Coupling
Gaussian fit to theoretical points
CEEIS-CBS without Spin Orbit
RMS DEV (theory vs experiment): 0.53 mh

Determination of Vibration Rotation Spectrum

Schrödinger equation with the analytical potential V(r)

$$[(\hbar^2/2\mu)(\partial/\partial r)^2 + J(J+1)/r^2]\, f(r) + V(r)\, f(r) = E_{v,J}\, f(r)$$

Solution for J = 1 to 10 by *discrete variable representation (Light, Miller)* on a 500 point grid yielded

23 theoretical vibrational levels for J = 0. The experimentalists had found 22, but had left open the existence of a 23th.

Organization of spectrum

$$E_{v,J} = V_{eq} + G_v + F_v(J)$$

$$F_v(J) = B_v\,[J\,(J+1)] - D_v\,[J\,(J+1)]^2 + \ldots$$

B_v , D_v determined by power series expansion in terms of J for J = 1-10.

Two terms are accurate to 10^{-6} cm^{-1} for v up to ≈ 10,
to 10^{-5} cm^{-1} for v up to ≈ 18, to 10^{-3} cm^{-1} for v = 23

Vibrational levels of F_2 (cm^{-1}): Deviations theory minus experiment

Val=Valence correlation. CV=Core-valence correlation.
SO=spin-orbit coupling. SR=scalar relativistic contribution

v	Experiment	VAL	VAL+CV	VAL+CV+SO	VAL+CV+SO+SR
0	0.00	0.00	0.00	0.00	0.00
1	893.90	3.14	2.45	-1.35	-1.82
2	1764.15	6.41	4.90	-2.02	-2.96
3	2610.22	9.69	7.24	-2.13	-3.52
4	3431.53	12.89	9.37	-1.79	-3.63
5	4227.43	15.94	11.23	-1.07	-3.35
6	4997.19	18.85	12.81	0.02	-2.73
7	5740.05	21.60	14.11	1.29	-1.84
8	6455.17	24.22	15.15	2.83	-0.71
9	7141.63	26.77	15.99	4.58	0.62
10	7798.48	29.29	16.66	6.44	2.07
11	8424.67	31.86	17.26	8.35	3.58
12	9019.11	34.55	17.82	10.18	5.00
13	9580.63	37.40	18.41	11.76	6.17
14	10108.02	40.45	19.04	12.78	6.79
15	10599.62	44.06	20.05	13.23	6.83
16	11053.90	48.34	21.57	12.73	5.91
17	11468.96	53.68	23.94	10.99	3.74
18	11842.62	60.57	27.63	7.62	-0.07
19	12172.25	69.79	33.39	2.21	-5.94
20	12452.98	84.18	43.99	-4.08	-12.72
21	12678.00	108.31	63.94	-9.13	-18.28
22	12830.38	156.70	107.61	-2.21	-11.93
Mean abs. deviation		33.68	17.65	5.87	4.00 cm^{-1}

Potential Energy Curve for $O_2(^3\Sigma_g^-) \rightarrow 2\ O(^3P)$

Zeroth order valence orbitals

$$2\sigma_g,\ 2\sigma_u,\ 3\sigma_g,\ 3\sigma_u,\ 2\pi x_u,\ 2\pi y_u,\ 2\pi x_g,\ 2\pi y_g$$

Multi-configurational zeroth-order reference function

Minimal

Ψ_o = $^3\Sigma_g^-$ function ($^3B_{1g}$ in D_{2h})

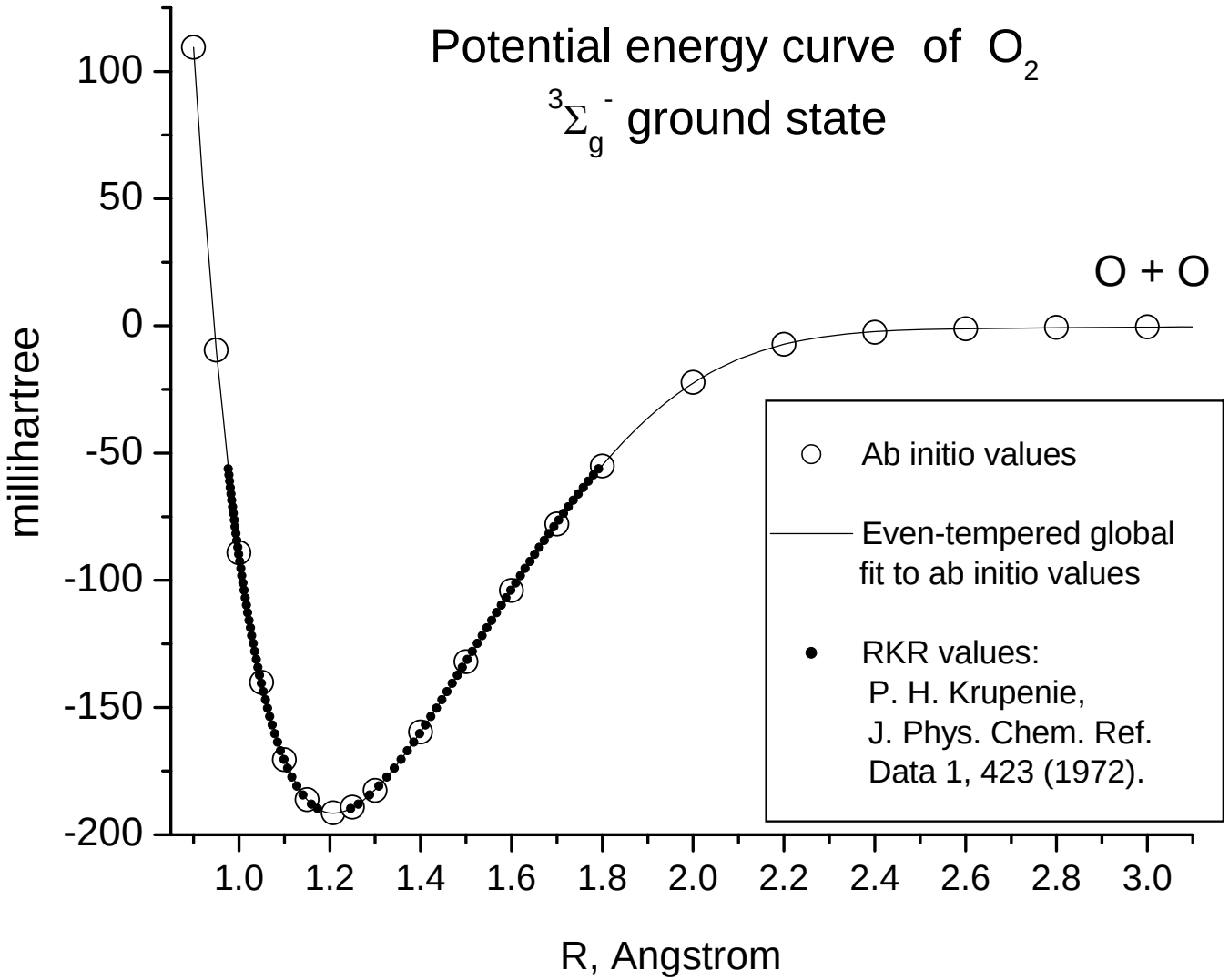
= superposition of 56 determinants in ORMAS space of

[6 electrons in full $\{(2\sigma_g)(2\sigma_u)(3\sigma_g)(3\sigma_u)\}$-space]

$\times$[6 electrons in full $\{(2\pi x_g)\ (2\pi y_g)\ (2\pi x_u)\ (2\pi y_u)\}$-space]

Alternative

Full [12/8] valence space: 60 determinants


Potential energy curve of O_2
$^3\Sigma_g^-$ ground state
O + O
millihartree
100
50
0
-50
-100
-150
-200
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
R, Angstrom
Ab initio values
Even-tempered global fit to ab initio values
RKR values:
P. H. Krupenie,
J. Phys. Chem. Ref. Data 1, 423 (1972).

Vibrational energy levels $G(v) = G_v - G_0$ from ab initio PE curve of O_2 compared with the experimental levels. Energies in cm^{-1}.

V	Theory	Theory–exp	v	Theory	Theory-exp
0	0.00	0.00	21	27838.22	-9.28
1	1563.91	7.53	22	28903.93	-10.12
2	3102.41	13.30	23	29943.20	-11.08
3	4615.82	17.21	24	30955.05	-12.53
4	6104.47	19.78	25	31938.33	-14.29
5	7568.69	21.00	26	32891.72	-16.65
6	9008.83	20.69	27	33813.68	-19.43
7	10425.21	18.33	28	34702.42	-21.27
8	11818.11	16.44	29	35555.81	-26.12
9	13187.82	14.22	30	36371.35	-28.28
10	14534.56	11.32	31	37146.02	-29.36
11	15858.51	6.09	32	37876.11	-20.89
12	17159.79	3.23	33	38556.98	4.98
13	18438.48	1.44	34	39182.59	2.59
14	19694.57	-0.63	35	39744.72	-15.28
15	20927.98	-2.92	36	40231.48	--
16	22138.58	-4.52	37	40623.94	--
17	23326.14	-5.36	38	40891.04	--
18	24490.33	-6.78	39	41030.67	--
19	25630.76	-7.77	40	41129.55	--
20	26746.93	-8.53	41	41204.62	--
Mean Absolute Deviation					12.84

Vibrational energy differences $G(v) = G_v - G_0$ of $^3\Sigma_g^-$ (O_2) (cm^{-1})

v	Experiment	Deviation from the experiment			
		VAL	VAL+SR	VAL+SR+SO	VAL+SR+SO+CV
0	0	0	0	0	0
1	1 556.39	1.59	-0.58	-0.79	7.53
2	3 089.11	1.62	-2.70	-3.14	13.30
3	4 598.61	-0.04	-6.50	-7.16	17.21
4	6 084.69	-2.89	-11.46	-12.34	19.78
5	7 547.69	-6.96	-17.61	-18.68	21.00
.....	.....	.....	.....	.....	.....
10	14 523.24	-41.72	-62.23	-63.62	11.32
.....	.....	.....	.....	.....	.....
15	20 930.90	-78.93	-108.14	-108.97	-2.92
.....	.....	.....	.....	.....	.....
20	26 755.46	-104.20	-141.00	-141.28	-8.53
.....	.....	.....	.....	.....	.....
25	31 952.62	-123.86	-167.47	-168.27	-14.29
.....	.....	.....	.....	.....	.....
30	36 399.63	-142.39	-192.76	-195.64	-28.28
31	37 175.38	-142.76	-194.58	-198.01	-29.36
32	37 897.00	-132.85	-186.19	-190.18	-20.89
33	38 552.00	-104.67	-159.62	-164.17	4.98
34	39 180.00	-103.66	-160.34	-165.40	2.59
35	39 760.00	-116.60	-175.18	-180.73	-15.28
MAD		80.24	112.39	113.89	12.84
ZPE	787.20	788.60	787.50	787.41	791.64
D_e	42 051.34	42 155.30	42 085.87	41 922.28	42 030.05
R_e (Å)	1.20752	1.21019	1.21043	1.21041	1.20781

Correlation Contribution to Binding in O_2 and F_2 (mh)

Theory	O_2	F_2
Zeroth order, complete basis (CBS)	–151.52	–29.65
Valence shell-correlation, (CBS)	–40.49	–32.7
Valence shell full CI, (CBS)	**–192.01**	**–62.35**
Core and core-valence correlation	**–0.50**	**0.31**
Spin-orbit coupling	**0.74**	**1.20**
Scalar relativistic corrections	**0.32**	**0.05**
Theoretical binding energy	**–191.45**	**–60.79**
Experiment		
Experimental dissociation energy	–188.0	–58.9
Experimental. zero-point vibration energy	3.6	2.1
Experimental electronic binding energy	**–191.6**	**–61.0**

Long Range van der Waals Interactions

- **Multipolar electrostatic interactions in homonuclear diatomics**

  Strongest: Interaction between atomic quadrupoles Θ

  $V_{quad}(R) = +6\,\Theta^2/R^5$ for Σ states: $\leftrightarrow\ \leftrightarrow$: repulsive

  $= -3\,\Theta^2/R^5$ for Π states: $\leftrightarrow\updownarrow + \updownarrow\leftrightarrow$: attractive

- **London dispersion interactions: Correlation effect**

  $V_{disp}(R) = -C_6/R^6 - C_8/R^8 - C_{10}/R^{10}\ \ldots\ldots$: attractive

- **Terra incognita**
  - *Transition* from short-range covalent binding regime to long-range van der Waals regime of weak forces
  - *Quantitative* relations between simultaneous long range multipolar and dispersion forces
  - Possible *competition* between quadrupolar repulsions and dispersion attractions in Σ states

Separating the Potential Energy Curve $F_2(^1\Sigma_g^+) \rightarrow 2F(^2P)$ into an Uncorrelated and a Correlated Contribution

- $\Psi = \Psi_o + \Psi_{corr} = \Psi_{rfors} + \Psi_{corr}$

$$\Psi_{rfors} = a(r)\,\mathcal{A}\{core^4\, 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 2\pi x_u^2 2\pi y_u^2 2\pi x_g^2 2\pi y_g^2\, (\alpha\beta)^9\}$$
$$+ b(r)\,\mathcal{A}\{core^4\, 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_u^2 2\pi x_u^2 2\pi y_u^2 2\pi x_g^2 2\pi y_g^2,\, (\alpha\beta)^9\}$$

= **"non-dynamic correlation"**
really uncorrelated dissociation

$\Psi_{corr} = \sum_x \Psi_x$ **"dynamic correlation", true correlation, 10^8 det's**

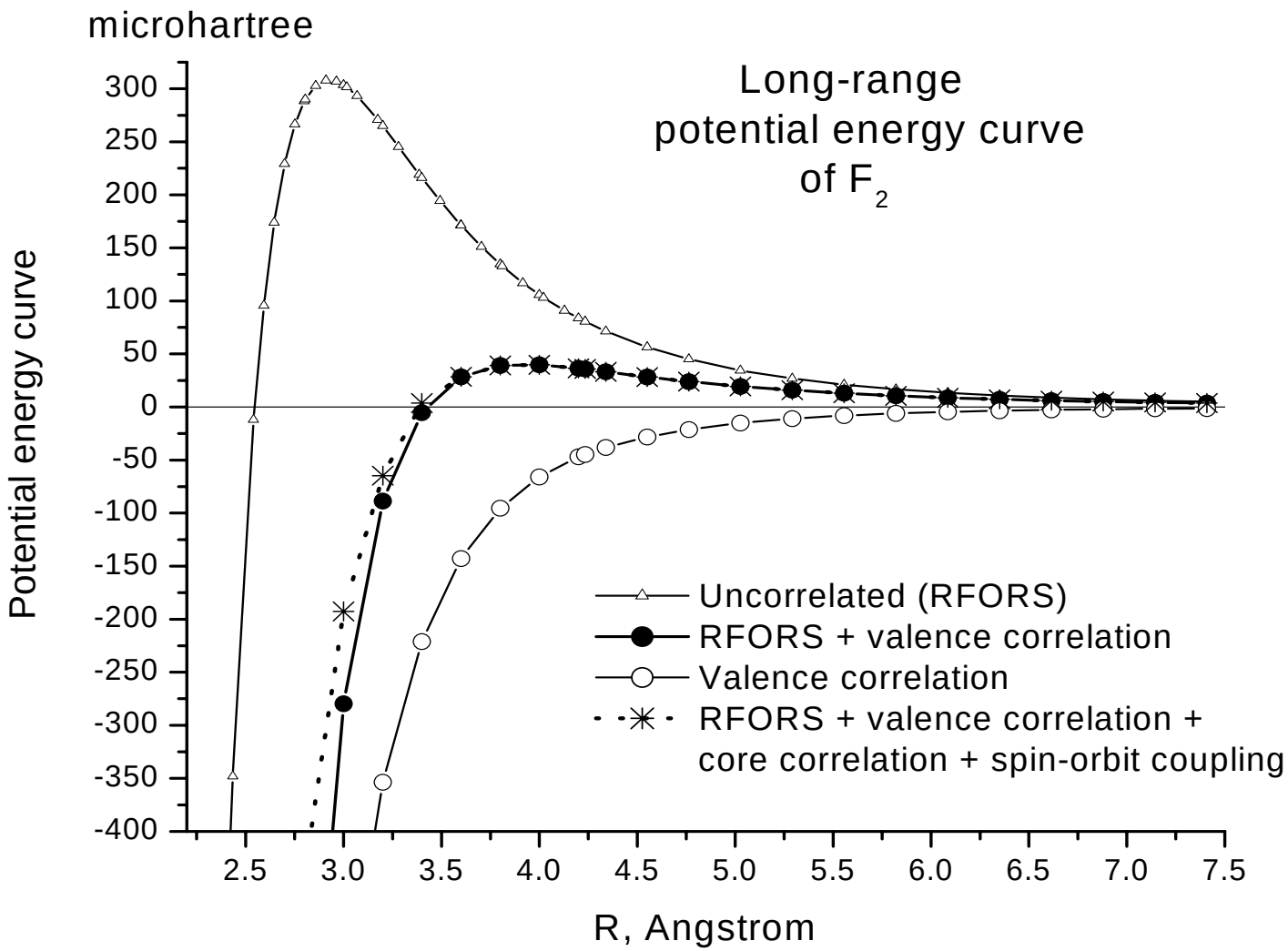
- $E(\Psi) = E(\Psi_{rfors}) + E_{corr}$ **E_{corr} is calculated as difference !**

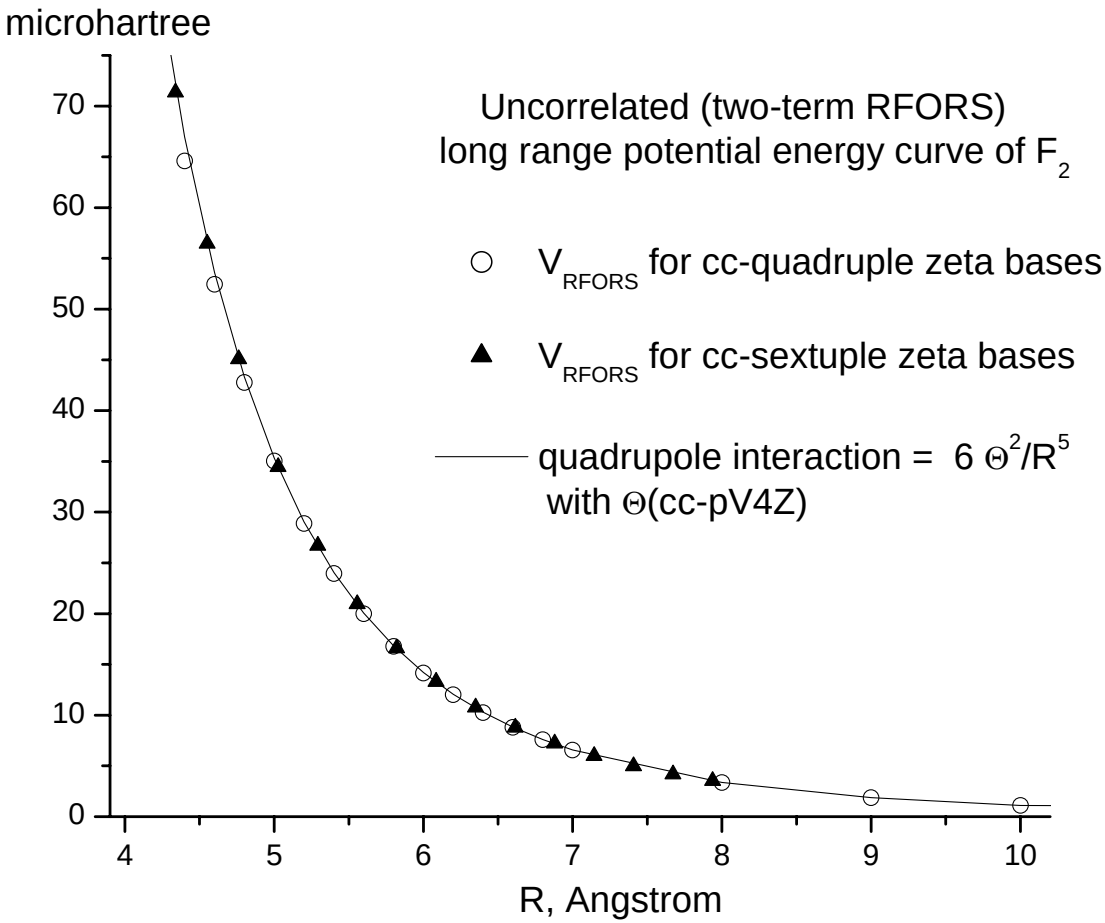
Hence

$V_{rfors}(R) = E_{rfors}(R) - E_{rfors}(\infty)$ **: Uncorrelated potential**

$V_{cor}(R) = E_{cor}(R) - E_{cor}(\infty)$ **: Correlation potential**

$V(R) = V_{rfors}(R) + V_{cor}(R)$ **: Potential energy curve**


microhartree
Long-range
potential energy curve
of F_2
Potential energy curve
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
R, Angstrom
Uncorrelated (RFORS)
RFORS + valence correlation
Valence correlation
RFORS + valence correlation +
core correlation + spin-orbit coupling



Quadrupole moment of F atom: Θ = 0.674[a], 0.68[b] (ea_o^2)

[a] Full CI, cc-pV4Z, This work

[b] CCSD(T), aug-cc-pV5Z, Gutsev, Jena, Bartlett, CPLett. **291**, 547 (1998)

Dispersion coefficients in $V_{disp}(R) = -C_6/R^6 - C_8/R^8$

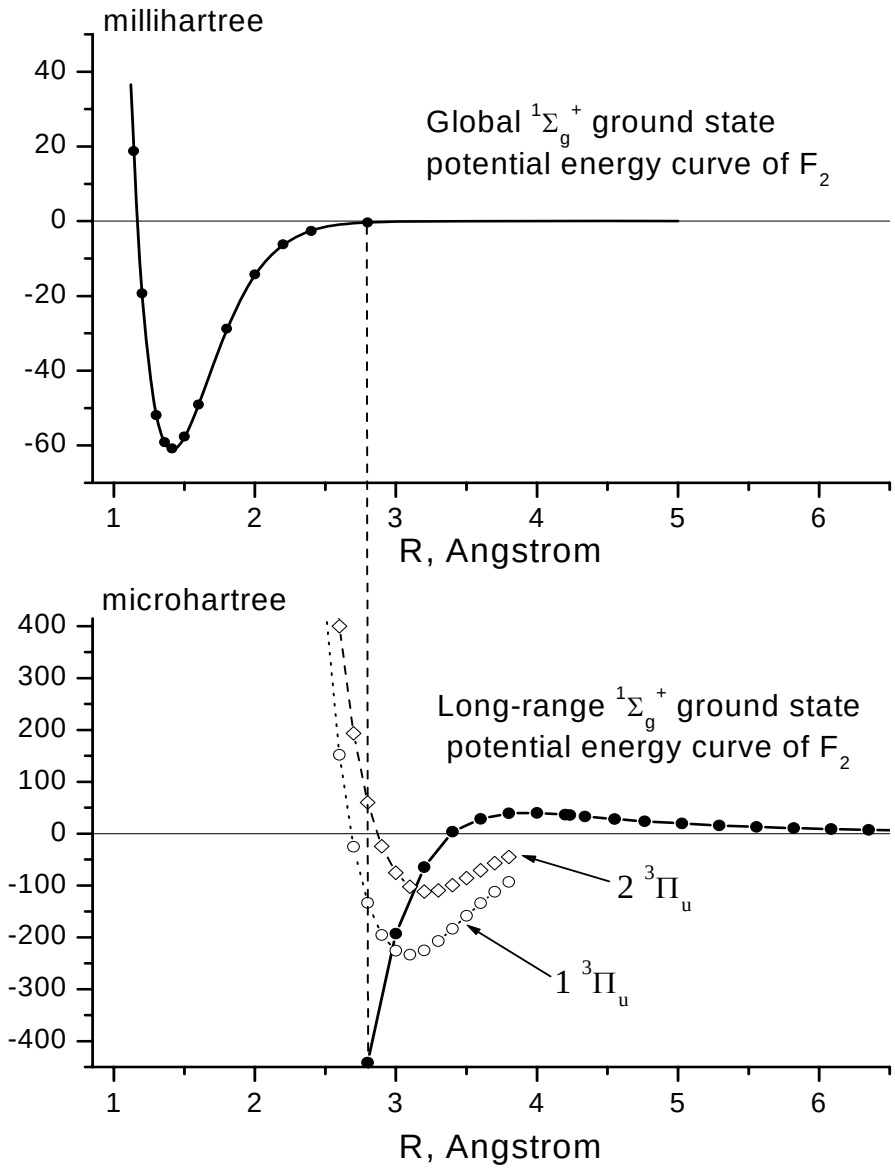
cc-pVXZ	Ne_2		F_2		
X	C_6 [a]	C_8 [b]	C_6 [a]	C_8 [b]	MAD [c]
2	0.646	4.269	1.281	21.968	0.0022
3	2.108	15.239	3.663	23.137	0.0004
4	3.493	29.105	5.504	52.453	0.0023
5	4.454	44.599	6.473	97.202	0.0061
6	5.167	57.434	7.294	117.733	0.0039
FCI-CBS	**6.535**	**83.204**	**8.954**	**146.018**	**0.0056**
Asymp.[d]			**8.6 - 9.5**	**150.7**	
Exper.[e]	**6.447**	**96.50**			

[a] (hartree×bohr^6) [b] (hartree×bohr^8).

[c] **Mean absolute deviations (microhartree) of $(-C_6/r^6 - C_8/R^8)$ from V_{corr} for R= 5 to 8 Å**

[d] Chu & Dalgarno, JCP 121, 4083 (2004), from complex atomic polarizability integration
Zatsarinny, Bartschat, Mitroy, Zhang, JCP 130, 124310 (2009), from atomic oscillator strengths

[e] R. A. Aziz, M. Slaman, Chem. Phys. 130, 187 (1989) from many experimental data


millihartree
40
20
0
-20
-40
-60
Global $^1\Sigma_g^+$ ground state
potential energy curve of F_2
1
2
3
4
5
6
R, Angstrom
microhartree
400
300
200
100
0
-100
-200
-300
-400
Long-range $^1\Sigma_g^+$ ground state
potential energy curve of F_2
$2\ ^3\Pi_u$
$1\ ^3\Pi_u$
1
2
3
4
5
6
R, Angstrom