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Quantum field theoretical methods in chemically bonded systems III

BCSLN–HL(N) potential energy curves for the ground states of H_2, LiH, FH and F_2*

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Summary. A new perturbative method is applied to single bonds. The starting model is the second-quantized self-consistent Heitler–London model. The unperturbed function is a four-determinant Bardeen–Cooper–Schrieffer function. Perturbative corrections are computed with renormalized Feynman diagrams. Convergence is satisfactory by third order. Calculated (experimental) dissociation energies in eV are 4.61 (4.75) for H_2, 2.37 (2.52) for LiH, 6.22 (6.13) for FH, and 1.88 (1.66) for F_2. Calculated (experimental) equilibrium bond distances in Å are 0.739 (0.741) for H_2, 1.598 (1.596) for LiH, 0.903 (0.917) for FH, and 1.395 (1.412) for F_2. Calculated (experimental) vibrational frequencies in cm^{-1} are 4578 (4401) for H_2, 1396 (1406) for LiH, 4447 (4138) for FH, and 927 (916) for F_2. Other spectroscopic constants agree with experiment to within 11% except for anharmonicities which differ from experiment by up to 20%.

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Key words: Perturbative methods – Potential energy curves – H_2 – LiH – FH – F_2 – Single bonds

1. Introduction

The self-consistent (SC) Heitler–London (HL) model is the simplest case of separated-pair [1], multiconfiguration self-consistent-field (optimized double configurations [2]) and generalized valence bond (GVB) [3] methods. Bardeen–Cooper–Schrieffer–Lipkin–Nogami–HL(N) (BCSLN–HL(N)) is Nth-order many-body perturbation theory (MBPT) starting from the SC HL model [4]. It is the simplest correct SC MBPT for chemical bonds. The energy corresponding to BCSLN–HL(N) theory is denoted by $E^{(N)}$. The choice of nomenclature is explained in Part I of this series [5].

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Spectroscopic constants calculated with BCSLN–HL(3) are reported in Part I for H_2, LiH, FH, F_2 and N_2. The selection of molecules is explained there. Renormalized Feynman diagrams (FD) used for the calculations are described in Part II of this series [6]. These FD are used in the present work.

BCSLN–HL(1–3) energy curves are reported in this paper for the four diatomic single bonds chosen in Part I.

$$\left.\begin{array}{c} H_2(X^1\Sigma_g^+) \rightarrow 2H(^2S) \quad 1a_0 \leqslant R \leq 8a_0 \\ LiH(X^1\Sigma^+) \rightarrow Li(^2S) + H(^2S) \quad 2a_0 \leqslant R \leqslant 15a_0 \\ FH(X^1\Sigma^+) \rightarrow F(^2P) + H(^2S) \quad 1.03a_0 \leqslant R \leqslant 9a_0 \\ F_2(X^1\Sigma_g^+) \rightarrow 2F(^2P) \quad 1.8a_0 \leqslant R \leqslant 6a_0 \end{array}\right\}. \tag{1}$$

Section 2 describes the computational details. Section 3 reports the results and compares them to other work.

2. Computational details

Bases of Slater-type atomic functions (STF) were taken from literature: H[$3s1p1d$] [2] (H_2); F[$4s3p1d1f$] [7] (F_2 and FH); and Li($6s4p\sigma 2d\sigma 5p\pi 2d\pi 3d\delta$] and H[$3s2p1d$] [8] (LiH). All except H[$3s1p1d$] have been used for perturbative calculations [7], [8].

Integrals were calculated with quantum chemical software [9–11]. Overlap and HL orbitals were computed with GVB [3]. FD were calculated with closed-shell single-determinant code [12–14]. In the largest case, F_2, calculation of the FD through third order requires about one minute for each value of the bond distance on an IBM 3090.

Normal energy is the first-order energy after the model correlation energy represented by renormalized FD is removed up to the order of the theory [6]. For the BCSLN–HL model, normal energy is denoted by $W^{(3)}_{HL}$. If the Hartree–Fock (HF) model is realistic, usually near R_e and at long bond distances, $W^{(3)}_{HL}$ and HF energies are similar. However, normal energy dissociates properly to atoms.

Dunham's method [15] was used to calculate spectroscopic constants [16]. Grids of twenty or more points were fitted to polynomials of degree nine. Grids around minima are of order 0.05 a_0 or smaller. Uncertainties in equilibrium bond distance due to fitting are of order $\pm$ 0.0005 a_0 [17], [18]. An approximate formula was used to compute dissociation energies (D_e).

$$D_e = E^{(N)}(R_{Max}) - E^{(N)}(R_e). \tag{2}$$

R_{Max} (R_e) is the longest (equilibrium) bond distance and N is the order of perturbation theory.

3. Accuracy of the perturbative results

3.1. $H_2(X^1\Sigma_g^+) \rightarrow 2H(^2S)$

Exact solutions were computed (*exact pairing* or *exact-pair*). Energies are reported in Table 1 and plotted in Fig. 1. Spectroscopic constants are reported in Table 2. Those for BCSLN–HL(3) are accurate approximations to exact

Table 1. Total energies for $H_2(X^1\Sigma_g^+) \rightarrow 2H(^2S)$

$\frac{R}{a_0}$	$\frac{W^{(3)}_{HL}}{\text{hartree}}$	$\frac{E^{(1)}}{\text{hartree}}$	$\frac{E^{(2)}}{\text{hartree}}$	$\frac{E^{(3)}}{\text{hartree}}$
1	−1.09085	−1.09795	−1.11471	−1.11942
1.1	−1.11714	−1.12449	−1.14098	−1.14505
1.2	−1.13275	−1.14035	−1.15654	−1.15993
1.25	−1.13759	−1.14531	−1.16134	−1.16438
1.3	−1.14087	−1.14871	−1.16457	−1.16726
1.35	−1.14281	−1.15078	−1.16646	−1.16879
1.4	−1.14367	−1.15175	−1.16725	−1.16922
1.45	−1.14359	−1.15178	−1.16708	−1.16870
1.5	−1.14271	−1.15102	−1.16612	−1.16738
1.55	−1.14117	−1.14959	−1.16447	−1.16539
1.6	−1.13911	−1.14761	−1.16227	−1.16285
1.7	−1.13368	−1.14234	−1.15654	−1.15646
1.8	−1.12703	−1.13580	−1.14951	−1.14882
2	−1.11173	−1.12053	−1.13323	−1.13150
2.5	−1.07299	−1.08049	−1.09074	−1.08765
3	−1.04312	−1.04791	−1.05619	−1.05322
3.5	−1.02363	−1.02594	−1.03278	−1.03042
4	−1.01206	−1.01300	−1.01881	−1.01694
4.5	−1.00578	−1.00615	−1.01127	−1.00966
5	−1.00264	−1.00279	−1.00747	−1.00597
5.5	−1.00115	−1.00122	−1.00561	−1.00416
6	−1.00048	−1.00050	−1.00471	−1.00328
6.5	−1.00018	−1.00019	−1.00428	−1.00287
7[a]	−1.00004	−1.00005	−1.00407	−1.00266
7.5[a]	−0.99999	−0.99999	−1.00397	−1.00256
8[a,b]	−0.99996	−0.99996	−1.00391	−1.00251

[a] Not used to fit the energy to a polynomial
[b] The value of R_{Max} used to calculate D_e in Eq. (2)

pairing. This is noteworthy in the case of ω_e: BCSLN–HL(1 and 2) are closer to experiment; BCSLN–HL(3) is much closer to exact pairing. Convergence is monotonic.

$E^{(3)}$ approaches a limiting value of −1.00251 hartree at long bond distances. This is about 0.07 eV smaller than the correct limiting value (−1.00000 hartree). Broken particle-number symmetry in the unperturbed excited states is responsible. All unperturbed BCSLN–HL excited states for H_2 break particle-number symmetry. For molecules with more electrons, most of the BCSLN–HL unperturbed excited states maintain particle-number symmetry. This may be expressed with FD. For molecules other than H_2 in a basis of dimension m, about $(1/m)$ FD come from unperturbed excited states with broken particle-number symmetry. Side conditions could be imposed and limiting behavior would be correct. However, accuracy of BCSLN–HL(3) with incorrect limiting behavior is commensurate with basis accuracy (compare BCSLN–HL(3) and exact pairing versus experiment).

Møller–Plesset partitioning has been applied to SC HL wave functions (GVB MP) [19]. GVB MP3 (perturbative corrections through third order) is close to the full CI limit for 6-31G**. BCSLN–HL(N) and GVB–MP are compared in Table 2. Agreement is excellent.

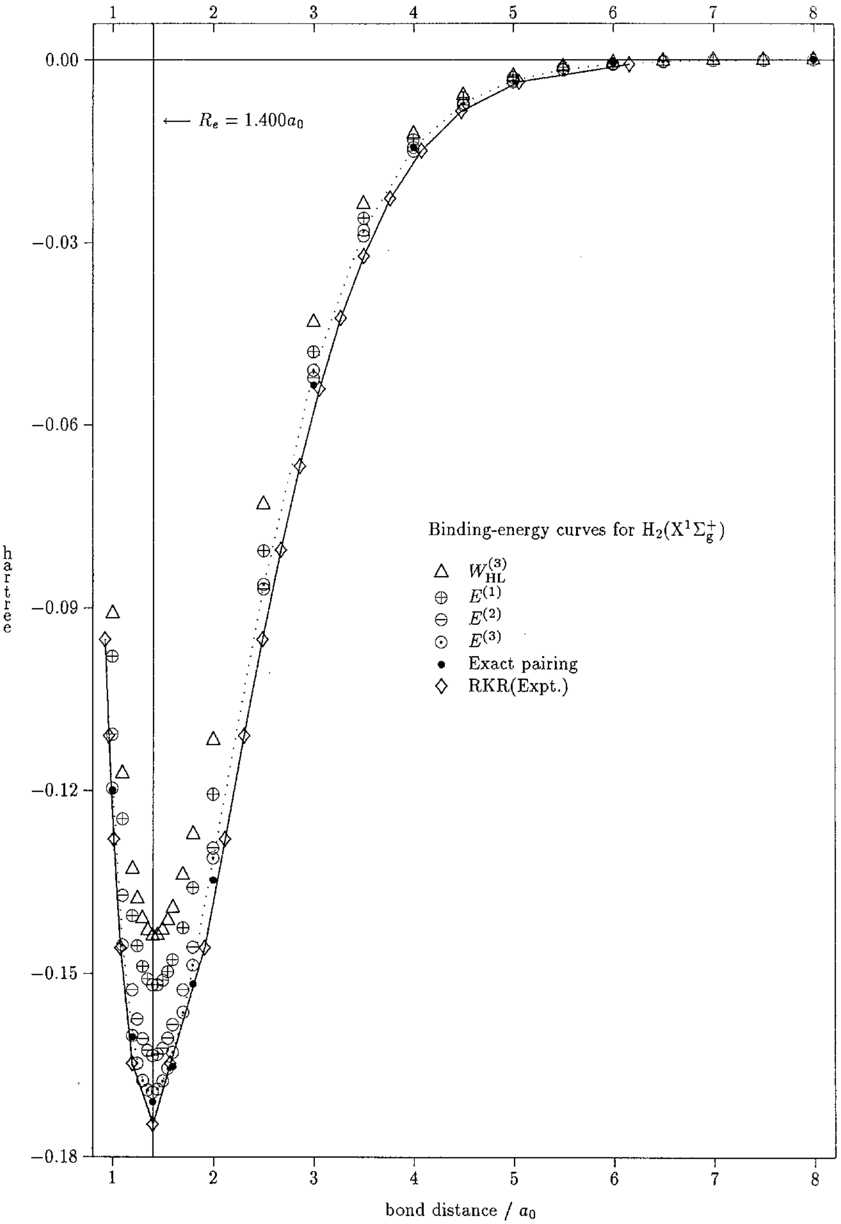

Fig. 1. Binding energies for $H_2(X^1\Sigma_g^+) \rightarrow 2H(^2S)$

3.2. LiH($X^1\Sigma^+$) → Li(^2S) + H(^2S)

Energies are reported in Table 3 and plotted in Fig. 2. Spectroscopic constants are reported in Table 4. MCCI-4 [20] is an approximate counterpart of exact pairing in H_2. BCSLN−HL(N) and MCCI-4 are compared in Table 4. Overall agreement is similar to H_2. BCSLN−HL(3) is an accurate approximation to the exact solution in the basis. Convergence is monotonic.

Table 2. Spectroscopic constants and comparison of BCSLN–HL(N) with other calculations for $H_2(X^1\Sigma_g^+)$

Basis/methods	R_e / Å	ω_e / cm^{-1}	$\omega_e x_e$ / cm^{-1}	B_e / cm^{-1}	α_e / cm^{-1}	$\bar{D}_e$ / cm^{-1} × 10^2	D_e / eV	E(.741 Å) / hartree	E(3.175 Å) / hartree
STF[3*s*2*p*1*d*]									
Normal energy	.751	4348	160	59.3	3.17	4.42	3.92	– 1.14367	– 1.00048
BCSLN–HL(1)	.755	4306	152	58.8	3.13	4.39	4.13	– 1.15175	– 1.00050
BCSLN–HL(2)	.749	4410	148	59.7	2.97	4.38	4.45	– 1.16725	– 1.00471
BCSLN–HL(3)	.739	4578	148	61.4	2.83	4.42	4.61	– 1.16922	– 1.00328
Exact pairing[a]	.744	4596	176	60.5	2.63	4.19	4.66	– 1.17098	– 1.00058
6-31G**[b]									
GVB	.7534						4.17	– 1.14954	– .99706
GVB MP2	.7419						4.51	– 1.16219	– .99707
GVB MP3	.7391						4.57	– 1.16448	– .99707
Experiment[c]	.741	4401	121	60.9	3.06	4.71	4.75		

[a] Present work
[b] [19]
[c] [26]

Table 3. Total energies for LiH($X^1\Sigma^+$) $\rightarrow$ Li(^2S) + H(^2S)

$\frac{R}{a_0}$	$\frac{W_{\mathrm{HL}}^{(3)}}{\text{hartree}}$	$\frac{E^{(1)}}{\text{hartree}}$	$\frac{E^{(2)}}{\text{hartree}}$	$\frac{E^{(3)}}{\text{hartree}}$
2	−7.92235	−7.92957	−7.98358	−7.98949
2.165	−7.94998	−7.95709	−8.01063	−8.01653
2.365	−7.97217	−7.97926	−8.03229	−8.03814
2.565	−7.98548	−7.99270	−8.04517	−8.05084
2.765	−7.99260	−8.00007	−8.05191	−8.05727
2.865	−7.99448	−8.00209	−8.05364	−8.05880
2.915	−7.99509	−8.00277	−8.05418	−8.05925
2.965	−7.99551	−8.00325	−8.05452	−8.05948
3.015	−7.99573	−8.00355	−8.05468	−8.05953
3.065	−7.99582	−8.00369	−8.05467	−8.05941
3.115	−7.99573	−8.00368	−8.05452	−8.05914
3.265	−7.99477	−8.00289	−8.05331	−8.05758
3.465	−7.99217	−8.00046	−8.05034	−8.05415
3.865	−7.98427	−7.99271	−8.04147	−8.04430
4.365	−7.97246	−7.98075	−8.02809	−8.02976
4.665	−7.96552	−7.97344	−8.02004	−8.02116
5.965	−7.95909	−7.96645	−8.01237	−8.01301
5.365	−7.95166	−7.95799	−8.00372	−8.00380
5.765	−7.94604	−7.95080	−7.99534	−7.99521
6.165	−7.94179	−7.94504	−7.98903	−7.98884
6.665	−7.93808	−7.93982	−7.98314	−7.98309
7.365	−7.93487	−7.93548	−7.97806	−7.97830
7.765	−7.93374	−7.93407	−7.97629	−7.97665
8.365[a]	−7.93266	−7.93279	−7.97457	−7.97504
10[a]	−7.93163	−7.93164	−7.97272	−7.97336
15[a,b]	−7.93139	−7.93139	−7.96997	−7.97075

[a] Not used to fit the energy to a polynomial

[b] The value of R_{Max} used to calculate D_e in Eq. (2)

Equation (2) is used where the binding-energy curve is not yet completely flat ($R_{Max} = 15\,a_0$). D_e reported for BCSLN–HL(N) are too small by ~0.01 eV.

Similar convergence patterns are found for H_2 and LiH because the 1*s* and bonding shells of LiH are almost completely separated. BCSLN–HL(1) treats 1*s* as a filled inner shell. Perturbative corrections to it are slowly varying functions of bond distance. Perturbative corrections to the bonding shell are similar to those of H_2.

GVB MP calculations were also reported for LiH [19]. BCSLN–HL(N) and GVB MP are compared in Table 4. The basis for BCSLN–HL is sufficiently more extensive that close agreement is not expected. What is significant is that BCSLN–HL(3) and GVB MP3 approach limits imposed by the particular basis sets chosen for the respective calculations.

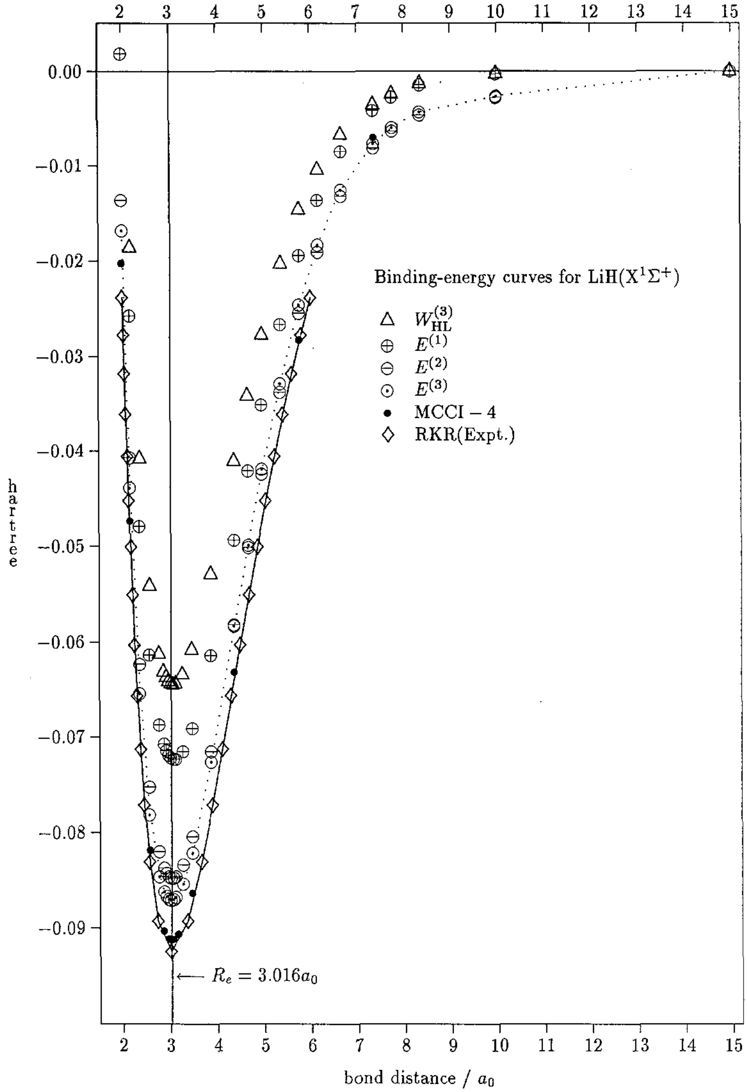

Fig. 2. Binding energies for LiH($X^1\Sigma^+$) → Li(^2S) + H(^2S)

3.3. FH($X^1\Sigma^+$) → F(^2P) + H(^2S)

Energies for FH are reported in Table 5 and plotted in Fig. 3. Spectroscopic constants are reported in Table 6. Overall agreement is comparable to BCSLN–HL(2) for H_2 and LiH.

Symmetry-restricted HF(1–3) (RHF(1–3)) and shifted RHF(1–3) ($\overline{RHF}$(1–3)) calculations were carried out for FH [21]. They are compared with BCSLN–HL(1–3) in Table 6. Convergence oscillates with order. $\overline{RHF}(N)$ oscillates most strongly, follwed by BCSLN–HL(N). BCSLN–HL converges monotonically for bond distances larger than about 3.3 a_0. Accuracy of the MBPT calculations is

Table 4. Spectroscopic constants and comparison of BCSLN–HL(N) with other calculations for LiH($X^1\Sigma^+$)

Basis/methods	R_e / Å	ω_e / cm^{-1}	$\omega_e x_e$ / cm^{-1}	B_e / cm^{-1}	α_e / cm^{-1}	$\bar{D}_e$ / cm^{-1} × 10^4	D_e / eV	E(1.595 Å) / hartree	E(3.897 Å) / hartree
STF Li[$6s4p\sigma 2d\sigma 5p\pi 2d\pi 3d\delta$]									
H[$3s2p1d$]									
Normal energy	1.621	1319	25.4	7.24	.249	8.72	1.53	−7.99573	−7.93487
BCSLN–HL(1)	1.633	1305	22.4	7.17	.226	8.66	1.97	−8.00355	−7.93548
BCSLN–HL(2)	1.609	1366	20.5	7.39	.205	8.64	2.31	−8.05468	−7.97806
BCSLN–HL(3)	1.598	1396	19.5	7.49	.202	8.63	2.37	−8.05953	−7.97830
CGTF Li[$7s5p3d$]H[$6s3p$]									
MCCI-4[a]	1.601	1392	21.7		.200		2.48	−8.05438	−7.97008
Li[3-21G]H[6-31G**][b]								$E(R_e)$ / hartree	
GVB	1.660						1.88	−7.95042	
GVB MP2	1.636						2.11	−7.95901	
GVB MP3	1.630						2.16	−7.96075	
Experiment[c]	1.596	1406	23.2	7.51	.213	8.62	2.52		

[a] [20]
[b] [19]
[c] [26]

Table 5. Total energies for $FH(X^1\Sigma^+) \rightarrow F(^2P) + H(^2S)$

R / a_0	$W^{(3)}_{HL}$ / hartree	$E^{(1)}$ / hartree	$E^{(2)}$ / hartree	$E^{(3)}$ / hartree
1.03[a]	−99.62261	−99.62759	−99.87802	−99.85842
1.23[a]	−99.91916	−99.92540	−100.17638	−100.15625
1.43	−100.03827	−100.0459	−100.29648	−100.27618
1.53	−100.06345	−100.07186	−100.32172	−100.30155
1.58	−100.07063	−100.07945	−100.32881	−100.30876
1.63	−100.07505	−100.08427	−100.33302	−100.31313
1.68	−100.07716	−100.08680	−100.33483	−100.31515
1.73	−100.07739	−100.08744	−100.33374	−100.31431
1.78	−100.07609	−100.08655	−100.33065	−100.31152
1.83	−100.07356	−100.08441	−100.32641	−100.30764
1.88	−100.07002	−100.08125	−100.32127	−100.30289
1.93	−100.06570	−100.07727	−100.26266	−100.24472
2.43	−100.00750	−100.01994	−100.22285	−100.21114
2.63	−99.98612	−99.99725	−100.19526	−100.18657
2.83	−99.96829	−99.97743	−100.17129	−100.16554
3.03	−99.95399	−99.96090	−100.15128	−100.14813
3.23	−99.94274	−99.94763	−100.13095	−100.12992
3.53	−99.93041	−99.93310	−100.11229	−100.11351
3.93	−99.92014	−99.92135	−100.09875	−100.10166
4.43	−99.91367	−99.91417	−100.09394	−100.09775
4.93	−99.91089	−99.91115	−100.08823	−100.09237
5.43	−99.90975	−99.90991	−100.08546	−100.08973
5.93	−99.90930	−99.90940	−100.08406	−100.08838
6.43	−99.90911	−99.90918	−100.08331	−100.08765
9[a,b]	−99.90895	−99.90896	−100.08231	−100.08667

[a] Not used to fit the energy to a polynomial

[b] The value of R_{Max} used to calculate D_e in Eq. (2)

comparable by third order. This suggests convergence. RHF(3) is in slightly better agreement with experiment, probably because of the larger *spd* basis.

In Table 6, BCSLN–HL(N) is also compared with UHF(N) and multi-reference CI (MRCI) calculations using extensive basis sets. UHF(N) refers to *N*th-order MP perturbation theory based on an unrestricted HF determinant. It is equivalent to *N*th-order MBPT based on an unrestricted HF determinant. Convergence oscillates between second and third order. D_e predicted by UHF(2) (BCSLN–HL(2)) is (is not) a useful approximation to the limit imposed by the use of a particular basis set. $D_e(R_e)$ computed with BCSLN–HL(3) is apparently about 0.1 eV (0.017 Å) larger (smaller) than such a limit. D_e computed with UHF(3) is about 0.2 eV smaller than the basis-set imposed limit. UHF(4) and MRCI are in excellent agreement. BCSLN–HL(4) will almost certainly yield spectroscopic constants near the limit within the basis set. Larger *s* and *p* functions might be needed to obtain close agreement between BCSLN–HL(4) and experiment.

Since BCSLN–HL(1) connects properly to both united- and separated-atom limits, need for fourth order to approach the limit achievable within a given basis set cannot be traced to interactions that ultimately break symmetry. It may be

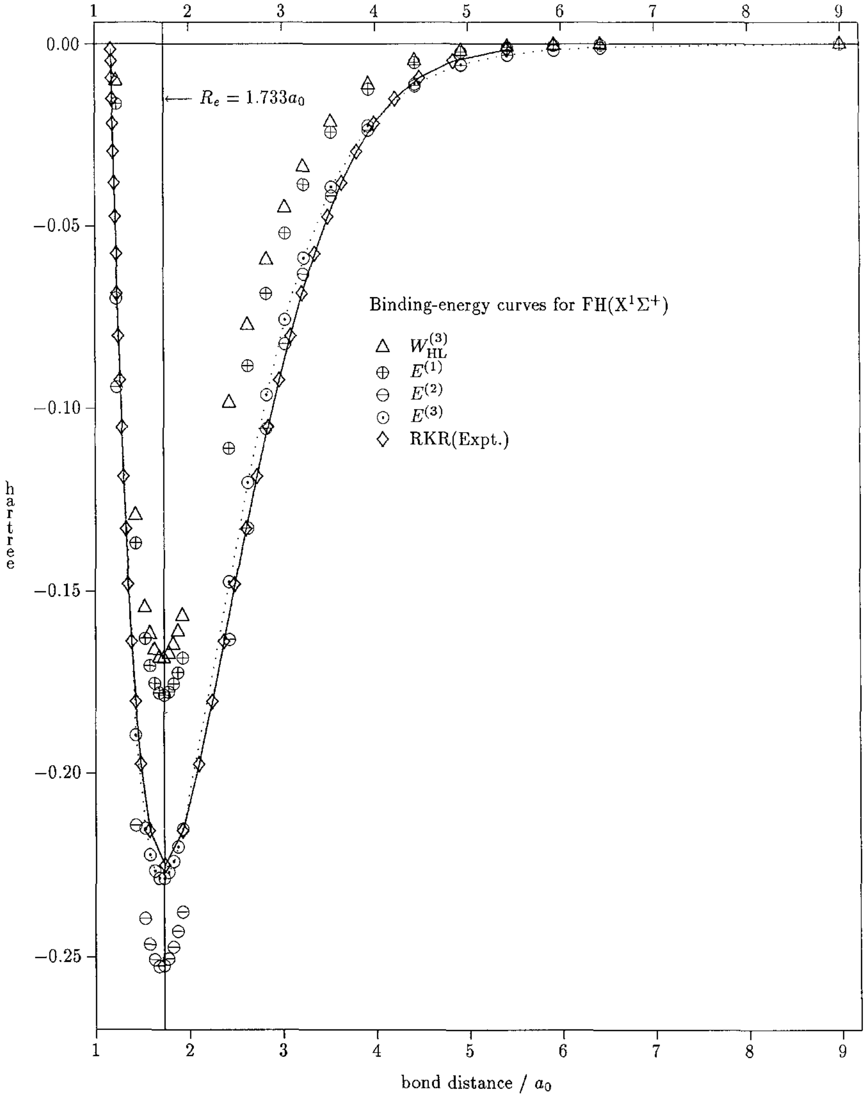

Fig. 3. Binding energies for $FH(X^1\Sigma^+) \rightarrow F(^2S) + H(^2P)$

that effects known to be important for the electron affinity of F [22] and the barrier height of the $F + H_2$ reaction [23, Sect. 2] and Ref. [19] will also accelerate the convergence of BCSLN. An unperturbed BCSLN model which includes these effects would pair the HL levels and two additional particle levels (5σ and 2π).

3.4. $F_2(X^1\Sigma_g^+) \rightarrow 2F(^2P)$

Energies are reported in Table 7 and plotted in Fig. 4. Spectroscopic constants are reported in Table 8. Overall agreement between BCSLN–HL(3) and experi-

Table 6. Spectroscopic constants and comparison of BCSLN–HL(N) with calculations using extensive basis sets for FH($X^1\Sigma^+$)

Basis/methods	R_e / Å	B_e / cm^{-1}	ω_e / cm^{-1}	$\omega_e x_e$ / cm^{-1}	α_e / cm^{-1}	$\bar{D}_e$ / cm^{-1} × 10^3	D_e / eV	E(.917 Å) / hartree	E(4.763 Å) / hartree
STF [4*s*3*p*1*d*1*f*][3*s*1*p*1*d*]									
Normal energy	.906	21.4	4310	118	.808	2.12	4.59	−100.0774	−99.9090
BCSLN–HL(1)	.913	21.1	4205	110	.798	2.13	4.86	−100.0874	−99.9090
BCSLN–HL(2)	.900	21.7	4552	88.7	.636	1.98	6.88	−100.3346	−100.0823
BCSLN–HL(3)	.903	21.6	4447	99.6	.713	2.04	6.22	−100.3151	−100.0867
STF[5*s*4*p*3*d*][3*s*2*p*1*d*][a,b]								E(.915 Å) / hartree	
RHF(1)	.897	21.91	4471	86.44	.756			−100.0693	
RHF(2)	.915	21.05	4165	89.96	.793			−100.3748	
RHF(3)	.908	21.35	4263	89.83	.787			−100.3726	
Shifted RHF(2) ($\overline{RHF}$(2))								−100.4229	
Shifted RHF(3) ($\overline{RHF}$(3))	.902	21.67	4388	86.21	.760			−100.3616	
6-311G++(3*df*, 3*pd*)[c]								E(.912 Å) / hartree	$E(\infty)$ / hartree
UHF(1)							4.27	−100.0578	−99.9009
UHF(2)							6.28	−100.3328	−100.1019
UFF(3)							5.98	−100.3319	−100.1121
UFF(4)	.92		4151				6.15	−100.3430	−100.1171
STF [7*s*5*p*3*d*2*f*][4*s*3*p*2*d*][d]									
MRCI	.92		4172				6.13		
STF [5*s*4*p*3*d*2*f*1*g*][4*s*3*p*2*d*1*f*][e]									
MRCI(222) + Q	.919						6.07		
Experiment[f]	.917	21.0	4138	89.9	.798	2.15	6.13		

[a] [27]
[b] [21]
[c] [28]
[d] [29]
[e] [23]
[f] [26]

Table 7. Total energies for $F_2(X^1\Sigma_g^+) \rightarrow 2F(^2P)$

R	$W_{HL}^{(3)}$	$E^{(1)}$	$E^{(2)}$	$E^{(3)}$
a_0	hartree	hartree	hartree	hartree
1.8	−198.42442	−198.43494	−198.89323	−198.86631
2	−198.64156	−198.65664	−199.11107	−199.08474
2.2	−198.74819	−198.76716	−199.21193	−199.18855
2.3	−198.77805	−198.79812	−199.23631	−199.21523
2.4	−198.79817	−198.81865	−199.24955	−199.23119
2.45	−198.80552	−198.82592	−199.25303	−199.23614
2.5	−198.81147	−198.83164	−199.2549	−199.23953
2.55	−198.81624	−198.83601	−199.25541	−199.24159
2.6	−198.82004	−198.83926	−199.25481	−199.24256
2.64	−198.82245	−198.84117	−199.25368	−199.24266
2.68	−198.82443	−198.84257	−199.25208	−199.24228
2.75	−198.82692	−198.84398	−199.24834	−199.2406
2.8	−198.82817	−198.84434	−199.24518	−199.23886
2.85	−198.82902	−198.84428	−199.24170	−199.23672
3	−198.82973	−198.84236	−199.23025	−199.22883
3.2	−198.82834	−198.83789	−199.21507	−199.21724
3.5	−198.82482	−198.83106	−199.19626	−199.20176
4	−198.82072	−198.82400	−199.17771	−199.18558
4.5	−198.81936	−198.82115	−199.16935	−199.17984
6[a]	−198.81827	−198.81947	−199.16249	−199.17135

[a] The value of R_{Max} used to calculate D_e in Eq. (2)

ment is comparable to BCSLN–HL(2) for H_2 and LiH. Second- and third-order perturbative corrections to D_e are almost the same as for FH. R_e predicted by BCSLN–HL(3) is about as accurate as for FH. BCSLN–HL(1) and BCSLN–HL(2) are not as good approximations as for FH.

BCSLN–HL(N) may be compared to CI and HF(N). CCI-6*a* (basis B) is the last step in a progression of accurate CI calculations [20, 24]. It uses as reference configurations the HL configurations plus configurations which arise from the excitations:

$$3\sigma_g 1\pi_g \rightarrow 3\sigma_u 2\pi_u. \tag{3}$$

RHF(N) calculations were also carried out with basis B [25]. Spectroscopic constants reported for RHF(4) are in excellent agreement with CCI-6a (basis B). Good agreement between RHF(4) and CCI-6a is a significant result. It shows that even when unbound a single determinant may be an excellent starting model by fourth order.

BCSLN–HL(N) is compared with CCI-6a and RHF(N) in Table 8. Convergence oscillates with order. BCSLN–HL(N) oscillates most strongly at R_e, but converges monotonically at bond distances larger than about 3.1 a_0. Except for R_e, BCSLN–HL(3) is an accurate approximation to RHF(4). R_e predicted by BCSLN–HL(3) is an accurate approximation to RHF(3). D_e (R_e) computed with BCSLN–HL(3) is apparently about 0.3 eV (0.02 Å) larger (smaller) than the limit achievable within the basis set. BCSLN–HL(4) in the present basis could reproduce the CCI-6a results in basis B; BCSLN–HL(4) in basis B would almost certainly reproduce the CCI-6a results.

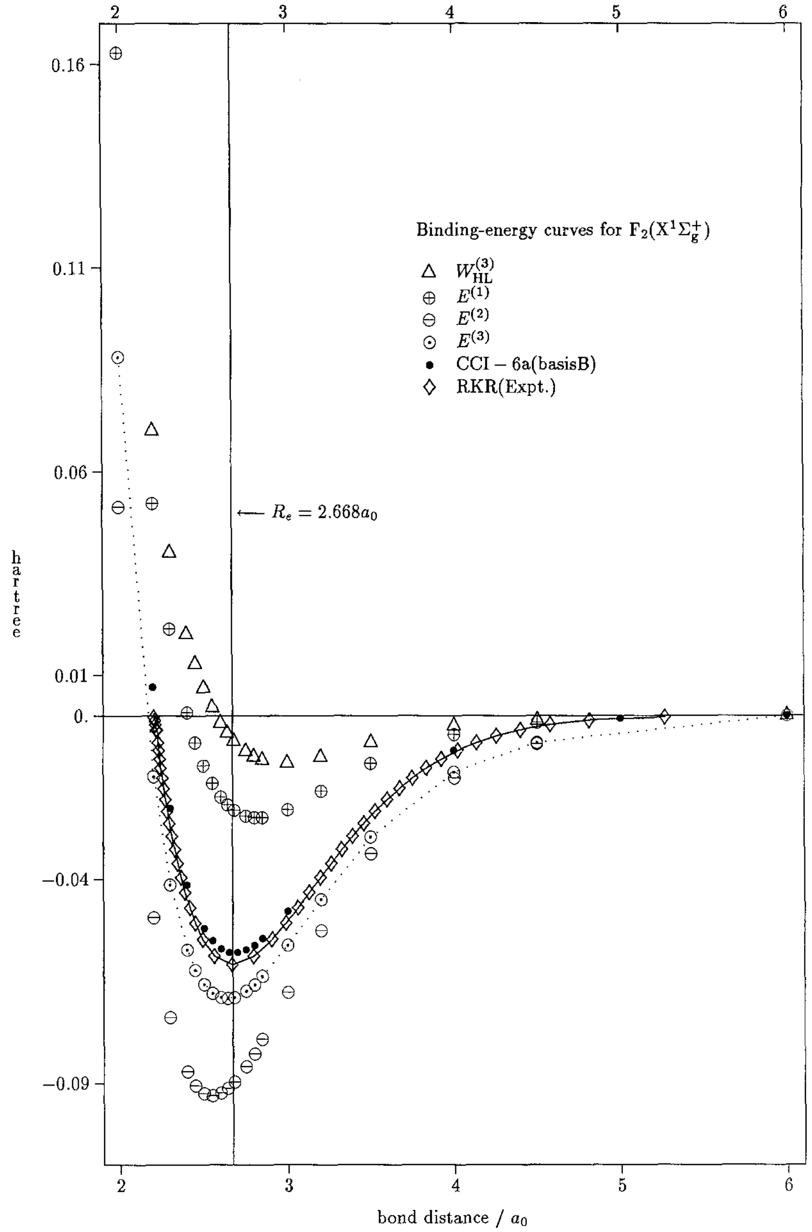

Fig. 4. Binding energies for $F_2(X^1\Sigma_g^+) \rightarrow 2F(^2P)$

Need for fourth-order correction to achieve the limit imposed by the basis set used in the calculation suggests that the starting model could be improved. The improved starting model would pair HL levels and the $1\pi_g$ hole and $2\pi_u$ particle levels of Eq. (3). From the viewpoint of broken symmetry, the $1\pi_g$ hole and $2\pi_u$ particle pairing interactions are needed to connect to the correct united-atom limit. They are also transpositions from FH to F_2 of many of the excitations

Table 8. Spectroscopic constants and comparison of BCSLN–HL(N) with calculations using extensive basis sets for $F_2(X^1\Sigma_g^+)$

Basis/methods	R_e / Å	ω_e / cm^{-1}	$\omega_e x_e$ / cm^{-1}	B_e / cm^{-1}	α_e / cm^{-1}	$\bar{D}_e$ / $cm^{-1} \times 10^6$	D_e / eV	$E(1.376$ Å$)$ / hartree	$E(3.175$ Å$)$ / hartree
STF [$4s3p1d1f$]									
Normal energy	1.575	465	6.0	.710	.022	6.63	0.31	− 198.82004	− 198.81827
BCSLN–HL(1)	1.490	659	15.5	.793	.019	4.60	0.68	− 198.83926	− 198.81947
BCSLN–HL(2)	1.348	1112	12.5	.970	.013	2.95	2.53	− 199.25481	− 199.16249
BCSLN–HL(3)	1.395	927	10.9	.905	.013	3.46	1.88	− 199.24256	− 199.17135
GTF [$5s4p2d1f$]									
RHF(1)[a]	1.329	1265	6.5		.008			− 198.76677	
RHF(2)[a]	1.400	1007	8.6		.010			− 199.29836	
RHF(3)[a]	1.386	1039	9.2		.010			− 199.29616	
RHF(4)[a]	1.420	913	11.7		.013			− 199.32227	
CCI-6a[b]	1.417	910	10.1				1.58	− 199.28375	− 199.22658
Experiment[c]	1.412	916	11.2	.890	.014	3.30	1.66		

[a] [25]
[b] [24]
[c] [26]

known to be important for the electron affinity of F and the barrier height of the $F + H_2$ reaction. The CCI-6a calculations showed that the excitations (3) become important in F_2 when the bond distance is shorter than R_e. Earlier calculations showed that they are also important in F_2 at longer bond distances [7].

4. Conclusions

The accuracy of BCSLN–HL(3) will be useful for many purposes. The BCSLN–HL(3) results for FH and F_2 are about as accurate as the BCSLN–HL(2) results for H_2 and LiH. The BCSLN–HL(3) description of explicit pairing correlation for H_2 and LiH is close to the limit achievable within the basis sets used in the respective calculations. For FH and F_2, the larger deviations of BCSLN–HL(3) from limits achievable with the basis sets chosen for the calculations show that accounts of all correlation in these molecules which are comparable to those recorded for H_2 and LiH require starting models for BCSLN that are more extensive than HL.

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References

1. Hurley AC, Lennard-Jones J, Pople JA (1953) Proc Roy Soc London A220:446
2. Das G, Wahl AC (1966) J Chem Phys 44:87
3. Hunt WJ, Hay PJ, Goddard WA (1972) J Chem Phys 57:738
4. Sorensen TE (1989) Bardeen–Cooper–Schrieffer–Lipkin–Nogami theory: A new method for electronic structure calculations with applications to potential energy curves for H_2, LiH, FH, F_2, and N_2. PhD thesis, University of Wisconsin-Milwaukee
5. Sorensen TE, England WB, Silver DM (1989) J Phys B 22:L539
6. Sorensen TE, England WB, Silver DM, Steinborn EO (1992) Quantum field theoretical methods in chemically bonded systems II. Diagrammatic perturbation theory. Theor Chim Acta 84:1–19
7. Das G, Wahl AC (1972) J Chem Phys 56:3532
8. Bartlett RJ, Silver DM (1975) J Chem Phys 62:3258
9. Hagstrom S (1975) QCPE 10:252
10. Lee YS (1980) Transformation from integrals based on complex spherical harmonics to integrals based on real spherical harmonics
11. Winter NW, Pitzer RM, Dunning TH (1973) Four-index integral transformation program
12. Silver DM (1978) Comput Phys Commun 14:71
13. Silver DM (1978) Comput Phys Commun 14:81
14. Wilson S (1978) Comput Phys Commun 14:91
15. Dunham JL (1932) Phys Rev 41:721
16. Hinze J (1975) Dunham analysis
17. Wahlgren U, Pacansky J, Bagus PS (1975) J Chem Phys 63:2874
18. Taylor PR, Bacskay GB, Hush NS, Hurley AC (1979) J Chem Phys 70:4481
19. Wolinski K, Sellers HL, Pulay P (1987) Chem Phys Lett 140:225
20. Jönsson B, Roos BO, Taylor PR, Siegbahn PEM (1981) J Chem Phys 74:4566
21. Wilson S (1979) Mol Phys 35:1
22. Botch BH, Dunning TH (1982) J Chem Phys 76:6046
23. Bauschlicher CW, Walsh SR, Langhoff SR, Taylor PR, Jaffe RL (1988) J Chem Phys 88:1743
24. Blomberg MRA, Siegbahn PEM (1981) Chem Phys Lett 81:4
25. Urban M, Noga J, Kellö V (1983) Theoret Chim Acta 62:549
26. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure, Vol. 4, Constants of diatomic molecules. Van Nostrand, Princeton
27. Wilson S, Silver DM, Bartlett RJ (1977) Mol Phys 33:1177
28. Frisch MJ, Binkley JS, Schaefer HF (1984) J Chem Phys 81:1882
29. Frisch MJ, Liu B, Binkley JS, Schaefer HF, Miller WH (1985) Chem Phys Lett 114:1