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REGULAR ARTICLE

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On the accuracy of numerical Hartree–Fock energies

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Abstract It is demonstrated that numerical Hartree–Fock (HF) energies reported in the literature in some cases have errors in the milliHartree range. The main cause of these errors is due to the use of too small a value for the 'practical infinity' parameter in the finite difference method for generating the results. By systematically investigating the convergence with respect to the computational parameters, HF energies accurate to at least 1 microHartree are generated for 42 diatomic systems containing first and second row elements, encompassing both cationic, neutral and anionic systems.

1 Introduction

The prediction of molecular stabilities by first-principle electronic structure methods is a subject that has attracted much attention over the last decade. The theoretical framework is conceptually simple: determine the minimum energy geometry, estimate the infinite-correlation infinite-basis-set limit for the electronic energy, and add vibrational zero-point energies and finite temperature corrections to give molecular heat of formation, which can be directly related to experimental results. A brute force approach for the second step, estimating the infinite-correlation infinite-basis-set limit, is not feasible, and composite methods are often used instead, as exemplified by the CBS-*n* [1], G*n* [2], W*n* [3] and focal point [4] methods. The computationally difficult part in these methods is estimating the correlation energy, but extrapolations [5] based on the correlation-consistent basis sets [6] or the use of explicitly correlated wave functions [7] have made a large step towards solving this problem. The basis set convergence of the Hartree–Fock (HF) energy is significantly faster than the correlation energy, and the HF basis set error is often assumed to be negligible, but as the effort towards higher accuracy continues, this error at some point must also be addressed.

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For atoms and diatomic systems, the limiting HF energy can be obtained by solving the integro-differential equations by finite difference or finite elements methods [8], and these results provide an absolute reference against which the results from finite basis sets can be evaluated. We have recently proposed a hierarchy of polarization-consistent basis sets [9, 10], which, although optimized for density functional methods, should also be suitable for estimating the HF basis set limit. In connection with this work, we have in several cases obtained energies by (large) basis set calculations that were significantly different or even lower than the limiting HF energies reported in the literature, casting doubt on the accuracy of these results. In the present paper, we examine the cause of these discrepancies, and report HF energies for a selection of diatomic systems composed of first and second row elements, which should be accurate to at least 1 microHartree.

2 Results and discussion

All calculations have been done using the *2dhf* program [11], which solves the integro-differential HF equations by a finite difference method [8]. The orbital densities are evaluated on a grid in the transformed prolate spheroidal coordinates ν and μ used for representing the radial wave function, while the angular part is solved analytically. The method in addition employs a 'practical infinity' distance parameter (R_∞) for estimating the asymptotic behavior in the μ coordinate. The accuracy of a finite difference HF calculation is thus determined by four parameters: the grid sizes for the ν and μ coordinates, the value for R_∞ and the convergence criteria for terminating the iterative procedure. If the increment between grid points in the ν and μ coordinates is chosen to be equal, the number of independent parameters is reduced to three, and this has been employed in the present case. A constant grid spacing determined by the number of ν grid points has as the consequence that the number of μ grid points increases with R_∞, as reflected in Tables 1, 2 and 3. The convergence criterion has in all cases been set to 10^{-12}, which is sufficient

Table 1 Convergence of the HF energy as a function of the grid size and R_∞ parameter for systems composed of first row elements. Grid is the number of grid points in the ν and μ coordinates, respectively

System	Grid	R_∞	HF energy
$^1CH^+$	169×193	30	−37.9099113[a]
$R = 2.137$ au	169×229	40	−37.9099112
	175×325	200	−37.9099112
	217×403	200	−37.9099112
$^3CH^-$	169×229	40	−38.2933200
$R = 2.20$ au	175×325	200	−38.2933200
	217×403	200	−38.2933200
^3NH	81×105		−54.978429[b]
$R = 1.9614$ au	169×235	40	−54.9784239
	175×331	200	−54.9784239
	217×409	200	−54.9784239
$^1OH^-$	211×211	45	−75.4188033[a]
$R = 1.781$ au	169×241	40	−75.4188031
	175×337	200	−75.4188031
	217×415	200	−75.4188031
^{1} FH	81×161		−100.07082[c]
$R = 1.7328$ au	169×193	30	−100.0708028[a]
	169×253	60	−100.0708025[d]
	169×241	40	−100.0708025
	175×337	200	−100.0708025
	217×421	200	−100.0708025
$^1C_2$			−75.406565[e]
$R = 2.358$ au	169×223	40	−75.4065652
	175×319	200	−75.4065652
	217×397	200	−75.4065652
^2CN	319×415	40	−92.2251341[f]
$R = 1.1718$ Å	169×229	40	−92.2251382
	175×325	200	−92.2251382
	217×403	200	−92.2251382
$^1CN^-$	211×211	50	−92.3489506[a]
$R = 2.214$ au	169×229	40	−92.3489505
	175×325	200	−92.3489505
	217×403	200	−92.3489506
$^1N_2$	57×105		−108.99381[c]
$R = 2.068$ au	229×229	25	−108.9938257[g]
	169×193	30	−108.9938260[a]
	169×229	40	−108.9938256
	175×325	200	−108.9938256
	217×409	200	−108.9938256
$^1NO^+$	169×193	30	−128.9780516[a]
$R = 2.007$ au	169×235	40	−128.9780515
	175×331	200	−128.9780515
	217×409	200	−128.9780515
^{1} NO$^-$	169×223	40	−129.2801373
$R = 2.36$ au	175×319	200	−129.2801743
	175×331	250	−129.2801744
	175×343	300	−129.2801745
	217×427	300	−129.2801745
^1CO	81×113		−112.79095[c]
$R = 2.132$ au	169×193	25	−112.790906[g]
	169×253	60	−112.7909072[d]
	169×229	40	−112.7909072
	175×325	200	−112.7909072
	217×403	200	−112.7909072

Table 1 (Contd.)

System	Grid	R_∞	HF energy
$^3O_2$	169×277	90	−149.6687531[d]
$R = 2.270$ au	169×223	40	−149.6687096
	175×325	200	−149.6687569
	175×337	250	−149.6687571
	175×343	300	−149.6687572
	217×427	300	−149.6687572
$^1CF^+$	169×193	30	−136.9001351[a]
$R = 2.322$ au	169×223	40	−136.9001348
	175×319	200	−136.9001348
	217×397	200	−136.9001348
$^3CF^-$	169×217	40	−137.2244623
$R = 2.78$ au	175×313	200	−137.2244560
	175×343	350	−137.2244562
	217×427	350	−137.2244562
^3NF	169×253	60	−153.8424180[d]
$R = 2.49$ au	169×223	40	−153.8424147
	175×319	200	−153.8424211
	175×343	300	−153.8424212
	217×397	300	−153.8424212
$^1OF^-$	169×211	40	−174.2362661
$R = 2.82$ au	175×313	200	−174.2363411
	175×331	300	−174.2363415
	175×343	350	−174.2363416
	217×427	350	−174.2363416
$^1F_2$			−198.773323[e]
$R = 2.668$ au	247×439	160	−198.7734430[d]
	169×193	30	−198.7724238[a]
	169×217	40	−198.7733129
	175×313	200	−198.7734439
	175×337	300	−198.7734446
	175×343	350	−198.7734447
	217×427	350	−198.7734448
$^2F_2^-$	169×205	40	−198.8621279
$R = 3.52$ au	175×301	200	−198.8623597
	175×331	350	−198.8623612
	175×337	400	−198.8623613
	217×421	400	−198.8623615
	259×499	400	−198.8623615

[a]Ref. [12]
[b]Ref. [13]
[c]Ref. [14]
[d]Ref. [9]
[e]Ref. [15]
[f]Ref. [16]
[g]Ref. [17]

to ensure convergence to at least ∼0.02 microHartree for the present systems.

Tables 1, 2 and 3 list HF energies for 42 diatomic species composed of first and second row elements having wave functions of $\sum$ symmetry. The total energy is given as a function of the ν grid size and the R_∞ parameter, and the last entry in each case should be within ∼0.2 microHartree of the limiting value. It should be noted that the energy does not vary monotonic with the R_∞ parameter. As a check of the accuracy of the final results, we have also estimated the HF limit by extrapolation of the results using the aug-pc-2, -3 and -4 basis sets, and these energies in each case agree with the numerical results to with a few tenths of a microHartree.

For the first row systems in Table 1, it is clear that a typical R_∞ value of 40 au is sufficient for species like C_2 and N_2, but inadequate for system like O_2 and F_2, where a cutoff value of ∼300 au is required for converging the results to a microHartree accuracy. We note that several literature values deviate by several tenths of a microHartree relative to the converged results. Furthermore, the employed R_∞ value

Table 2 Convergence of the HF energy as a function of the grid size and R_∞ parameter for systems composed of first and second row elements. Grid is the number of grid points in the ν and μ coordinates, respectively

System	Grid	R_∞	HF energy
^{3}SiH$^-$	169×211	40	−289.4646220
$R = 2.94$ au	175×307	200	−289.4646297
	175×331	300	−289.4646298
	217×409	300	−289.4646301
	259×493	300	−289.4646301
^{1}SH$^-$	211×211	50	−398.1497921[a]
$R = 2.551$ au	169×217	40	−398.1497798
	175×319	200	−398.1497904
	175×337	300	−398.1497904
	217×421	300	−398.1497908
	259×505	300	−398.1497909
^{1}HCl	169×223	40	−460.1124388
$R = 2.44$ au	175×319	200	−460.1124488
	175×343	300	−460.1124489
	217×427	300	−460.1124493
	259×505	300	−460.1124493
^{2}CP	169×211	40	−378.4745976
$R = 3.08$ au	175×307	200	−378.4746077
	175×331	300	−378.4746078
	217×409	300	−378.4746084
	259×487	300	−378.4746084
^{1}CP$^-$	169×211	40	−378.5615775
$R = 3.00$ au	175×307	200	−378.5615880
	175×331	300	−378.5615881
	217×409	300	−378.5615886
	259×493	300	−378.5615887
^{1}CS	121×121		−435.36273[b,c]
$R = 2.89964$ au	193×229	40	−435.3624198[d]
	169×211	40	−435.3624291
	175×307	200	−435.3624195
	175×331	300	−435.3624195
	217×415	300	−435.3624202
	259×493	300	−435.3624203
^{2}SiN	121×137	30	−343.353489[e]
$R = 1.575$Å	169×211	40	−343.2970349
	175×307	200	−343.2970265
	175×331	300	−343.2970265
	217×409	300	−343.2970268
	259×493	300	−343.2970269
^{1}SiN$^-$	169×211	40	−343.3623749
$R = 2.94$ au	175×307	200	−343.3623652
	175×331	300	−343.3623652
	217×409	300	−343.3623655
	259×493	300	−343.3623656
^{1}NP	121×121		−395.18864[b]
$R = 2.8173$ au	169×211	40	−395.1884040
	175×313	200	−395.1883950
	175×331	300	−395.1883949
	217×415	300	−395.1883953
	259×493	300	−395.1883954

Table 2 (Contd.)

System	Grid	R_∞	HF energy
^{3}SN$^-$	169×211	40	−451.9875815
$R = 3.12$ au	175×307	200	−451.9876478
	175×325	300	−451.9876481
	175×337	350	−451.9876482
	217×415	350	−451.9876492
	259×499	350	−451.9876493
^{3}NCl	169×211	40	−513.9069810
$R = 3.14$ au	175×307	200	−513.9070118
	175×325	300	−513.9070118
	217×409	300	−513.9070133
	259×487	300	−513.9070135
^{1}SiO	121×121		−363.85548[b]
$R = 2.853$ au	169×211	40	−363.8553486
	175×313	200	−363.8553415
	175×331	300	−363.8553414
	217×415	300	−363.8553418
	259×493	300	−363.8553418
^{3}PO$^-$	169×211	40	−415.6564135
$R = 2.90$ au	175×307	200	−415.6564649
	175×319	250	−415.6564651
	175×331	300	−415.6564652
	217×415	300	−415.6564657
	259×493	300	−415.6564658
^{3}SO	169×211	40	−472.3990425
$R = 2.87$ au	175×307	200	−472.3991036
	175×331	300	−472.3991039
	175×343	350	−472.3991040
	217×421	350	−472.3991047
	259×505	350	−472.3991048
^{1}SF$^-$	169×205	40	−497.0283170
$R = 3.22$ au	175×301	200	−497.0283455
	175×313	250	−497.0283456
	175×325	300	−497.0283457
	217×403	300	−497.0283469
	259×487	300	−497.0283470
^{3}PF	169×211	40	−440.2339052
$R = 3.015$ au	175×307	200	−440.2339244
	175×331	300	−440.2339245
	217×409	300	−440.2339251
	259×487	300	−440.2339252
^{1}ClF	169×211	40	−558.9175082
$R = 3.14$ au	175×307	200	−558.9176239
	175×325	300	−558.9176245
	175×337	350	−558.9176247
	175×343	400	−558.9176247
	217×415	350	−558.9176261
	259×499	350	−558.9176263

[a] Ref. [12]
[b] Ref. [18]
[c] $R = 2.9006$ au. The corresponding converged value at this geometry is −435.3623913
[d] Ref. [19]
[e] Ref. [20]

and convergence criterion for terminating the iterative procedure is often not given, making it difficult to reproduce the reported values. For systems involving second row elements (Tables 2 and 3), the cutoff value must in some cases be even larger, and a significantly larger grid is also required in order to converge the results to within 1 microHartree. For some of the systems (SiN and P_2), the converged results deviate from the literature value by several milliHartrees.

A priori, it might have been expected that anions with loosely bound electrons would require larger values for R_∞ in order to obtain converged results. The results in Tables 1, 2 and 3, however, only show a weakly trend in this direction. The R_∞ value required for systems like F_2 and Cl_2 is already so large that it also suffices for the corresponding anion. Cations are not expected to have requirements different from the neutral species, and only a few have been included for comparison with literature values.

Table 3 Convergence of the HF energy as a function of the grid size and R_∞ parameter for systems composed of second row elements. Grid is the number of grid points in the ν and μ coordinates, respectively

System	Grid	R_∞	HF energy
^{1}SiS	121×137	30	−686.516707[a]
$R = 1.93$ Å	169×199	40	−686.5162620
	175×295	200	−686.5162806
	175×307	250	−686.5162807
	175×319	300	−686.5162808
	259×475	300	−686.5162842
	277×505	300	−686.5162842
$^1P_2$	61×61		−681.508[b]
$R = 3.578$ au	169×199	40	−681.5000151
	175×295	200	−681.5002505
	175×331	350	−681.5002523
	175×337	400	−681.5002523
	259×499	400	−681.5002552
	295×571	400	−681.5002553
$^3PS^-$	169×199	40	−738.3396168
$R = 3.80$ au	175×295	200	−738.3397021
	175×319	300	−738.3397027
	175×325	350	−738.3397026
	259×481	350	−738.3397073
	295×553	350	−738.3397074
$^3S_2$	169×199	40	−795.0911928
$R = 3.642$ au	175×295	200	−795.0915518
	175×319	300	−795.0915540
	175×325	350	−795.0915541
	259×481	350	−795.0915589
	295×553	350	−795.0915590
$^1SCl^-$	169×193	40	−857.1042706
$R = 4.06$ au	175×289	200	−857.1044078
	175×331	400	−857.1044093
	175×337	450	−857.1044093
	259×487	400	−857.1044184
	295×559	400	−857.1044186
$^1Cl_2$	169×199	40	−919.0083635
$R = 3.86$ au	175×295	200	−919.0089219
	175×325	350	−919.0089254
	175×331	400	−919.0089255
	259×493	400	−919.0089343
	295×565	400	−919.0089345
$^1Cl_2^-$	169×181	40	−919.0785465
$R = 5.00$ au	175×277	200	−919.0795182
	175×319	400	−919.0795280
	175×325	450	−919.0795279
	259×469	400	−919.0795631
	277×505	400	−919.0795635
	295×535	400	−919.0795637

[a]Ref. [20]
[b]Ref. [18]

3 Summary

Numerical Hartree–Fock energies with an accuracy of at least 1 μ Hartree are reported for 42 diatomic species composed of first and second row elements. It is shown that literature values in some cases are in error by several microHartrees for first row systems and by several milliHartrees for second row systems.

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