

# Effects of Coulomb attenuation on chemical properties<sup>1</sup>

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## Abstract

We have implemented the recently introduced Coulomb-attenuated CAP(*m*) potentials in the Q-CHEM program and have performed attenuated SCF and correlation calculations on a wide variety of molecular systems. We find that chemical energetics predicted using the higher CAP(*m*) agree well with those from the Coulomb operator. The half-integer approximations are especially effective, despite their unphysical asymptotic behaviour. © 1997 Elsevier Science B.V.

*Keywords:* Coulomb attenuation; Chemical properties; CAP(*m*)

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## 1. Introduction

One of the major obstacles inhibiting the application of quantum chemical methods to large molecular systems is the ubiquitous Coulomb problem. The essential difficulty is that the Coulomb interaction involves pairs of particles and the cost of evaluating the Coulomb energy, if treated in the most obvious way, naturally scales quadratically with the size of the system.

The Coulomb interaction decays very slowly with the interparticle distance and is still roughly a microhartree even for two electrons a millimeter apart. Recent research, however, has found that it can be very effective computationally to split the Coulomb problem into short- and long-range contributions and then to treat these using entirely different approaches [1–3]. In the FMM [1] and CFMM [2], a split is achieved by determining

which pairs of charge distributions are “well-separated” and which are not (i.e. by partitioning physical space) and by then treating well-separated pairs via multipole expansions. In the KWIK algorithm [3], the Coulomb operator itself is split into a singular short-range operator and a smooth long-range operator; the latter may then be handled in Fourier space.

More recently, we have investigated whether or not chemical properties depend equally on the short- and long-range KWIK components and were intrigued to find properties such as atomization energies and electron and proton affinities to be remarkably insensitive to the latter. This led us to the CASE (Coulomb-attenuated Schrödinger equation) approximation [4], in which the long-range KWIK component is systematically omitted from every Coulomb term in the Schrödinger equation. Because only short-range interactions remain, the cost of evaluating the attenuated Coulomb energy scales only linearly with the size of the system [5].

Subsequently, we rederived the Dirac-Slater exchange functional under the assumption that the

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Coulomb operator is replaced by the short-range CASE operator. Our derivation yields an attenuated Dirac-Slater exchange functional and enables us to perform Coulomb-attenuated Hartree-Fock-Slater (HFS) calculations [6].

Although we found that the CASE approximation has surprisingly little effect on many chemical properties, there are others (e.g. ionization energies) that are very strongly affected. Obviously therefore, it was desirable to devise a mechanism by which CASE results could be systematically improved toward exactitude. In a recent letter [7], we showed that CASE may be regarded as the first and crudest member of a family of approximations, Coulomb-attenuated potentials CAP(*m*), that bridge the gap between the CASE and Coulomb operators and we examined the effects of the CAP(*m*) approximations on two model problems, namely the energy of a hydrogen atom and the Madelung constant of the NaCl lattice. The results obtained were encouraging and suggested that the CAP(*m*) might prove to be generally useful approximations to the Coulomb operator.

In the present paper, we apply the CAP(*m*) to a much wider array of problems. We report the effects of the approximations on a large number of atomization energies, ionization energies and proton affinities computed at the Hartree-Fock and Hartree-Fock-Slater levels and on correlation energies computed via second-order Møller-Plesset perturbation (MP2) theory. All calculations were performed using Q-CHEM 1.0 [8].

## 2. CAP(*m*) approximations

The CAP(*m*), which are defined [7] only for integer and half-integer *m*, are given by

$$\frac{1}{r} \approx \frac{\text{erfc}(\omega r)}{r} + \frac{2\omega}{\sqrt{\pi}} \sum_{j=1}^{[m+1/2]} a_{mj} \exp(-\omega^2 \alpha_{mj}^2 r^2) \quad (1)$$

where  $\omega$  is an attenuation parameter and the  $\alpha_{mj}$  and  $a_{mj}$  (Table 1) are the roots and weights [9] of Gauss-Legendre quadrature. CAP(0) is the CASE approximation and higher CAP(*m*) afford progressively more accurate models of the Coulomb singularity and its neighborhood.

Table 1

The defining parameters of the CAP(*m*) approximations, Eq. (1)

<i>m</i>	$\alpha_{mj}$	$a_{mj}$
1/2	0.00000 00000	1.00000 00000
1	0.57735 02692	1.00000 00000
3/2	0.00000 00000	0.44444 44444
	0.77459 66692	0.55555 55555
2	0.33998 10436	0.65214 51549
	0.86113 63116	0.34785 48451
5/2	0.00000 00000	0.28444 44444
	0.53846 93101	0.47862 86705
	0.90617 98459	0.23692 68851
3	0.23861 91861	0.46791 39346
	0.66120 93865	0.36076 15730
	0.93246 95142	0.17132 44924
7/2	0.00000 00000	0.20897 95918
	0.40584 51514	0.38183 00505
	0.74153 11856	0.27970 53915
	0.94910 79123	0.12948 49662

The first four approximations are given by

$$\text{CAP}(0) \frac{1}{r} \approx \frac{\text{erfc}(\omega r)}{r} \quad (2)$$

$$\text{CAP}(1/2) \frac{1}{r} \approx \frac{\text{erfc}(\omega r)}{r} + \frac{2\omega}{\sqrt{\pi}} \quad (3)$$

$$\text{CAP}(1) \frac{1}{r} \approx \frac{\text{erfc}(\omega r)}{r} + \frac{2\omega}{\sqrt{\pi}} \exp\left(\frac{-\omega^2 r^2}{3}\right) \quad (4)$$

$$\text{CAP}(3/2) \frac{1}{r} \approx \frac{\text{erfc}(\omega r)}{r} + \frac{2\omega}{\sqrt{\pi}} \left[ \frac{4}{9} + \frac{5}{9} \exp\left(\frac{-3\omega^2 r^2}{5}\right) \right] \quad (5)$$

When *m* is an integer (half-integer), CAP(*m*) is a rigorous lower (upper) bound to 1/*r*. Graphs of the first six CAP(*m*) may be found elsewhere [7].

When the CAP(*m*) are used in molecular orbital calculations employing a Gaussian basis set, the nuclear-attraction and two-electron repulsion integrals are modified. All such integrals, however, can be evaluated in terms of the error function and the associated formulae have been reported elsewhere [7,10,11].

## 3. Results and discussion

In our preliminary study [7], we applied the CAP(*m*) to the H atom and the NaCl lattice. The

Table 2  
 HF/6-31G\* atomization energies and CAP(m) errors (kJ mol<sup>-1</sup>)

Molecule	Exact	CAP(0)	CAP(1/2)	CAP(1)	CAP(3/2)	CAP(2)	CAP(5/2)	CAP(3)	CAP(7/2)
LiH	361.9	-57.2	-57.2	11.7	-21.2	6.1	-5.6	2.4	-1.1
BeH	215.6	-118.5	-118.5	29.4	-21.6	13.8	-7.5	3.4	-1.4
CH	225.1	37.7	37.7	-42.3	2.2	5.4	-3.0	1.1	-0.4
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	640.9	-62.0	-62.0	-39.6	-2.5	8.6	-4.3	1.6	-0.5
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	511.6	48.0	48.0	-76.8	4.9	9.9	-5.7	2.3	-0.7
CH <sub>3</sub>	1006.5	-69.5	-69.5	-62.7	-0.6	12.0	-6.7	2.7	-0.9
CH <sub>4</sub>	1368.6	-65.3	-65.3	-98.7	8.2	15.1	-9.8	4.2	-1.5
NH	198.4	41.0	41.0	-34.1	-0.6	4.4	-2.0	0.6	-0.2
NH <sub>2</sub>	460.5	60.4	60.4	-62.3	-0.8	8.3	-3.8	1.3	-0.4
NH <sub>3</sub>	797.3	45.4	45.4	-79.3	-1.7	11.6	-5.5	1.9	-0.6
OH	261.7	17.2	17.1	-29.0	-0.4	3.0	-1.2	0.3	-0.1
OH <sub>2</sub>	602.3	15.7	15.7	-50.6	-1.6	5.9	-2.3	0.7	-0.2
FH	365.2	-17.9	-17.9	-23.6	-0.1	2.0	-0.7	0.2	0.0
SiH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	450.1	-135.0	-135.0	-91.9	36.9	8.4	-13.3	7.9	-3.4
SiH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	431.3	-116.7	-116.7	-63.9	25.7	9.7	-11.5	6.4	-2.7
SiH <sub>3</sub>	734.0	-228.0	-228.0	-98.2	38.1	13.9	-17.4	10.0	-4.3
SiH <sub>4</sub>	1051.0	-354.6	-354.6	-128.1	48.9	17.9	-23.2	13.7	-6.1
PH <sub>2</sub>	427.4	-36.0	-36.0	-121.7	41.9	9.4	-12.7	6.9	-2.8
PH <sub>3</sub>	690.1	-74.2	-74.2	-175.6	63.8	12.2	-18.2	10.2	-4.2
SH <sub>2</sub>	511.1	7.0	7.0	-139.8	44.3	7.8	-10.1	5.1	-1.9
ClH	298.4	22.7	22.7	-75.6	21.9	3.3	-3.9	1.8	-0.6
Li <sub>2</sub>	10.9	8.8	8.8	55.2	21.6	-10.6	18.9	-8.2	4.2
LiF	361.9	-363.8	-363.8	56.2	-10.6	1.7	-6.5	3.1	-1.3
C <sub>2</sub> H <sub>2</sub>	1200.9	65.8	65.8	-237.7	24.7	21.7	-15.1	7.0	-2.9
C <sub>2</sub> H <sub>4</sub>	1775.9	-14.2	-14.2	-270.8	75.5	12.9	-23.3	14.6	-6.8
C <sub>2</sub> H <sub>6</sub>	2303.6	-165.4	-165.4	-249.2	128.0	-8.6	-26.8	22.0	-11.7
CN	360.1	308.7	308.6	-257.5	7.9	31.5	-16.8	6.2	-1.9
HCN	802.5	286.1	286.1	-284.4	26.2	25.1	-15.7	6.7	-2.5
CO	708.0	354.2	354.2	-288.7	-8.0	41.8	-20.6	7.1	-2.1
HCO	740.8	330.2	330.2	-304.7	20.6	34.3	-21.3	8.9	-3.1
H <sub>2</sub> CO	1056.6	270.5	270.5	-323.1	42.1	30.4	-23.6	11.2	-4.3
H <sub>3</sub> COH	1513.5	36.7	36.7	-303.7	84.4	19.5	-29.0	16.7	-7.1
N <sub>2</sub>	431.9	518.3	518.3	-309.9	-13.3	44.0	-20.7	7.0	-2.0
H <sub>2</sub> NNH <sub>2</sub>	1061.2	148.5	148.5	-305.6	78.5	19.1	-26.9	15.2	-6.4
NO	204.6	514.6	514.6	-297.3	-21.5	45.2	-19.9	6.3	-1.7
O <sub>2</sub>	102.3	451.0	451.0	-314.5	1.1	39.7	-19.3	6.3	-1.7
HOOH	514.0	154.5	154.5	-301.7	60.3	25.1	-23.3	10.5	-3.6
F <sub>2</sub>	-149.9	244.7	244.7	-258.4	26.5	28.2	-17.0	5.9	-1.6
CO <sub>2</sub>	996.8	595.9	595.9	-574.4	62.4	41.1	-42.3	25.8	-12.6
Na <sub>2</sub>	-3.1	11.8	11.8	114.7	17.9	-20.2	48.1	-25.4	10.9
Si <sub>2</sub>	145.0	-206.9	-206.9	225.8	339.4	-251.0	53.1	19.9	-30.7
P <sub>2</sub>	105.0	-118.5	-118.5	-232.8	437.7	-156.3	-22.2	46.4	-30.1
S <sub>2</sub>	166.7	-133.8	-133.8	-336.5	432.9	-120.3	-44.2	53.5	-30.1
Cl <sub>2</sub>	43.7	-172.0	-172.0	-248.0	384.3	-117.6	-42.0	52.7	-29.6
NaCl	289.4	592.7	592.7	463.6	22.1	-123.3	49.6	-8.3	-3.7
SiO	418.4	-146.1	-146.1	-366.7	134.2	13.5	-34.9	20.0	-8.3
SC	385.4	157.2	157.2	-490.9	189.8	12.4	-44.9	26.7	-11.2
SO	168.5	224.5	224.5	-495.8	134.0	35.9	-44.3	21.8	-8.0
ClO	0.4	162.8	162.8	-451.5	145.0	29.3	-44.7	22.9	-8.5
FCI	13.7	89.1	89.1	-390.1	136.3	23.5	-40.4	20.9	-7.7
Si <sub>2</sub> H <sub>6</sub>	1711.6	-979.4	-979.3	170.3	292.8	-211.9	42.2	19.1	-34.2
CH <sub>3</sub> Cl	1232.4	-223.8	-223.8	-208.6	230.7	-55.8	-26.0	30.2	-17.1

Table 2 Continued

Molecule	Exact	CAP(0)	CAP(1/2)	CAP(1)	CAP(3/2)	CAP(2)	CAP(5/2)	CAP(3)	CAP(7/2)
H <sub>3</sub> CSH	1444.7	-249.7	-249.7	-211.6	252.2	-70.1	-23.6	32.5	-20.0
HOCl	288.9	14.3	14.3	-335.2	177.3	-4.2	-36.8	24.2	-10.4
SO <sub>2</sub>	299.5	487.2	487.2	1049.0	272.9	57.8	-91.2	53.6	-24.7
BF <sub>3</sub>	1515.3	-0.6	-0.6	-630.6	206.8	3.4	-66.9	51.5	-26.1
BCl <sub>3</sub>	1019.3	-877.4	-877.4	125.8	591.5	-457.2	163.3	-8.9	-65.5
AlF <sub>3</sub>	1305.8	-1118.0	-1118.0	-651.2	332.0	-44.5	-70.3	63.0	-40.5
AlCl <sub>3</sub>	984.9	-1167.6	-1167.6	265.7	870.9	-507.5	128.6	-32.6	-35.1
CF <sub>4</sub>	1314.9	565.0	565.0	-1089.3	418.5	-2.4	-123.5	92.0	-43.7
CCl <sub>4</sub>	714.4	-1045.3	-1045.3	961.8	976.3	-981.8	370.3	-7.3	-137.8
COS	827.3	418.9	418.9	-585.0	231.5	-42.0	-27.7	33.1	-24.5
CS <sub>2</sub>	658.2	123.5	123.5	-601.9	349.2	-99.1	13.5	4.4	-19.1
COF <sub>2</sub>	1091.2	608.7	608.7	-835.7	217.8	27.8	-79.9	55.0	-26.2
SiF <sub>4</sub>	1722.8	-810.7	-810.7	-1131.3	575.8	-84.8	-117.7	112.9	-68.0
SiCl <sub>4</sub>	1111.1	-2007.8	-2007.8	636.7	1294.8	-927.4	346.5	-88.5	-82.8
N <sub>2</sub> O	284.3	1014.6	1014.6	-622.6	65.8	38.8	-39.8	24.7	-12.4
CINO	140.8	442.4	442.4	-268.3	237.7	-117.3	1.9	29.9	-26.7
NF <sub>3</sub>	135.5	643.8	643.8	-863.7	254.3	33.8	-85.0	53.7	-23.6
PF <sub>3</sub>	898.4	-119.4	-119.4	-1087.3	476.6	-1.6	-124.6	89.9	-43.9
O <sub>3</sub>	-298.6	914.8	914.8	-665.1	107.3	41.4	-45.7	25.4	-11.1
F <sub>2</sub> O	-181.7	441.5	441.5	-529.9	116.6	32.0	-42.1	23.2	-9.6
ClF <sub>3</sub>	-165.4	245.8	245.8	-1099.8	561.6	-28.9	-119.4	84.7	-42.0
C <sub>2</sub> F <sub>4</sub>	1549.3	490.8	490.8	-950.5	418.6	-120.4	-50.7	72.8	-55.1
C <sub>2</sub> Cl <sub>4</sub>	1179.0	-974.8	-974.8	264.9	855.6	-704.0	311.3	-89.2	-58.3
CF <sub>3</sub> CN	1654.4	683.5	683.5	-1077.6	513.7	-116.6	-63.7	76.8	-57.0
CH <sub>3</sub> CCH (propyne)	2169.7	3.7	3.7	-408.4	110.7	6.6	-21.8	15.4	-10.2
CH <sub>2</sub> =C=CH <sub>2</sub> (allene)	2165.0	86.9	86.9	-438.2	113.1	7.2	-21.2	14.5	-9.8
C <sub>3</sub> H <sub>4</sub> (cyclopropene)	2064.3	81.5	81.5	-548.6	191.2	15.2	-46.6	30.9	-15.2
CH <sub>3</sub> CH=CH <sub>2</sub> (propylene)	2727.1	-132.8	-132.8	-364.7	190.9	-36.4	-22.1	25.8	-18.3
C <sub>3</sub> H <sub>6</sub> (cyclopropane)	2695.2	-129.5	-129.5	-500.4	266.0	-16.0	-52.5	42.3	-22.1
C <sub>3</sub> H <sub>8</sub> (propane)	3242.0	-307.1	-307.1	-292.3	256.3	-77.1	-18.9	33.5	-25.4
CH <sub>2</sub> CHCHCH <sub>2</sub> (butadiene)	3164.5	-101.9	-101.9	-514.9	270.7	-55.8	-22.5	27.6	-20.7
C <sub>4</sub> H <sub>6</sub> (2-butyne)	3134.3	-116.8	-116.8	-599.7	177.8	14.8	-35.0	18.9	-10.5
C <sub>4</sub> H <sub>6</sub> (methylene cyclopropane)	3081.4	-42.4	-42.4	-594.7	287.0	-42.7	-27.8	31.1	-24.6
C <sub>4</sub> H <sub>6</sub> (bicyclobutane)	3040.2	-20.1	-20.1	-766.2	433.7	-44.6	-72.1	63.3	-35.5
C <sub>4</sub> H <sub>6</sub> (cyclobutene)	3113.0	-224.5	-224.5	-639.3	445.7	-78.9	-58.5	60.3	-36.1
C <sub>4</sub> H <sub>8</sub> (cyclobutane)	3641.9	-417.3	-417.3	-518.2	529.3	-135.7	-53.3	70.6	-45.4
C <sub>4</sub> H <sub>8</sub> (isobutene)	3676.9	-293.0	-293.0	-345.3	321.3	-132.3	3.5	32.0	-33.6
C <sub>4</sub> H <sub>10</sub> (trans butane)	4180.1	-470.4	-470.4	-354.8	375.8	-125.6	-13.6	36.0	-30.4
C <sub>4</sub> H <sub>10</sub> (isobutane)	4181.4	-499.1	-499.1	-220.1	402.7	-194.4	13.3	40.9	-43.4
C <sub>5</sub> H <sub>8</sub> (spiropentane)	4009.1	-235.1	-235.1	-638.8	445.7	-131.1	-5.3	35.8	-40.4
C <sub>6</sub> H <sub>6</sub> (benzene)	4272.9	-356.0	-356.0	-708.5	587.6	-234.8	0.6	58.4	-57.5
CH <sub>2</sub> F <sub>2</sub>	1280.1	235.1	235.1	-541.0	149.9	29.4	-53.5	32.8	-14.3
CHF <sub>3</sub>	1300.2	245.8	245.8	-1099.8	561.6	-28.9	-119.4	84.7	-42.0
CH <sub>2</sub> Cl <sub>2</sub>	1080.9	-415.1	-415.1	-114.5	462.5	-241.6	31.4	34.2	-44.6
CHCl <sub>3</sub>	909.9	-678.3	-678.3	260.2	709.8	-549.3	163.3	21.3	-84.9
CH <sub>3</sub> NH <sub>2</sub> (methylamine)	1710.9	6.7	6.7	-289.5	103.0	8.9	-28.9	19.2	-9.0
CH <sub>3</sub> CN (methyl cyanide)	1786.9	233.0	233.0	-450.1	144.4	-13.3	-18.1	18.8	-14.2
CH <sub>3</sub> NO <sub>2</sub> (nitromethane)	1378.0	725.1	725.1	-748.2	308.0	-51.2	-52.6	55.9	-34.1
CH <sub>3</sub> ONO (methyl nitrite)	1393.5	573.9	573.9	-664.2	264.8	-48.2	-44.1	49.3	-32.0
CH <sub>3</sub> SiH <sub>3</sub> (methyl silane)	2022.1	-672.5	-672.5	-118.4	228.9	-80.2	-17.6	32.7	-23.9
HCOOH (formic acid)	1348.0	387.9	387.9	-559.6	139.4	20.0	-48.4	33.1	-16.2
HCOOCH <sub>3</sub> (methyl formate)	2266.3	311.0	311.0	-609.7	254.6	-49.9	-39.1	45.8	-31.3
CH <sub>3</sub> CONH <sub>2</sub> (acetamide)	2497.5	107.2	107.2	-526.9	308.4	-89.2	-27.9	46.7	-33.6

Table 2 Continued

Molecule	Exact	CAP(0)	CAP(1/2)	CAP(1)	CAP(3/2)	CAP(2)	CAP(5/2)	CAP(3)	CAP(7/2)
C <sub>2</sub> H <sub>4</sub> NH (aziridine)	2097.7	110.3	110.3	-612.2	247.0	11.3	-60.5	41.2	-19.5
NCCN (cyanogen)	1169.0	744.2	744.2	-705.4	170.9	-16.1	-23.5	22.8	-19.4
(CH <sub>3</sub> ) <sub>2</sub> NH (dimethylamine)	2633.9	-45.5	-45.5	-394.0	224.7	-42.4	-30.0	33.3	-22.1
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> (trans ethylamine)	2656.9	-124.7	-124.7	-326.9	243.4	-70.9	-20.4	34.3	-25.6
CH <sub>2</sub> CO (ketene)	1521.8	376.5	376.5	-493.4	99.3	12.5	-28.4	21.6	-13.2
C <sub>2</sub> H <sub>4</sub> O (oxirane)	1908.2	194.6	194.6	-653.5	209.5	32.4	-61.3	37.0	-16.4
CH <sub>3</sub> CHO (acetylaldehyde)	2034.5	151.9	151.9	-445.0	188.9	-26.4	-30.6	31.3	-19.7
HCOCOH (glyoxal)	1733.8	442.7	442.7	-642.4	258.2	-54.4	-35.0	41.8	-30.8
CH <sub>3</sub> CH <sub>2</sub> OH (ethanol)	2466.2	-95.1	-95.1	-397.5	223.2	-32.1	-37.1	35.5	-20.7
CH <sub>3</sub> OCH <sub>3</sub> (dimethylether)	2437.3	50.5	50.5	-445.7	190.5	-16.6	-35.3	31.2	-19.0
C <sub>2</sub> H <sub>4</sub> S (thiooxirane)	1879.5	-262.1	-262.1	-447.5	495.5	-116.4	-53.7	63.1	-36.5
(CH <sub>3</sub> ) <sub>2</sub> SO (dimethyl sulfoxide)	2428.4	-340.1	-340.1	-531.2	643.5	-235.9	-19.9	73.1	-60.0
C <sub>2</sub> H <sub>5</sub> SH (ethanethiol)	2384.3	-408.5	-408.5	-192.8	379.1	-164.4	3.3	36.7	-34.8
CH <sub>3</sub> SCH <sub>3</sub> (dimethyl sulfide)	2383.4	-534.5	-534.5	-214.4	448.9	-171.6	-15.3	49.9	-38.2
CH <sub>2</sub> =CHF	1731.1	140.9	140.9	-450.2	142.9	2.1	-35.4	27.4	-15.0
C <sub>2</sub> H <sub>5</sub> Cl (ethyl chloride)	2180.0	-371.5	-371.5	-180.1	359.9	-157.1	3.2	35.6	-33.7
CH <sub>2</sub> =CHCl (vinyl chloride)	1650.2	-141.1	-141.1	-315.6	285.5	-94.8	-10.6	30.7	-25.7
CH <sub>2</sub> =CHCN (acrylonitrile)	2203.5	285.2	285.2	-579.7	226.2	-45.4	-11.3	19.1	-18.6
CH <sub>3</sub> COCH <sub>3</sub> (acetone)	3003.4	-67.1	-67.1	-450.5	335.2	-122.3	-13.4	44.3	-37.5
CH <sub>3</sub> COOH (acetic acid)	2322.3	183.1	183.1	-613.6	298.1	-61.5	-46.6	53.6	-34.4
CH <sub>3</sub> COF (acetyl fluoride)	2073.3	230.3	230.3	-620.9	290.3	-58.1	-45.9	52.5	-33.5
CH <sub>3</sub> COCl (acetyl chloride)	1943.9	-69.1	-69.1	-327.3	443.5	-224.8	14.6	50.1	-51.4
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl (propyl chloride)	3118.8	-551.7	-551.7	-241.7	488.6	-205.1	10.9	32.0	-34.4
(CH <sub>3</sub> ) <sub>2</sub> CHOH (isopropanol)	3417.1	-281.2	-281.2	-350.6	384.6	-149.4	-13.5	49.7	-41.1
C <sub>2</sub> H <sub>5</sub> OCH <sub>3</sub> (methyl ethyl ether)	3389.4	-97.0	-97.0	-552.9	316.5	-51.7	-41.1	37.2	-23.6
(CH <sub>3</sub> ) <sub>3</sub> N (trimethylamine)	3560.6	-119.4	-119.4	-387.2	380.3	-146.6	-10.9	47.1	-41.0
C <sub>4</sub> H <sub>4</sub> O (furan)	2946.1	77.2	77.2	-932.3	506.2	-84.0	-76.9	76.1	-45.3
C <sub>4</sub> H <sub>4</sub> S (thiophene)	2877.2	-475.7	-475.7	-647.9	772.5	-283.3	-28.6	87.7	-69.2
C <sub>4</sub> H <sub>5</sub> N (pyrrole)	3165.9	-38.1	-38.1	-844.5	507.9	-99.7	-65.0	70.3	-43.4
C <sub>5</sub> H <sub>5</sub> N (pyridine)	3709.4	-61.2	-61.2	-805.8	604.3	-233.8	-9.5	68.3	-62.4
H <sub>2</sub>	342.2	-24.3	-24.3	4.9	-3.4	1.1	-0.3	0.1	0.0
HS	236.6	11.7	11.7	-72.2	21.8	4.4	-5.2	2.5	-0.9
CCH	688.9	172.3	172.3	-268.9	29.2	26.4	-18.3	8.4	-3.3
C <sub>2</sub> H <sub>4</sub> ( <sup>2</sup> A')	1396.6	14.4	14.4	-256.3	55.1	19.6	-22.2	12.4	-5.5
CH <sub>3</sub> CO( <sup>2</sup> A')	1720.6	191.5	191.5	-437.3	157.2	-15.4	-28.5	27.3	-17.2
H <sub>2</sub> COH( <sup>2</sup> A)	1177.0	95.8	95.8	-291.0	57.8	26.0	-26.2	13.4	-5.4
CH <sub>3</sub> O( <sup>2</sup> A')	1210.0	88.2	88.2	-333.5	78.2	25.8	-30.1	16.1	-6.4
CH <sub>3</sub> CH <sub>2</sub> O( <sup>2</sup> A'')	2151.6	-39.0	-65.7	-397.2	239.6	-43.6	-36.8	38.7	-23.4
CH <sub>3</sub> S( <sup>2</sup> A')	1180.8	-238.7	-234.3	-178.8	230.8	-64.8	-22.5	30.2	-18.2
C <sub>2</sub> H <sub>5</sub> ( <sup>2</sup> A')	1953.4	-144.2	-144.2	-241.9	104.7	0.3	-25.3	18.8	-9.7
(CH <sub>3</sub> ) <sub>2</sub> CH( <sup>2</sup> A')	2902.4	-263.4	-263.4	-320.1	210.9	-52.0	-18.5	26.8	-20.7
(CH <sub>3</sub> ) <sub>3</sub> C (t-butyl radical)	3851.1	-415.9	-415.9	-289.2	329.2	-149.6	13.5	28.5	-35.2
NO <sub>2</sub>	179.7	891.6	891.6	-642.5	71.9	48.8	-46.5	26.0	-11.6
RMS Error		417.4	417.4	488.2	326.4	167.6	66.8	39.2	30.7

results were encouraging but it is obviously now important to examine the performance of the approximations when applied to molecules. A de facto standard for such investigations, the G2 dataset, has been widely used and has recently been significantly extended [12]. It now contains 148 atomization

energies, 40 ionization energies and 8 proton affinities for a variety of small molecules and we have adopted it for this work.

The goal of this paper is to assess the errors that the CAP(*m*) introduce when applied to Hartree–Fock (HF), Hartree–Fock–Slater (HFS) and second-order

Table 3  
HF/6-31G\* ionization potentials and CAP(*m*) errors (kJ mol<sup>-1</sup>)

Molecule	Exact	CAP(0)	CAP(1/2)	CAP(1)	CAP(3/2)	CAP(2)	CAP(5/2)	CAP(3)	CAP(7/2)
H	1308.1	-1220.0	261.2	-33.4	5.2	-0.8	0.1	0.0	0.0
He	2261.9	-1388.8	92.5	-2.4	-0.6	0.2	0.0	0.0	0.0
Li	514.2	-666.0	815.2	-184.1	94.1	-24.0	10.1	-3.2	1.2
Be	765.1	-1041.6	439.7	-56.6	-8.6	8.7	-4.7	2.0	-0.8
B	756.1	-1336.6	144.7	55.3	-46.5	18.2	-6.1	1.9	-0.6
C	1033.9	-1530.6	-49.3	91.4	-44.0	13.7	-3.7	1.0	-0.2
N	1347.5	-1644.5	-163.3	105.7	-37.4	9.8	-2.3	0.5	-0.1
O	1158.6	-1674.9	-193.7	114.8	-34.2	7.7	-1.6	0.3	-0.1
F	1504.1	-1772.5	-291.2	114.7	-26.1	4.7	-0.8	0.1	0.0
Ne	1897.4	-1832.8	-351.5	107.1	-19.8	3.0	-0.4	0.1	0.0
Na	478.2	-594.1	887.2	-166.3	110.1	-13.8	7.9	-1.4	0.5
Mg	637.4	-836.5	644.8	-64.1	-3.8	18.0	-12.4	6.4	-3.1
Al	536.1	-899.5	581.7	8.0	-60.6	45.6	-25.4	12.2	-5.4
Si	736.4	-1205.5	275.8	92.9	-113.7	57.0	-24.5	10.0	-3.7
P	959.4	-1476.0	5.3	169.6	-129.1	54.4	-19.4	6.7	-2.2
S	882.4	-1540.4	-59.1	206.3	-134.7	52.6	-17.3	5.5	-1.6
Cl	1136.7	-1761.4	-280.2	255.0	-129.0	43.9	-12.7	3.6	-1.0
Ar	1414.3	-1948.0	-466.8	290.1	-118.1	35.0	-9.0	2.2	-0.5
CH <sub>4</sub>	1156.9	-1463.8	17.5	81.3	-81.9	34.6	-12.4	4.1	-1.2
NH <sub>3</sub>	816.7	-1394.8	86.4	60.5	-53.4	21.4	-6.9	2.0	-0.5
OH	1085.4	-1606.2	-125.0	117.1	-44.6	11.5	-2.5	0.5	-0.1
OH <sub>2</sub>	1038.0	-1547.3	-66.0	108.9	-49.8	14.3	-3.5	0.8	-0.2
FH	1347.0	-1665.3	-184.0	119.3	-37.8	8.2	-1.5	0.3	0.0
SiH <sub>4</sub>	1004.6	-1397.7	83.6	-4.9	-181.1	109.4	-47.4	18.1	-6.2
PH	934.6	-1467.1	14.2	158.1	-141.8	63.2	-23.7	8.6	-2.9
PH <sub>2</sub>	900.9	-1450.8	30.5	143.7	-152.6	71.1	-27.7	10.3	-3.5
PH <sub>3</sub>	830.9	-1403.7	77.5	88.7	-142.4	75.5	-32.8	13.2	-4.7
SH	883.7	-1532.1	-50.9	185.1	-144.5	60.0	-20.6	6.8	-2.1
SH <sub>2</sub>	893.8	-1530.9	-49.6	168.9	-153.8	66.9	-23.9	8.1	-2.6
CH	1118.5	-1729.1	-247.8	234.5	-141.1	51.7	-15.7	4.6	-1.3
HCCCH	930.6	-1511.9	-30.6	107.4	-108.6	44.7	-17.2	6.4	-2.3
H <sub>2</sub> CCH <sub>2</sub>	838.1	-1404.1	77.1	32.5	-127.7	65.9	-29.4	11.8	-4.4
CO	1244.5	-1664.4	-183.1	147.0	-110.3	47.9	-17.4	5.6	-1.6
N <sub>2</sub>	1449.6	-1809.0	-327.7	217.4	-117.3	40.2	-12.1	3.5	-1.0
O <sub>2</sub>	1249.3	-2000.0	-518.7	224.5	-95.6	34.1	-11.2	3.4	-0.9
P <sub>2</sub>	905.8	-1563.8	-82.6	-0.8	-234.7	155.0	-86.1	38.8	-15.5
S <sub>2</sub>	924.4	-1764.7	-283.5	244.0	-267.0	123.0	-64.8	32.7	-14.8
Cl <sub>2</sub>	1082.3	-1967.5	-486.2	360.0	-280.5	106.9	-52.3	27.3	-13.0
ClF	1143.3	-1998.7	-517.5	350.5	-172.2	64.2	-27.5	11.4	-4.1
SC	960.3	-1626.2	-144.9	116.6	-140.4	80.1	-44.4	20.8	-8.3
RMS errors		1532.3	328.6	161.1	123.0	56.6	26.2	11.6	4.7

Møller–Plesset (MP2) theories. Attenuated HF/6-31G\* thermochemical data and attenuated MP2/6-31G\* correlation energies are presented in Tables 2–5, respectively. Table 6 summarizes these results and, also, those for the analogous HFS/6-31G\* thermochemical data. All of the calculations have been performed using  $\omega = 0.5 \text{ a}_0^{-1}$ . It should be noted that this yields much more attenuation than the  $0.1 \text{ a}_0^{-1}$

used in our earlier study of the CASE approximation [4].

Table 2 lists HF/6-31G\* atomization energies and the corresponding attenuation errors. It can be proven that CAP(0) and CAP(1/2) atomization energies are always identical but it is clear that, using  $\omega = 0.5 \text{ a}_0^{-1}$ , they are both very inaccurate approximations. Typically, their errors are comparable to the atomization

Table 4  
HF/6-31G\* proton affinities and CAP(*m*) errors (kJ mol<sup>-1</sup>)

Molecule	Exact	CAP(0)	CAP(1/2)	CAP(1)	CAP(3/2)	CAP(2)	CAP(5/2)	CAP(3)	CAP(7/2)
H <sub>2</sub>	387.1	34.9	34.9	-25.9	7.8	-1.5	0.3	-0.1	0.0
HCCH	678.6	344.5	344.5	-205.0	137.5	-46.8	15.5	-5.3	1.8
NH <sub>3</sub>	908.8	164.4	164.4	-119.9	71.9	-23.9	6.6	-1.7	0.4
H <sub>2</sub> O	730.3	242.4	242.4	-139.8	55.2	-14.6	3.3	-0.7	0.2
SiH <sub>4</sub>	625.6	58.7	58.7	-47.6	204.6	-113.3	46.1	-16.6	5.3
PH <sub>3</sub>	823.0	106.3	106.3	-151.9	172.5	-80.0	31.5	-11.7	3.9
H <sub>2</sub> S	720.0	285.3	285.3	-245.9	189.8	-71.9	22.7	-7.0	2.0
HCl	542.7	489.3	489.3	-318.8	177.7	-56.6	14.9	-3.8	1.0
RMS errors		260.1	260.1	181.7	144.2	61.8	22.8	8.0	2.5

energy itself and, thus, they are of no predictive value. This contrasts with our earlier work [4] which demonstrated that, using  $\omega = 0.1 a_0^{-1}$ , CAP(0) was a surprisingly accurate approximation. Curiously, using  $\omega = 0.5 a_0^{-1}$ , CAP(1) actually turns out to be *worse* than CAP(0). However, proceeding to still higher *m* values, the CAP(*m*) results improve steadily. Generally, as we observed in our earlier study [7], we find that CAP(*m* + 1/2) is superior to CAP(*m*). This is significant because a CAP(*m* + 1/2) calculation is actually less expensive than a CAP(*m*) one [5]. It is also worth noting that, as *m* increases, the CAP(*m*) and CAP(*m* + 1/2) atomization energies often bracket the unattenuated result. In the final analysis, however, we must conclude that even the most sophisticated approximation that we have studied, CAP(7/2) using  $\omega = 0.5 a_0^{-1}$ , gives mixed results for atomization energies.

Table 3 lists HF/6-31G\* ionization potentials and the corresponding attenuation errors. As we have noted previously [4], ionization involves the loss of a charged particle and CAP(0) performs very poorly with the *w* value used. Proceeding to CAP(1/2), however, we observe a marked improvement, the RMS error dropping by roughly 80%. Each further increase in *m* roughly halves the RMS error and, as a consequence, CAP(7/2) is a very good approximation. Once again, we note that CAP(*m*) and CAP(*m* + 1/2) very often bracket the unattenuated result.

Table 4 lists eight HF/6-31G\* proton affinities and the corresponding attenuation errors. Proton addition has a relatively small effect on electronic structure and, consequently, even CAP(0) affords qualitative accuracy. The RMS errors drop monotonically as *m*

increases and CAP(7/2) is an excellent approximation. Again, we note the now familiar bracketing effect.

We conclude from these Hartree–Fock thermochemical results, as we did from our NaCl and H atom study [7], that it is very worthwhile to proceed beyond the CASE approximation to the higher CAP(*m*). Of course, it is interesting to ask whether this conclusion applies equally to density functional theory (DFT) calculations. We have shown elsewhere [6] how to generalize the Dirac/Slater exchange functional to accommodate attenuation of the Coulomb operator to the CASE operator. By analogous constructions, we have recently derived generalizations of the functional appropriate for any CAP(*m*) operator and this has enabled us to perform CAP(*m*) HFS calculations. Using the SG-1 grid [13] to integrate the exchange functionals, we find that the effects of the CAP(*m*) on HFS/6-31G\* thermochemistry are very similar to those presented in Tables 2–4. For this reason, we do not report the analogous HFS tables here but the tables are available upon request from the authors and are summarized in Table 6.

Table 5 lists MP2/6-31G\* correlation energies and the corresponding attenuation errors for the first-row neutral molecules from the G2 dataset. The MP2 energies are obtained [4] by using CAP(*m*) to compute MO integrals over unattenuated orbitals. CAP(0) and CAP(1/2) systematically underestimate correlation energies, CAP(1) systematically overestimates, and the higher CAP(*m*) rapidly converge to the unattenuated results. Such results certainly support the notion that electron correlation, at least in these molecules, is a short-range phenomenon.

Table 5  
 3MP2/6-31G\* correlation energies and CAP(*m*) errors (kJ mol<sup>-1</sup>)

Molecule	Exact	CAP(0)	CAP(1/2)	CAP(1)	CAP(3/2)	CAP(2)	CAP(5/2)	CAP(3)	CAP(7/2)
H <sub>2</sub>	45.6	-14.6	-14.6	4.5	-0.8	0.1	0.0	0.0	0.0
H <sub>2</sub> CCH <sub>2</sub>	691.1	-262.1	-262.1	104.1	-8.5	-1.4	2.8	-1.3	0.6
H <sub>2</sub> CO	817.1	-251.3	-251.3	76.1	-4.8	-1.4	1.5	-0.6	0.2
H <sub>2</sub> NNH <sub>2</sub>	883.2	-273.6	-273.6	80.8	0.9	-4.5	3.0	-1.2	0.5
H <sub>3</sub> CCH <sub>3</sub>	723.1	-264.6	-264.6	103.6	-6.0	-2.4	3.5	-1.6	0.7
H <sub>3</sub> COH	837.8	-248.0	-248.0	73.8	-0.1	-3.6	2.7	-1.1	0.4
HCCCH	684.2	-274.5	-274.5	110.8	-13.9	0.7	1.7	-0.9	0.4
HCN	779.1	-288.4	-288.4	103.4	-13.5	0.9	0.9	-0.5	0.2
HCO	774.9	-239.9	-239.9	72.1	-5.7	-0.8	1.1	-0.4	0.2
HOOH	984.0	-258.1	-258.1	60.2	1.6	-3.4	1.8	-0.6	0.2
Li <sub>2</sub>	52.4	-43.6	-43.6	26.9	-23.1	17.0	-7.9	5.0	-2.1
LiF	512.7	-101.8	-101.8	15.7	1.5	-1.1	0.5	-0.2	0.1
LiH	41.1	-20.1	-20.1	10.4	-3.3	1.2	-0.3	0.1	0.0
BeH	63.3	-27.2	-27.2	14.2	-3.5	1.0	0.0	-0.1	0.1
CH	203.6	-67.8	-67.8	20.9	-1.4	-0.5	0.4	-0.2	0.1
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	267.3	-90.3	-90.3	28.6	-1.6	-0.9	0.7	-0.3	0.1
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	225.8	-76.2	-76.2	22.9	0.1	-1.4	0.8	-0.3	0.1
CH <sub>3</sub>	299.6	-102.3	-102.3	32.4	-0.4	-1.6	1.0	-0.4	0.1
CH <sub>4</sub>	372.7	-130.3	-130.3	43.3	-0.9	-2.0	1.4	-0.5	0.2
CN	579.7	-193.4	-193.4	62.7	-7.1	0.2	0.6	-0.3	0.1
CO	771.1	-237.5	-237.5	70.1	-7.8	0.3	0.5	-0.2	0.1
CO <sub>2</sub>	1286.3	-378.7	-378.7	110.8	-9.7	-0.4	1.6	-0.7	0.3
N <sub>2</sub>	856.4	-294.0	-294.0	93.7	-12.3	1.0	0.4	-0.2	0.1
NH	268.3	-76.4	-76.4	17.3	0.4	-1.0	0.4	-0.1	0.0
NH <sub>2</sub>	358.2	-104.5	-104.5	24.8	0.9	-1.6	0.7	-0.2	0.1
NH <sub>3</sub>	455.6	-136.1	-136.1	33.5	1.4	-2.3	1.1	-0.3	0.1
NO	832.7	-243.5	-243.5	65.0	-4.6	-0.9	0.7	-0.3	0.1
O <sub>2</sub>	912.4	-262.0	-262.0	69.3	-5.1	-0.8	0.7	-0.3	0.1
OH	371.1	-86.9	-86.9	14.9	1.2	-1.0	0.3	-0.1	0.0
OH <sub>2</sub>	497.4	-122.0	-122.0	22.3	1.8	-1.6	0.6	-0.2	0.0
F <sub>2</sub>	960.9	-205.5	-205.5	40.4	-0.4	-1.3	0.6	-0.2	0.1
FH	477.5	-90.1	-90.1	12.1	1.1	-0.7	0.2	0.0	0.0
BF <sub>3</sub>	1568.6	-322.3	-322.3	65.1	2.7	-3.0	2.3	-0.8	0.3
CF <sub>4</sub>	2154.7	-460.2	-460.2	103.0	4.5	-5.9	3.9	-1.5	0.6
COF <sub>2</sub>	1719.2	-417.6	-417.6	104.7	-1.5	-3.7	2.9	-1.1	0.4
N <sub>2</sub> O	1445.5	-491.8	-491.8	173.4	-28.7	6.0	0.2	-0.4	0.3
NF <sub>3</sub>	1850.1	-428.0	-428.0	102.9	0.7	-4.5	3.1	-1.1	0.4
O <sub>3</sub>	1676.9	-528.9	-528.9	174.1	-25.5	3.8	0.8	-0.6	0.3
F <sub>2</sub> O	961.7	-205.9	-205.9	40.6	-0.4	-1.3	0.6	-0.2	0.1
C <sub>2</sub> F <sub>4</sub>	2491.6	-596.6	-596.6	165.6	-3.5	-2.2	6.3	-2.5	1.2
CF <sub>3</sub> CN	2480.9	-675.5	-675.5	216.1	-14.4	-2.4	6.6	-3.1	1.7
CH <sub>3</sub> CCH (propyne)	1035.3	-407.7	-407.7	173.9	-18.7	0.1	4.8	-2.5	1.5
CH <sub>2</sub> =C=CH <sub>2</sub> (allene)	1019.7	-397.6	-397.6	171.5	-16.0	-0.4	5.4	-2.8	1.6
C <sub>3</sub> H <sub>4</sub> (cyclopropene)	1044.4	-415.0	-415.0	179.9	-21.5	1.7	3.7	-1.9	1.0
CH <sub>3</sub> CH=CH <sub>2</sub> (propylene)	1047.5	-400.5	-400.5	170.1	-15.3	-0.4	5.1	-2.6	1.5
C <sub>3</sub> H <sub>6</sub> (cyclopropane)	1061.5	-406.5	-406.5	175.1	-15.1	-1.2	5.3	-2.6	1.3
C <sub>3</sub> H <sub>8</sub> (propane)	1079.4	-403.2	-403.2	169.6	-13.2	-1.0	5.6	-2.7	1.5
CH <sub>2</sub> CHCHCH <sub>2</sub> (butadiene)	1374.6	-539.8	-539.8	241.0	-27.3	4.1	6.5	-3.5	2.6
C <sub>4</sub> H <sub>6</sub> (2-butyne)	1387.6	-542.0	-542.0	237.8	-24.0	0.6	7.7	-4.1	2.7
C <sub>4</sub> H <sub>6</sub> (methylene cyclopropane)	1390.2	-543.9	-543.9	245.2	-24.0	0.8	8.0	-4.2	2.6
C <sub>4</sub> H <sub>6</sub> (bicyclobutane)	1414.3	-561.7	-561.7	257.8	-30.2	3.5	6.3	-3.3	2.0
C <sub>4</sub> H <sub>6</sub> (cyclobutene)	1393.6	-551.1	-551.1	252.5	-28.5	3.0	6.7	-3.6	2.1



Table 5 Continued

Molecule	Exact	CAP(0)	CAP(1/2)	CAP(1)	CAP(3/2)	CAP(2)	CAP(5/2)	CAP(3)	CAP(7/2)
C <sub>4</sub> H <sub>8</sub> (cyclobutane)	1419.4	-548.4	-548.4	250.9	-23.3	0.7	8.4	-4.3	2.5
C <sub>4</sub> H <sub>8</sub> (isobutene)	1408.8	-542.9	-542.9	241.4	-24.3	2.5	7.4	-3.8	2.6
C <sub>4</sub> H <sub>10</sub> ( <i>trans</i> -butane)	1436.3	-542.3	-542.3	235.8	-20.7	1.4	7.5	-3.6	2.4
C <sub>4</sub> H <sub>10</sub> (isobutane)	1442.3	-547.0	-547.0	242.3	-22.7	2.4	7.6	-3.9	2.6
C <sub>5</sub> H <sub>8</sub> (spiropentane)	1764.5	-692.4	-692.4	321.5	-33.4	3.9	10.1	-5.3	3.6
C <sub>6</sub> H <sub>6</sub> (benzene)	2061.4	-847.1	-847.1	422.3	-65.2	20.6	7.5	-4.8	4.1
CH <sub>2</sub> F <sub>2</sub>	1256.2	-290.4	-290.4	70.1	1.8	-3.8	2.5	-0.9	0.3
CHF <sub>3</sub>	1706.0	-375.2	-375.2	86.4	2.9	-4.7	3.1	-1.2	0.4
CH <sub>3</sub> NH <sub>2</sub> (methylamine)	801.6	-267.2	-267.2	90.8	-2.1	-3.7	3.3	-1.4	0.6
CH <sub>3</sub> CN (methyl cyanide)	1125.9	-418.6	-418.6	163.0	-17.7	0.2	3.7	-1.9	1.0
CH <sub>3</sub> NO <sub>2</sub> (nitromethane)	1815.8	-575.6	-575.6	198.7	-17.3	-0.5	4.4	-2.1	1.0
CH <sub>3</sub> ONO (methyl nitrite)	1783.9	-555.5	-555.5	186.3	-13.5	-1.6	4.4	-2.0	1.0
HCOOH (formic acid)	1295.0	-373.8	-373.8	109.1	-4.9	-2.6	2.7	-1.1	0.5
HCOOCH <sub>3</sub> (methyl formate)	1643.4	-505.4	-505.4	169.8	-9.3	-2.7	5.1	-2.3	1.2
CH <sub>3</sub> CONH <sub>2</sub> (acetamide)	1605.4	-524.7	-524.7	188.9	-12.5	-2.0	5.8	-2.8	1.5
C <sub>2</sub> H <sub>4</sub> NH (aziridine)	1144.1	-413.0	-413.0	163.2	-12.2	-2.2	4.8	-2.2	1.1
NCCN (cyanogen)	1566.8	-601.2	-601.2	242.5	-38.0	7.5	2.7	-1.7	1.4
(CH <sub>3</sub> ) <sub>2</sub> NH (dimethylamine)	1155.5	-404.4	-404.4	156.0	-8.5	-3.0	5.5	-2.6	1.4
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> ( <i>trans</i> -ethylamine)	1159.1	-406.8	-406.8	156.7	-9.4	-2.4	5.3	-2.4	1.3
CH <sub>2</sub> CO (ketene)	1150.8	-387.5	-387.5	139.3	-13.8	0.2	2.9	-1.4	0.8
C <sub>2</sub> H <sub>4</sub> O (oxirane)	1182.2	-392.8	-392.8	142.6	-9.4	-2.5	4.0	-1.8	0.8
CH <sub>3</sub> CHO (acetylaldehyde)	1169.5	-386.1	-386.1	137.3	-10.3	-1.4	3.6	-1.7	0.8
HCOCOH (glyoxal)	1620.6	-510.9	-510.9	172.9	-14.5	-0.4	4.0	-1.9	1.0
CH <sub>3</sub> CH <sub>2</sub> OH (ethanol)	1193.5	-385.4	-385.4	138.3	-6.2	-3.4	5.0	-2.3	1.2
CH <sub>3</sub> OCH <sub>3</sub> (dimethyl ether)	1187.2	-381.0	-381.0	134.7	-4.9	-3.8	5.0	-2.2	1.1
CH <sub>2</sub> =CHF	1140.6	-345.2	-345.2	118.9	-7.4	-2.2	3.4	-1.6	0.7
CH <sub>2</sub> =CHCN (acrylonitrile)	1454.8	-559.1	-559.1	234.5	-29.0	3.5	5.3	-3.0	2.0
CH <sub>3</sub> COCH <sub>3</sub> (acetone)	1525.4	-523.8	-523.8	203.0	-17.5	0.3	5.7	-2.8	1.7
CH <sub>3</sub> COOH (acetic acid)	1646.0	-507.9	-507.9	172.2	-10.6	-2.3	5.1	-2.4	1.3
CH <sub>3</sub> COF (acetyl fluoride)	1623.4	-469.1	-469.1	151.8	-8.7	-2.4	4.4	-1.9	1.0
(CH <sub>3</sub> ) <sub>2</sub> CHOH (isopropanol)	1556.0	-528.3	-528.3	209.0	-14.8	-1.0	7.1	-3.5	2.1
C <sub>2</sub> H <sub>5</sub> OCH <sub>3</sub> (methyl ethyl ether)	1544.1	-519.4	-519.4	200.4	-11.6	-2.5	7.2	-3.4	2.0
(CH <sub>3</sub> ) <sub>3</sub> N (trimethylamine)	1518.0	-548.2	-548.2	229.7	-17.7	-0.2	7.8	-3.8	2.4
C <sub>4</sub> H <sub>4</sub> O (furan)	1865.0	-688.9	-688.9	303.3	-38.0	6.6	6.3	-3.5	2.2
C <sub>4</sub> H <sub>5</sub> N (pyrrole)	1833.3	-713.9	-713.9	329.6	-42.8	8.4	7.1	-4.0	2.7
C <sub>5</sub> H <sub>5</sub> N (pyridine)	2144.8	-854.4	-854.4	410.4	-62.0	18.4	6.9	-4.3	3.6
CCH	539.5	-210.3	-210.3	80.3	-9.4	0.0	1.2	-0.6	0.2
C <sub>2</sub> H <sub>3</sub> ( <sup>2</sup> A')	590.3	-219.5	-219.5	84.5	-6.0	-1.6	2.4	-1.0	0.5
CH <sub>3</sub> CO ( <sup>2</sup> A')	1140.4	-381.8	-381.8	135.8	-12.2	-0.8	2.9	-1.5	0.7
H <sub>2</sub> COH ( <sup>2</sup> A)	776.0	-225.4	-225.4	64.2	0.3	-3.3	2.3	-0.9	0.3
CH <sub>3</sub> O ( <sup>2</sup> A')	716.0	-213.6	-213.6	64.5	-0.9	-2.8	2.1	-0.8	0.3
CH <sub>3</sub> CH <sub>2</sub> O ( <sup>2</sup> A'')	1255.6	-429.0	-429.0	163.8	-22.6	5.6	1.2	-0.5	0.4
(CH <sub>3</sub> ) <sub>2</sub> CH ( <sup>2</sup> A')	1028.8	-387.5	-387.5	162.8	-14.9	-0.6	4.6	-2.7	1.3
C <sub>2</sub> H <sub>5</sub> ( <sup>2</sup> A')	1390.4	-532.0	-532.0	235.6	-25.4	3.0	6.3	-3.9	2.3
(CH <sub>3</sub> ) <sub>3</sub> C ( <i>t</i> -butyl radical)	1390.4	-532.0	-532.0	235.6	-25.4	3.0	6.3	-3.9	2.3
NO <sub>2</sub>	1435.8	-442.9	-442.9	138.2	-15.4	0.7	1.5	-0.7	0.3
RMS errors		416.4	416.4	164.3	17.9	4.2	4.4	2.3	1.4

Table 6  
CAP(*m*) error summary (kJ mol<sup>-1</sup>)

Property	CAP(0)	CAP(1/2)	CAP(1)	CAP(3/2)	CAP(2)	CAP(5/2)	CAP(3)	CAP(7/2)
HF atomization energies	417.4	417.4	488.2	326.4	167.6	66.8	39.2	30.7
HF ionization potentials	1532.3	328.6	161.1	123.0	56.6	26.2	11.6	4.7
HF proton affinities	260.1	260.1	181.7	144.2	61.8	22.8	8.0	2.5
HFS atomization energies	257.7	257.7	237.5	109.3	56.1	44.7	25.5	21.4
HFS ionization potentials	1488.9	321.4	152.2	102.5	50.3	20.3	9.2	9.7
HFS proton affinities	273.7	273.7	187.4	143.7	62.0	20.7	7.3	1.6
MP2 correlation energies	416.4	416.4	164.3	17.9	4.2	4.4	2.3	1.4

#### 4. Conclusions

The CAP(*m*) operators are a well-defined and systematic family of approximations to the Coulomb operator  $1/r$ . When used in quantum chemical calculations employing a Gaussian basis set, they yield analytically evaluable integrals. Unlike the Coulomb operator, CAP(*m*) operators are short-range and therefore computationally inexpensive to utilize [5].

We find, however, that the errors introduced by the CAP(*m*) approximations are strongly dependent on the property in question. It is clear from Table 6 that the largest errors are found for atomization energies, irrespective of whether these are computed at the HF or HFS levels. Ionization potentials and proton affinities are generally more accurately treated (except that CAP(0) is hopeless for the former). MP2 correlation energies (and, we suspect, higher-level correlation energies) are remarkably well reproduced, even by CAP(5/2) with  $\omega = 0.5$ . This result is probably the most significant of the present work and appears to offer an inexpensive computational route to post-SCF calculations. We will report further on this elsewhere.

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