(22) Hybridization was determined by Mulliken population analysis of the GVB orbitals. We did not include the contribution of d functiions to the hybridization, since in all cases the contribution was small, e.g., in the N–N σ bond the hybridizations are actually $sp^{1.5}d^{0.02}$ and $sp^{5.0}d^{0.12}$.
(23) (a) One approach[18b] has been to build in only those correlations that do not disappear at $R = \infty$ (leading to HF wave functions for the separated fragments). Such an approach can lead to inconsistent levels of correlations and tends to provide too large a bond energy; (b) W. J. Stevens, G. Das, A. C. Wahl, M. Krauss, and P. Newmann, *J. Chem. Phys.*, **61**, 3686 (1974), and references cited therein.
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A Study of One-Electron Functionals for Molecular Correlation Energies

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Abstract: The Carr–Gordon–Kim electron correlation functional is applied to a series of hydrides for C, O, N, and F, and to a selection of small molecules using several basis sets. Excellent agreement of calculated correlation energies with experiment is generally found and the results are essentially independent of the basis set used. Calculated correlation energies for successive reactions of C, N, O, and F with H are in good agreement with experimental values. The results indicate that one-electron density functionals show promise for the economical estimation of electron correlation energies of large molecular systems.

In recent years, ab initio molecular orbital (MO) calculations have been applied even to relatively large molecular systems, such as those common in organic chemistry. These calculations have generally been of the single-determinant LCAO-MO-SCF type for which a specific limitation is set on the energy by the variational principle. The difference between this lower bound, the Hartree–Fock limit, and the true or experimental energy is the correlation energy, a relatively large quantity (many eV) that is often not considered explicitly.

The successful treatment of isodesmic reactions even with minimal basis sets[2,3] demonstrates that correlation energy differences can be quite small for closed shell systems having equal numbers of similar kinds of bonds. However, where bonds are broken, or severely altered, as in the study of reaction transition states, this approach may be less satisfactory, and explicit consideration of the correlation energy may be required. For large molecular systems the application of configuration interaction (CI) techniques becomes prohibitively expensive.

Correlation energies have been related to the numbers and types of electrons as in the IEPA (independent electron pair approximation)[4] and the CEPA (coupled electron pair approximation)[5] methods. While one may obtain disastrous[5] results with the former, accurate variational type correlation energies may be obtained with the latter method, at a cost somewhat less than that of a good CI, but this method too can become time consuming for large systems. Recently, however, the use of functionals has been reintroduced[6-9] as an alternative to CI methods.

The procedure considered here represents the correlation energy (CE) as a functional $f(\rho)$ of the self-consistent field (SCF) single-determinant electron density distribution, ρ. A rather simple analytical, one-electron function of ρ is typically used for $f(\rho)$, particularly if ρ is slowly varying.

$$F \approx \int \rho f(\rho) \mathrm{d}\tau \tag{1}$$

Furthermore, if the function itself varies slowly with ρ, then ρ might be well enough approximated with rather limited LCAO basis sets, e.g., Slater orbitals, whose SCF energy may in fact be rather far from the Hartree–Fock limit. In principle, eq 1 can be applied to systems containing two or more electrons with rather unsophisticated computational effort.

Wigner first proposed that such a functional should exist[9] and Slater[10] successfully used a functional dependent on $\rho^{1/3}$ to calculate exchange energies, which are a type of correlation energy (i.e., the difference in energy between a simple product wave function and an antisymmetrical one).

Of course, electron correlation is a two-electron phenomenon and recently a two-electron functional has been shown to provide excellent evaluations of correlation energies for small molecules.[11] In this paper we explore the possible application of one-electron functions to simple open and closed shell molecular systems with an eye to treating larger organic systems. We also are interested in a functional that is of an intensive nature rather than having a mixture of intensive and extensive character. We discuss briefly two different such functionals that have been proposed in the literature,[6-8] indicate some limitations, propose some changes, and finally show that these functionals can give satisfactory estimates of molecular correlation energies under the specified conditions.

Lie–Clementi (LC) Functional. Lie and Clementi[8] have recently explored the use of a functional first given by Gombas.[12,13]

$$f(\rho) = a_1\rho^{1/3}(a_2 + \rho^{1/3})^{-1} + b_1 \ln (1 + b_2\rho^{1/3}) \tag{2}$$

Lie and Clementi parameterized eq 2 using atomic SCF-LCAO-MO's to fit the correlation energies for the closed shell atoms He, Be, and Ne. Consideration was next given to the fact that an unpaired electron contributes less to the total correlation energy than it would if its orbital were doubly occupied. Lie and Clementi generalized eq 1 by replacing the electron density with the LCAO expansion

Table I. Comparison of Correlation Energies

	Lie-Clementi	This work				Expt[a]
		6-311G + BF	4-31G	STO-3G	Hybrid atoms	
CH_4	−0.307[b]	−0.309	−0.308	−0.309	−0.309	−0.296
NH_3	−0.324[b]	−0.326	−0.326	−0.325	−0.324	−0.326
H_2O	−0.344[b]	−0.344	−0.344	−0.344	−0.342	−0.365
HF	−0.368	−0.371	−0.368	−0.365	−0.364	−0.377
Ne	−0.381			−0.385		−0.381
Ar	−0.759			−0.760		−0.732

[a] Reference 18. [b] Personal communication from George Lie.

$$\rho'_i = \sum_{i=1}^{\text{occ}} \eta_i \bar{\rho}_i \tag{3}$$

$$\bar{\rho}_i = \left| \sum_j c_{ij} \chi_j(\mathbf{r}) \right|^2 \tag{4}$$

Here η_i is the MO occupation number, and $\bar{\rho}_i$ is the density of the ith spin orbital. The LCAO coefficients are c_{ij} and χ_j is the atomic orbital basis function. Lie and Clementi prescribed a weighted density for systems with partially occupied MO's

$$\rho \equiv \sum_i \rho'_i e^{-d(2-\mu_i)^2} \tag{5}$$

where μ_i allows for the fractional weighting character of the occupation number. In a restricted Hartree-Fock[14] (RHF) example μ_i and η_i would be 2 and 1, for closed and open shell MO's respectively, while for the unrestricted Hartree-Fock[15] (UHF) analogue for which the mean value of S^2 is near the exact one, the near-equivalent α and β spin MO's would be approximated to have $\eta_i = 1$ and $\mu_i = 2$, the unpaired MO being treated the same as the open shell MO in the RHF case. For the basis set used by Lie and Clementi, d was found to be 0.5 for F(^{2}P). It is interesting to note that the effect of the nodal properties of the SCF MO's on the density, and hence the correlation energy, is readily judged by evaluating eq 4 explicitly as given.

Lie and Clementi applied eq 2 to first-row neutral monohydride and diatomic molecules. As they were concerned with the shape of potential functions in their work they were required to use a multideterminant wave function in order to have proper dissociation; this procedure, of course, introduces some correlation energy and, consequently, so as to compensate for this, the nonintegral MO occupation numbers derived from the MCSCF processed were used for $\eta_i = \mu_i$. This has the effect of reducing the contribution of the already partially correlated MO's. This procedure involves three kinds of problems in our proposed subsequent extension to large organic systems. First, MCSCF calculations are not currently feasible for large systems. Second, the procedure amounts to deriving a correlation energy from an already partially correlated density function, even though correction for this is inherent in eq 5. Third, particularly for multiatomic molecules, it would be desirable to estimate correlation energies without becoming involved in problems of proper dissociation. Nevertheless, the treatment of open shell MO's in this method can be very useful.

Carr-Gordon-Kim (CGK) Functional. A second, more general functional, derived by Carr et al.,[7] has been used recently by Kim and Gordon[6] in the study of weak/rare gas interactions. Their functional is more complete in the sense that it leads directly to the total energy.

The Carr-Gordon-Kim correlation functional piece[6] is separated into regions of high, medium, and low electron density, based on the volume of unit density represented in

$$4\pi r_s^3 \rho/3 = 1 \tag{6}$$

or to allow comparison with eq 2

$$r_s = 0.62035\rho^{-1/3}$$

In a high density region, such as is found in an atomic core and in some covalent bonds, e.g., C_2, N_2, and F_2, $f(\rho)$ is derived from the electron gas approximation:

$$f(\rho_{\text{high}}) = (0.311 + 0.00558\rho^{-1/3})(\ln \rho^{-1/3} + 0.47747) - 0.00620\rho^{-1/3} - 0.048 \tag{7a}$$

The form in low density regions, such as at the outer regions of an atom or molecule, is derived from the energy of electrons in a Wigner crystal lattice and is expressed as a power series in $r_s^{-1/2}$, or using eq 6

$$f(\rho_{\text{low}}) = -0.2717\rho^{1/3} + 0.8220\rho^{1/2} - 0.9119\rho^{2/3} - 0.248\rho^{5/6} \tag{7b}$$

These two functions do not intersect and Gordon and Kim have chosen an intersecting linear interpolation in the intermediate density region between the values of $0.7 \leq r_s \leq 10$, or $1.128 \leq \rho^{1/3} \leq 16.12$,

$$f(\rho_{\text{med}}) = -0.0615697 + 0.018981\,(\ln \rho^{-1/3} + 0.47747) \tag{7c}$$

Unfortunately, most of the typical valence density lies in this region. A similar but nonlinear interpolation was proposed by Carr et al.[7]

Modified Carr-Gordon-Kim Functional. Kim and Gordon have reinvestigated their functional and its correlation part in some detail.[6b] In particular, they report that the ratio of experimental to calculated correlation energies appears to approach a limiting value of two for polyelectronic atoms as the atomic number or number of the electrons goes up. They have offered an explanation as to why the calculated values are too high, but the piecewise definition and, especially, the ad hoc nature in the "medium density" region, suggested to us a more empirical approach. In order to evaluate whether a functional of the Carr-Gordon-Kim (CGK) type can be usefully applied to molecular systems, we have compared the calculated correlation energy divided by two (hereafter referred to as the "CGK/2" functional) with experimental values for several ten-electron systems of chemical interest, e.g., CH_4, NH_3, H_2O, HF, and Ne. It was especially important to see whether this functional would reproduce the trend of increasing magnitude of correlation energy along this series.

Ordinary CI calculations depend significantly on the flexibility of basis sets; hence, in the present study of functionals we explored several basis sets. For a minimal basis set we have used for the most part the STO-3G basis set.[16] The next level was the split valence-shell basis set, 4-31G,[17] that has only one function for the core. Lastly, in an effort to obtain a density corresponding reasonably closely to the Hartree-Fock limit we used a triply split valence-shell basis with a single core function, 6-311G.[18] To compensate for the absence of d-type orbitals with the 6-311G basis, we incorporated bond functions

Table II. CGK/2 Correlation Energies

	STO-3G	4-31G	Expt[c]
CH_3-CH_3	−0.572	−0.565	−0.557
CH_3-NH_2	−0.591		−0.599
CH_3-OH	−0.625		−0.620
NH_2-NH_2	−0.618	−0.624	−0.637
HO-OH	−0.683		−0.699
F-F	−0.670	−0.670[a]	−0.737
$CH_2{=}CH_2$	−0.518	−0.518	−0.522
$CH_2{=}O$	−0.545	−0.557	−0.586
HN=NH	−0.567	−0.579	−0.583
HN=O	−0.575	−0.580	−0.627
C_6H_6	(−1.385)[b]		−1.412[d]
C≡C		−0.401	−0.512[e]
HC≡CH		−0.451	−0.491
C≡O		−0.486	−0.538
HC≡N	−0.472	−0.466	−0.517
N≡N		−0.492	−0.542

[a] 6-31G: −0.670. [b] From atomic densities. [c] Derived from ref 21 and 18. [d] Reference 23. [e] Derived using the Hartree–Fock value in ref 8.

Table III. Hydride UHF-SCF Energies

	6-311G**[a]	6-311G + BF	Difference
$C(^3P)$	−37.68732	−37.68456	−0.00276
$CH(^2\pi)$	−38.27558	−38.27109	−0.00449
$CH_2(^3B_1)$	−38.93339	−38.93025	−0.00314
$CH_3(^2A_1')$	−39.57268	−39.56784	−0.00484
$CH_4(^1A_1)$	−40.20842	−40.20221	−0.00621
$N(^4S)$	−54.39613	−54.39603	−0.00010
$NH(^3\Sigma^-)$	−54.97431	−54.96878	−0.00553
$NH_2(^2A)$	−55.57703	−55.56229	−0.01574
$NH_3(^1A_1)$	−56.20854	−56.19700	−0.01154
$O(^3P)$	−74.80363	−74.80075	−0.00288
$OH(^2\pi)$	−75.40897	−75.39561	−0.01286
$OH_2(^1A_1)$	−76.04519	−76.02207	−0.02232
$F(^2P)$	−99.39519	−99.33512	−0.06007
$HF(^1A_1)$	−100.04588	−99.98867	−0.05721

[a] Reference 18.

in all X–H bonds. Each bond function[22] was a single 1s-Gaussian function, at ⅓ and ⅔ bond distance, and had an exponent of 0.6, the optimal for C–H. Finally, in the Heitler–London sense, sums of atomic densities for CH_4, NH_3, H_2O, and HF were constructed from STO-3G SCF-AO's for $C(^5S)$, $N(^4S)$, $O(^3P)$, $F(^2P)$, and $H(^2S)$. These states were chosen so as to correspond approximately to the hybridization or valence states of the atoms in the molecules. Standard geometries[19] were used throughout. Numerical integration was performed using small trapezoidal areas. The areas were kept small enough to obtain an accuracy of ±0.001 au in the calculated correlation energy. The results are summarized in Table II. The results are extremely good considering the simplicity of the approach. The numbers are all close to the results of Lie and Clementi who used a near Hartree–Fock-limit basis, and to the experimental values. Moreover, an unexpected and important outcome of this study is the finding that the results are virtually independent of basis set. Minimum basis atomic densities give virtually the same results as a near Hartree–Fock LCAO-MO density. This result suggests that the CGK/2 functional may provide useful estimates of correlation energies for large molecular systems using only the most simple determinant LCAO-SCF wave functions.

Application to sp ^{n} Hybridized Systems. The application to still further compounds is summarized in Table III, which is divided into several classes of compounds. The first group consists of those in which the heavy atoms have approximately sp^3 hybridization. In the second group, the heavy atoms are approximately sp^2, and in the third group, sp. We have compared calculated results with experiment using densities from both STO-3G and 4-31G basis sets in several cases, particularly when a minimum basis was thought to be insufficiently flexible to describe the anisotropy of the electron distribution.

In the singly bonded systems the calculated values generally agree well with experiment. There is a relatively large error for F_2. Since an identical value is obtained using the STO-3G and 6-31G[20] LCAO-MO's, and 4-31G atomic densities, the effect is apparently not due to a possible poor representation of the core region by the basis set. With the exception of F_2, this group has a mean absolute error of ±0.011 au (±6.9 kcal mol^{-1}).

With both hydrazine and ethane slight improvement is obtained on using the 4-31G basis rather than the STO-3G basis. The correlation energy of hydrazine was also calculated using STO-6G Slater basis orbitals in conjunction with the STO-3G LCAO-SCF-MO's. Since the net overlap between basis AO's is little affected by using STO-6G vs. STO-3G, the largest effect, if any, should be in the vicinity of the core where $\rho(\mathbf{r})$ is largest in magnitude. However, the STO-6G basis orbitals give −0.618, identical with the STO-3G value. This comparison as well as the case of F_2 demonstrates further that deviations do not depend seriously on basis set.

The calculated correlation energies for the sp^2, ethylene type systems as a group deviate from the experimental values more than the sp^3 systems, particularly at the minimal basis level, ±0.028 au (±18 kcal mol^{-1}). The use of the 4-31G basis, where feasible, lowers the mean deviation to ±0.023 au (±14 kcal mol^{-1}). The largest deviation is 27.6 kcal mol^{-1} for HNO. Especially significant is the case of formaldehyde. The error is 18.2 kcal mol^{-1}. We note that the energy change for the hydrogenation reaction $CH_2O + 2H_2 \rightarrow CH_4 + H_2O$ reported for the 6-31G** basis set,[21] which has a d orbital set on the heavy atom and a p set on hydrogen, is in good agreement with that determined using solely Hartree–Fock limit energies, ~61.4 kcal mol. Consequently, it seems clear that for two additional examples, HNO and CH_2O, the functional itself is predominantly responsible for the error in the calculated correlation energies.

The sp-hybridized systems show errors of even larger average magnitude than found for F_2, HNO, and CH_2O. These errors also do not seem to be related to basis set since additional correlation energy calculations using various basis sets for N_2 again showed no large difference, the variations being only 0.005–0.010 au. A similar result is found for HCN. The sp systems, as well as CH_2O and HNO, all have heavy atom bond distances between 1.25 and 1.13 Å. It appears that the CGK/2 functional underestimates the correlation energy for valence electron densities found in rather short bonds between the heavy atoms C, N, and O, in which the electron density may not vary slowly. It is possible that the large deviation for F_2 is related even though the F–F bond distance is somewhat larger. Analysis shows significant contribution of the valence density to the high density region, eq 7a, for all the sp systems and also F_2, whereas nearly all of the other typical valence densities fall in the range of eq 7c.

The values found in parentheses in Table II were determined from sums of atomic densities constructed from the appropriately hybridized atoms. There is then generally good agreement with results obtained for SCF-MO's and those from atomic densities. Of particular interest is the case of benzene; here we find a good agreement with experiment for an sp^2 system of 42 electrons where it was possible to represent the total density by using only three pseudonatural orbitals. As a result the total computation effort was reduced by a factor of 7.

Table IV. Correlation Energy Partitioning for Methane

	4-31G			6-311G + BF			
d	0.5	0.72	1.125	1.445	1.125	Expt[a]	|Δ|
C	−0.163	−0.157	−0.149	−0.151	−0.155	−0.154	0.001
$C + H \rightarrow CH$	−0.033	−0.038	−0.044	−0.046	−0.049	−0.043 ± 0.003	0.006
$CH + H \rightarrow CH_2$	−0.029	−0.023	−0.016	−0.011	−0.010	−0.012 ± 0.008	0.002
$CH_2 + H \rightarrow CH_3$	−0.040	−0.043	−0.048	−0.047	−0.046	−0.043 ± 0.011	0.003
$CH_3 + H \rightarrow CH_4$	−0.041	−0.044	−0.049	−0.052	−0.050	−0.041 ± 0.008	0.009
Total	−0.306	−0.305	−0.306	−0.309	−0.310	−0.293	
CH_4 (calcd direct)		−0.308			−0.309		

[a] Reference 18.

Table V. Correlation Energy Partitioning for Hydrides of N, O, F, H with 6-311G + BF, *d* = 1.125

	Calcd	Expt[a]
N	−0.178	−0.185 ± 0.001
$N + H \rightarrow NH$	−0.049	−0.062 ± 0.007
$NH + H \rightarrow NH_2$	−0.049	−0.049 ± 0.18
$NH_2 + H \rightarrow NH_3$	−0.049	−0.038 ± 0.016
Total	−0.325	−0.334
NH_3 (calcd direct)	−0.326	
O	−0.251	−0.252 ± 0.001
$O + H \rightarrow OH$	−0.030	−0.059 ± 0.003
$OH + H \rightarrow OH_2$	−0.066	−0.054 ± 0.005
Total	−0.348	−0.365
H_2O (calcd direct)	−0.347	
F	−0.314	−0.315 ± 0.001
$F + H \rightarrow FH$	−0.057	−0.062 ± 0.003
Total	−0.371	−0.377
HF (calcd direct)		

[a] Reference 18.

Application to First-Row Hydrides. We next discuss the results given by the CGK/2 functional for the neutral hydrides of C, N, O, and F. The densities were derived from the SCF MO's obtained with the 6-311G + BF basis set. The UHF-SCF energies are given in Table III and compared with those for 6-311G**. (Note in passing that although d-type orbitals should not lower the energy with respect to the sp Hartree-Fock limit, the 6-311G** atomic energies[18] are lower than those for 6-311G because of the partial population of a 3s-type function which is brought into the calculation with the 3d orbitals.) Among the hydrides of a given first-row atom, the differences between the UHF energies for the 6-311G** basis set and for the 6-311G + BF basis set tend to increase with the number of hydrogens. Among the saturated hydrides CH_4, NH_3, H_2O, and HF, the UHF energy differences increase with the number of unshared electron pairs. This latter effect is to be expected, particularly in the molecule HF where the variational space of the lone pairs is restricted and the absence of p functions on H does not allow for π-type interactions between H and F. Similar arguments hold for the other members of the series studied as a significant number of basis orbitals have been deleted in nearly all cases.

A comment is necessary on the procedure for calculating correlation energies using functionals for open shell systems. As inferred by Lie and Clementi, and discussed above, the open shell weighting factor is formally for a completely orthonormal MO basis set. We have already seen an insensitivity of the CGK/2 functions to basis sets, at least for hydrides. Qualitatively, this means that the functional is not very sensitive to moderate local changes in the density. Consequently, we shall reasonably assume that for our purposes the results from the *total* density for the UHF-SCF-MO's will not differ significantly from those expected for the RHF-SCF-MO density since the mean value of the spin operator S^2 was always near the theoretical one.

In order to use the UHF-SCF-MO's for correlation energy calculations it is now necessary to determine *d* in eq 4 after first assigning $\mu_i{}^\alpha = \mu_i{}^\beta = 2$ for the corresponding spin orbitals. As our interest is predominantly in carbon systems the value of *d* was adjusted to reproduce the correlation energy of $C(^3P)$. The value of $d = 1.125$ was found for 6-311G + BF, and $d = 0.72$ for the 4-31G basis set. These values may be compared with the value $d = 0.5$ determined previously for $F(^2P)$ using a large basis set.[8] We also investigated the effect of *d* on the correlation energy of the reactions

$$CH_n + H \rightarrow CH_{n+1}$$

for $n = 0, 1, 2, 3$, and for both the 4-31G and 6-311G + BF basis sets using a value of zero for the correlation energy of $H(^2S)$. In Table V we see the effect of basis set in the partitioning of the correlation energy, though the total for the net reaction, C + 4H, is constant. The following reaction is especially significant in this set:

$$CH(^2\pi) + H(^2S) \rightarrow CH_2(^3B_1)$$

For it the 6-311G + BF basis set in particular closely reproduces the experimental change in correlation energy. In this reaction the number of electron pairs does not change and the calculated correlation energy change is small compared to the other steps in which changes in the number of electron pairs occur; that is, the modified CGK/2 expression reproduces an important experimental trend. In order to obtain comparable agreement with the 4-31G basis an unreasonable value would be derived for $C(^3P)$. Nevertheless, if estimated errors in the experimental values are taken into account, the 4-31G basis set values for $d = 0.72$ are acceptable on the whole.

In Table V we report the results for the reaction of N, O, and F with H. There is good agreement with experiment on the whole, with the most serious exception being for the formation of OH. Furthermore, in Tables IV and V the sum of correlation energy changes for successive hydride reactions of a given first-row heavy atom has the same value as when the correlation energy is determined directly from the total molecular density, and indicates that our round-off errors are small.

Comparison of Results from CGK/2 and LC Functionals. To a certain extent it is difficult to compare our results directly with all of the results of Lie and Clementi using their functional. For the first-row atoms and monohydrides given, Table VI, the comparison may be made directly for the single-determinant SCF densities. Similar results are obtained using either the CGK/2 functional and the 4-31G basis, or a Hartree–Fock limit basis set with the LC functional for the atomic correlation energies for the heavy atoms. For the monohydrides the CGK/2 results are about 10% larger than those from the LC functional, and are somewhat closer to experiment. This difference is of the same magnitude as the correlation energy obtained from the MCSCF process. For the heavy atom diatomic molecules the CGK/2 functional is in error by 10–20%

Table VI. Comparison of CGK/2 and LC Functionals

	ΔE(MCSCF-HF)	ϵ(MCSCF)	ϵ(total)	ϵ(HF)	ϵ(this work)[d]	ϵ(exact)[a]
C(^{3}P)				−0.155	−0.157	−0.155
CH	−0.018	−0.189	−0.207	−0.182	−0.204	−0.194
CH$_4$			−0.307[c]		−0.309	−0.296[b]
C$_2$	−0.123	−0.360	−0.483		−0.401	−0.512
N(^{4}S)				−0.189	−0.178	−0.186
NH	−0.023	−0.222	−0.245	−0.214	−0.227	−0.232
NH$_3$			−0.324[c]		−0.326	−0.326[b]
N$_2$	−0.077	−0.454	−0.531		−0.492	−0.542
O(^{3}P)				−0.246	−0.251	−0.254
OH	−0.023	−0.282	−0.305	−0.273	−0.281	−0.310
OH$_2$			−0.341[c]		−0.347	−0.365[b]
O$_2$	−0.094	−0.525	−0.619		−0.545	−0.647
F(^{2}P)				−0.311	−0.314	−0.316
FH	−0.022	−0.348[b]	−0.370[c]	−0.338	−0.371	−0.377[b]
F$_2$	−0.079	−0.647	−0.726		−0.670	−0.741

[a] Reference 8. [b] Reference 18. [c] Private communication, George C. Lie. [d] UHF or RHF 4-31G SCF MO's.

when compared to experimental values. The average MCSCF correlation energies for the monohydrides is −0.022 au whereas for the homonuclear diatomic molecules it is about −0.093 au. This is what makes a direct comparison between the LC and CGK/2 results difficult. The fact that the latter gives results that are larger than the former, which incorporates the MCSCF density, is undoubtedly related to the exponential weighting in eq 5, where nonintegral values of μ_i are used as obtained for occupation numbers in the MCSCF process. One should recall that the LC functional is parameterized for atomic densities, and as such, gives rise to larger correlation energies by about 5% when the MCSCF density is used.

One should also note that the directly calculated (MCSCF-HF) correlation energies for the first-row monohydrides decrease from 8.7 to 5.9% on going from CH to FH, whereas for the corresponding homonuclear diatomics the decrease is from 25 to 11%. The deviation from experiment of the results of the CGK/2 functional parallels this balance also, the error being 21% for C$_2$ and 9% for F$_2$. In these latter molecules, as we have stated before, an increasing portion (~10%) of the valence density falls into the "core region" in terms of magnitude of $\rho^{-1/3}$.

Conclusions

We draw several conclusions from the above results. First, the CGK/2 functional is very simple in that no calibration is involved except for open shells. Even such calibration also appears to be a rather simple one, since the values of the parameter d determined for C(^{3}P) appear to apply sufficiently well for ground state N, O, and F. Second, functionals derived for use with one-electron density matrices are relatively insensitive to substantial variation of basis sets and, therefore, have potential use with large molecular systems. Finally, the calculated correlation energy values for several types of molecules are sufficiently accurate to suggest that rather simple one-electron density matrix functionals may be a satisfactory approach to the calculation of correlation energies. Indeed, since the division of the CGK functional by two represents an element of empiricism, the results suggest an extension to a still more empirical functional. We have followed this approach to derive a purely empirical one-electron functional capable of giving more accurate correlation energies and will report these results in a subsequent paper.

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