Table II. Maximum Absolute Values of Bond Density as a Function of R[a]

R	maximum bond density r space	 p space
2.0	0.0451	0.192
1.8	0.0593	−0.0769
1.6	0.0792	−0.122
1.5	0.0930	−0.197
1.4	0.113	−0.276
1.3	0.142	−0.354
1.2	0.178	−0.433
1.0	0.281	−0.585

[a] R and the bond density are in atomic units. Note that the equilibrium internuclear separation is 1.4 a_0.

notable is the change between R = 1.8 and 1.6 a_0. Below the equilibrium internuclear distance (1.4 a_0) closer approach of the H atoms results in the transfer of momentum density back into the antibinding bond-parallel high p region. The enclosure of the negative lobe by the positive lobe generates the unstable oval structure at R = 1.0 a_0.

The difference in density relocation in r-space and p-space is in accord with the Virial property.[2,18] The formation of a stable system must be accompanied by the lowering of the total energy or equivalently by the raising of the kinetic energy. The kinetic energy (T) can be increased more effectively by transferring the density into the high-momentum bond-perpendicular region because the parallel component ($T_\parallel$) of the kinetic energy of a diatomic is smaller than the perpendicular component ($T_\perp$).[9-11] The phenomenological change in p-space bond density upon bond formation is indicative of this Virial requirement.[2] In this regard, Bader and Preston[9] have shown earlier that the difference between the bond-perpendicular and bond-parallel components of the kinetic energy, $(T_\perp - T_\parallel)/T$, reaches its maximum in H_2 between R = 2.0 and 1.4 a_0. The results of the present investigations are entirely consistent with the theoretical analysis of kinetic energy density in H_2 given by Bader and Preston.[9] The presently reported experimental studies of the distribution of bond density in momentum space are also consistent with the predictions made in the pioneering theoretical work of Coulson and Duncanson[17] in 1941 concerning the electron momentum distribution in a single bond. Finally, the p-space bond density maps complement the r-space bond density maps to provide a more complete bonding picture. Namely, the formation of a stable σ bond in molecular hydrogen can be regarded as a transformation of the "slow" charge moving with a low momentum along the bond axis at the ends of the molecule to "fast" charge moving with a high momentum perpendicular to the bond axis in the internuclear space of the molecule. Clearly bond formation is manifested, in the present study, much more dramatically in momentum-space than in position-space. Since measurements are possible in p-space but thus far not in r-space, the use of momentum-space concepts and binary (e,2e) spectroscopy promises new vistas of chemical bonding in both experimental and theoretical work.

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Correlation Effects and Bond-Correlation Energies in the Series of Molecules Including C_1 to C_4 Hydrocarbons. Fourth-Order MB-RSPT Calculations

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Abstract: The MB-RSPT up to the fourth order was applied to the calculations of the correlation energies in the series of molecules (including C_1 to C_4 hydrocarbons and the oxygen-containing molecules) using the Gaussian DZ+P basis set. We analyzed the correlation effects which arise from individual types of excitations (single, double, triple, and quadruple) as a function of the number of electrons and the bonding situation in the molecule. The lowest value of the correlation energy per electron pair was found from a series of C_1 to C_3 alkanes. The correlation energy increases in molecules with a double C═C bond, oxygen-containing single bond, adjacent double C═C bonds (CH_2CCCH_2), and triple C≡C bonds and is highest in molecules with multiple carbon–oxygen bonds adjacent to another multiple bond (CH_2CCO). We also present the bond-correlation energies and examine the additivity of the bond-correlation contributions.

Attempts to estimate the correlation energy in large molecules already have a rather long history. The simplest conceivable approach is based on the assumption of a constant value of the correlation energy for each type of bonding in the molecules.[1-6] Using the principle of additivity (or implicitly the linear dependence of an appropriate type) the correlation energy is given as a sum of these bond contributions. Although this method cannot be applied in all problems where the correlation effects are important, it may be useful at least in one important topic, namely in estimation of reaction energies.

The naive principle of additivity is not new. In the present context it has been used for a long time in thermodynamics (see,

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e.g., ref[7]) being based on the observed regularities in the enthalpy of formation for several homologous series. Deviations from simple additivity are taken into account by including data on the related structural environment for each increment.

In calculations of bond correlation energies various authors[3,4,6] usually use the combination of estimated Hartree–Fock (HF) limits and the "experimental" nonrelativistic energies of small molecules to obtain the "experimental" correlation energies. This approach, semiempirical in its nature, suffers from some drawbacks. First, both HF limits and "experimental" nonrelativistic energies are determined with errors which may be different for various molecules in the series and are hardly controllable. Second, it is not possible to obtain reliable HF limits for a sufficiently large number of members in the homologous series, namely for larger molecules. Nor is it possible to obtain HF limits for various molecules with related structural environments to take into account the nonadditivity. Finally, this method leads to total correlation energies. Therefore, it is not capable of providing detailed insight into physical effects from which correlation energies arise. It is mainly this last point which led us to the idea of investigating correlation energies in a series of molecules using the many body Rayleigh–Schrödinger perturbation theory (MB-RSPT) up to the fourth order. MB-RSPT is known[8–15] as a very suitable method for the detailed analysis of correlation effects. Using this method we are able to calculate directly the effect of single, double, triple, and quadruple excitations for relatively large molecules with a sufficiently stable accuracy. The analysis of individual types of excitations in molecules with different bonds and different "bond environments" and the dependence of their contributions (especially those which arise from triple and quadruple excitations) on the number of electrons in molecules is of primary interest in this paper. Regarding the analysis of the dependence of the correlation energy on the number of electrons it is important to stress the fact that MB-RSPT is "size-extensive" (see ref 9 and 10 and citations therein) in contrast to the variational configurational interaction method[16,17] restricted to double excitations. This aspect of the method is also important for intended applications of our correlation energies to the evaluation of correlation effects of reaction energies. Another advantage of MB-RSPT lies in its usefulness in the comparison of various approaches to the correlation problem and also in its relative computational simplicity.

Some of our results partly overlap with previous calculations by Frisch, Krishnan, and Pople,[18,19] who also presented complete fourth-order results for a series of molecules. Since our results cover molecules with larger numbers of atoms and electrons, we are able to extend the findings presented in the cited papers. In comparison with ref 18 and 19 we also used a larger basis set.

Bearing in mind the difficulties with the estimation of nonadditivity effects, the decomposition of correlation energies into the bond contributions presented in the last part of this paper is only tentative. We could calculate systematically hydrocarbons up to three heavy atoms and only in some cases molecules with four carbons. For a serious estimate of nonadditivity effects this is still insufficient. From the work of Cremer[6] it appears that the additivity principle for bond-correlation energies is quite well satisfied, but his conclusions follow from calculations of molecules which contain no more than three heavy atoms. Moreover, they are based on second-order MB-RSPT which is capable of recovering only the dominant part of double excitations but no higher excitations. Therefore, it is interesting to see whether the many-body effects in higher orders of MB-RSPT and the inclusion of higher excitations have some influence on additivity of the correlation energy.

Computational Details

MB-RSPT Calculations. The theoretical and computational aspects of MB-RSPT were described in several review articles[8–15] and need not be repeated here.

We preformed the majority of our calculations on the AMDAHL 470V/6 computer in Garching using the MUNICH system of programs[20] for the SCF part and the transformation of integrals and the POLYCOR system of programs[21–24] for MB-RSPT calculations. In most calculations we used double precision arithmetic. Only in three cases (propane, butadiene, and butatriene molecules) did we use single precision arithmetic for the most difficult step, the calculation of triple excitations. We performed a numerical test on ethylene and propene and this showed no loss of accuracy to the reported figures. In these three cases we disregarded integrals over molecular orbitals less than 10^{-5}. In all other cases integrals less than 10^{-7} were disregarded. For the whole series of molecules we calculated only the valence-shell correlation energies. This means that the inner-shell orbitals were excluded from correlation. Correspondingly, the highest unoccupied orbitals were also omitted. The consequence of this will be discussed later.

Basis Set. In all calculations we used the (9s 5p 1d/4s 1p) Gaussian basis[25] contracted to a [4s 2p 1d/2s 1p] set.[26] Exponents of hydrogen p functions were $\alpha_{p(H)} = 1.0$, without optimization. Exponents of carbon d functions were optimized by using CH_4 and C_2H_2 as model systems. With SCF plus total fourth-order valence-correlation energy we obtained $\alpha_{d(C)} = 0.64$ for CH_4 and 0.72 for C_2H_2, which differ only slightly from values obtained already with the second-order energy and which are approximately 0.15 smaller than at the SCF level.[27]

The dependence of the $\alpha_{d(C)}$ exponent on the actual bonding situation is well-known from SCF calculations.[27] Since it is more convenient to use the same exponents for all carbon atoms we chose the standard value $\alpha_{d(C)} = 0.7$. The error introduced by this may be estimated from the shape of the potential surface in the present optimization of $\alpha_{d(C)}$ for methane and acetylene and the experience with optimization of $\alpha_{d(C)}$ for a wider class of molecules at the SCF level. This error should not be larger than 0.5–1.0 mhartree for our series of molecules. Since the dependence of the correlation energy on $\alpha_{d(C)}$ is involved mainly in the second-order energy, the error in individual fourth-order contributions is lower by at least an order of magnitude.

Our $\alpha_{d(C)}$ is very close to (more precisely, slightly lower than) the value recommended by Ahlrichs and Taylor[28] for the carbon atom. Accordingly, for the oxygen atom we used the standard exponent $\alpha_{d(O)} = 1.2$ which is slightly lower than that prescribed by the cited authors.[28]

Our DZ+P basis is the smallest possible basis which conforms to the combined requirement of computational tractability and accuracy. Certainly with a smaller set, say of the DZ quality, it would be possible to calculate much larger molecules. Unfortunately, such a basis may lead to unbalanced values for individual correlation contributions. For example,[22] in H_2O the total contribution of fourth-order quadruple excitation diagrams, $E_{QR}^{(4)}$ (which is the sum of the net effect of negative quadruple excitations, $E_Q^{(4)}$, and the positive renormalization term, $E_R^{(4)}$), is negative with the DZ basis, while with DZ+P and larger bases it is positive. The relative importance of triple excitations also depends considerably on the basis set.[29]

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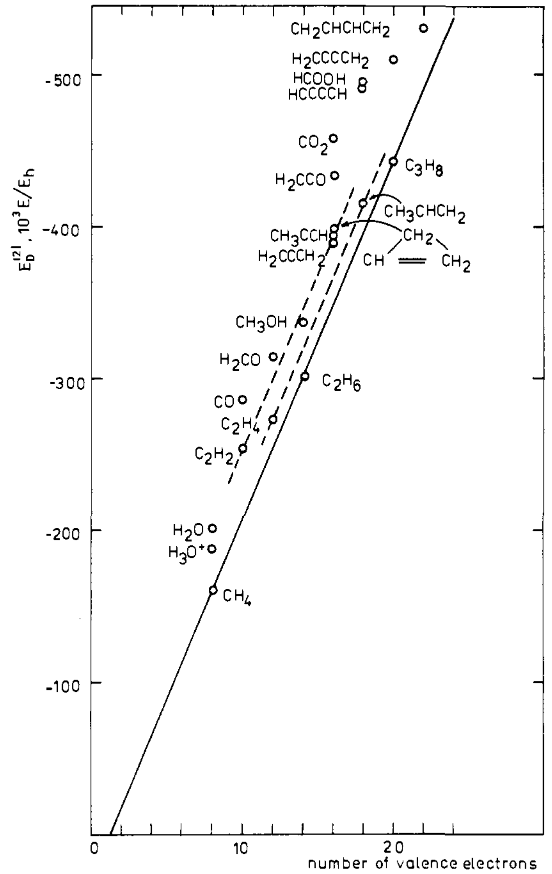

Figure 1. Molecular second-order correlation energies as a function of the number of electrons. The solid line connects the correlation energies of alkanes, while the broken lines connect the energies of molecules with one double bond and one triple bond, respectively.

Geometries. In most cases we used geometries of molecules presented in the review of Harmony et al.[30] The exception was ethane, where we used the geometry published by Shaw et al.[31] and the H_3O^+ ion, where the theoretical prediction of Rodwell and Radom[32] was adopted. For several molecules complete geometries might not be obtained from spectroscopic data so that some parameters were assumed.[30] The precise geometry specifications used in this paper may be obtained from the present authors by request.

Results and Discussion

Influence of Inner-Shell Orbitals and Highest Unoccupied Orbitals. In order to elucidate the influence of a different bonding environment on the inner-shell correlation energy we present calculations for CH_4, C_2H_2, and C_2H_4 in Table I. Comparing for each molecule the first row where all molecular orbitals were taken into account with the next one (with inner-shell orbitals excluded from correlation) we may see that the inner-shell correlation energy and its coupling with the valence shell correlation energy per one carbon atom is 16.1, 15.8, and 15.9 mhartree, that is almost constant. The effect of inner-shell orbitals is almost completely recovered in the second order. This agrees with our finding for the fluorine molecule.[33]

The influence of the highest unoccupied orbitals is very small, 0.026–0.028 mhartree per carbon atom, and is practically completely additive. Thus, if necessary, the corresponding energy might be added to the correlation energy of molecules which are calculated without the highest unoccupied orbitals. Even for molecules with four carbon atoms the contribution from these orbitals is approximately 0.1 mhartree, which is far below the uncertainty caused by incomplete optimization of the basis set and geometry.

Table I. The Influence of the Inner Shell and the Higher Unoccupied Molecular Orbitals on the Correlation Energy (in 10^{-3} hartree)[a]

	restrictions[b]	$-E_D^{(2)}$	$-E_D^{(3)}$	$-E_{SDTQR}^{(4)}$	$-E_{SDTQR}^{(2)-(4)}$
CH_4	0 + 0	174.806	19.995	5.495	200.296
	1 + 0	159.656	19.116	5.409	184.181
	1 + 1	159.627	19.123	5.405	184.155
C_2H_2	0 + 0	282.006	13.047	14.884	309.936
	2 + 0	252.340	11.332	14.661	278.333
	2 + 2	252.275	11.349	14.652	278.276
C_2H_4	0 + 0	301.633	25.770	12.133	339.535
	2 + 0	271.805	24.031	11.938	307.773
	2 + 2	271.742	24.046	11.930	307.718

[a] In this preliminary study we used the basis with $\alpha_{d(C)} = 0.8$. [b] First (last) number denotes the number of omitted inner (higher unoccupied) molecular orbitals. [c] Subscript indices denote the inclusion of double (D), single (S), triple (T), and quadruple (Q) excitations and the renormalization term (R); superscript indices denote the order of MB-RSPT included.

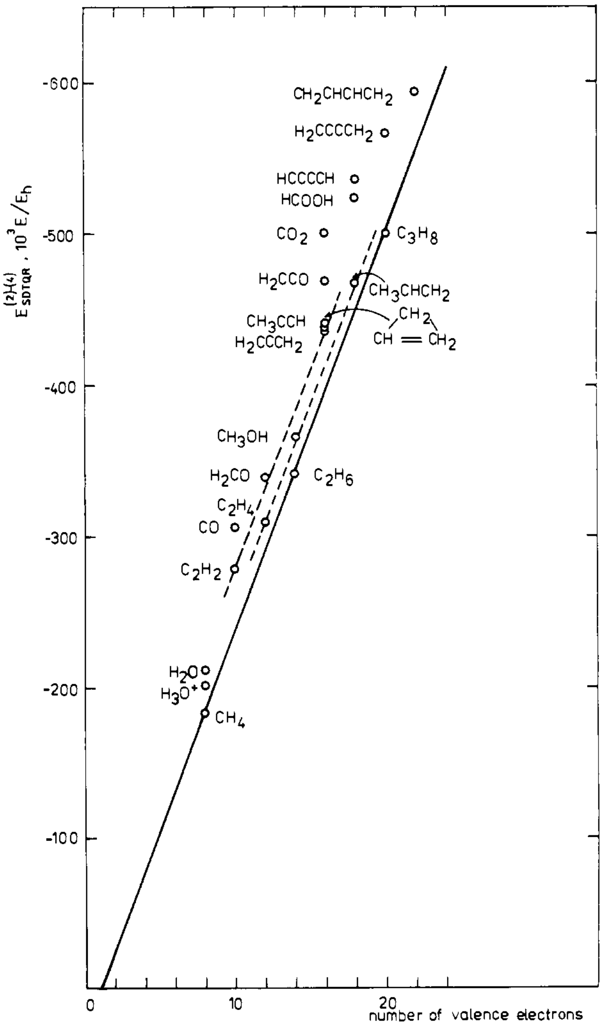

Figure 2. The fourth-order correlation energy of molecules as a function of the number of electrons. For further comments, see Figure 1.

The Dependence of the Correlation Energy on the Number of Electrons and on the Bonding Environment. The main body of information of this paper is included in Table II. The tabulated material may be useful for precise numerical comparisons, but it does not provide a sufficiently transparent basis for a discussion. Figures 1 and 2 serve this purpose better.

It is seen clearly that the lowest correlation energy per electron pair is found in the alkane series CH_4, C_2H_6, C_3H_8. This is valid

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for $E_D^{(2)}$ energies as well as for total fourth-order energies $E_{SDTQR}^{(2)-(4)}$. For alkanes, the dependence of the $E_D^{(2)}$ energy on the number of electron pairs is remarkably linear. With $E_{SDTQR}^{(2)-(4)}$ this linearity remains unchanged, but the slope is slightly larger due to the higher order contributions. From the correlation energies in the first three alkanes it follows clearly that the correlation effects for this type of hydrocarbon are additive. This fully corresponds to strict additivity of the bond energies of alkanes in thermodynamics. Of course the analogy with thermodynamics may be drawn only from the total energy. This implies that SCF energies of alkanes also lie on a straight line, which is really the case. Since in thermodynamics the additivity becomes increasingly more accurate with the increasing number of $-CH_2-$ groups, it is expected that the linearity of correlation energies for alkanes also holds for higher members of the series, which we are not able to calculate at present.

Next let us look at other molecules presented in Table II and Figures 1 and 2. Our discussion may be based on the observation that all molecules have larger negative correlation energies than alkanes with a corresponding number of valence electrons, i.e., they all lay above the straight line for $E_D^{(2)}$ and $E_{SDTQR}^{(2)-(4)}$ energies of alkanes. Taking the straight line for alkanes as a basis for the comparison and taking into account the sequence of correlation energies of molecules with an equal number of valence electrons, we arrive at the estimation of effects which lead to the exaltation of the correlation energy. In the increasing order they are approximately as follows: double $C{=}C$ bond < oxygen-containing single bond < adjacent double $C{=}C$ bonds < triple $C{\equiv}C$ bonds < multiple carbon–oxygen bonds < multiple carbon–oxygen bonds adjacent to another multiple bond.

It is interesting that the overall picture of correlation effects in Figure 2 is approximately the same as that in Figure 1, which apparently indicates that the third- and fourth-order effects do not play any important role. We may notice only minor changes in the relative position of various points going from the second to the full fourth order. The most remarkable is the interchange of positions for HCOOH and HCCCCH. $E_D^{(2)}$ energy of formic acid is very slightly more negative than that of butadiyne, but with $E_{SDTQR}^{(2)-(4)}$ the correlation energy of butadyine is by 13 mhartree more negative than that of HCOOH. The inspection of values in Table II shows us that this effect may be explained already at the level of double excitations in the third order. Nevertheless, the fourth-order contributions are also important, but they cancell each other out: triple excitations differ in both molecules by 9 mhartree, but this difference is cancelled out by the high positive renormalization term $E_R^{(4)}$ (this term may be obtained from Table II as the difference of $E_{QR}^{(4)}$ and $E_Q^{(4)}$ values).

Significant shifts in relative positions with energies and $E_{SDTQR}^{(2)-(4)}$ are also exhibited by systems with 16 valence electrons, although in this case no change in the order of positions for these five molecules is observed. There are considerable differences in some individual correlation contributions in these molecules. At the second-order level the most negative is the energy of CO_2 and the least negative is the energy of allene (the difference of $E_D^{(2)}$ for CO_2 and allene is −88 mhartree). With $E_D^{(3)}$ the situation is completely reversed, the $E_D^{(3)}$ energy for allene being the most negative while $E_D^{(3)}$ for CO_2 is 42 mhartree higher and is positive. This effect of $E_D^{(3)}$ is partly compensated by the fourth order single and mainly triple excitations (with the limiting values $E_T^{(4)} = -23$ mhartree for CO_2 and $E_T^{(4)} = -14$ mhartree for H_2CCCH_2) while $E_D^{(4)}$ and $E_{QR}^{(4)}$ are almost constant for all five molecules. To visualize the behavior of some higher order contributions we present the dependence of $E_D^{(3)}$ on the number of valence electrons in Figure 3 and similar dependence for $E_{TQR}^{(4)}$ in Figure 4. These energies were chosen as representative of many-body interactions ($E_D^{(3)}$) and higher excitations ($E_{TQR}^{(4)}$). Let us recall that $E_D^{(2)}$ contains only double excitation pair correlation contributions and that the $E_D^{(3)}$ energy also contains non-pair-separable many-body effects which arise from double excitations. Finally, the term $E_{TQR}^{(4)}$ involves the sum of energies which arise from the connected fourth-order triple (T) and quadruple (QR) excitation diagrams, i.e., it includes also the renormalization term.[22,23] It is clear that no obvious correlation of $E_D^{(3)}$ or $E_{TQR}^{(4)}$ with the number of electrons may be observed. Only alkanes

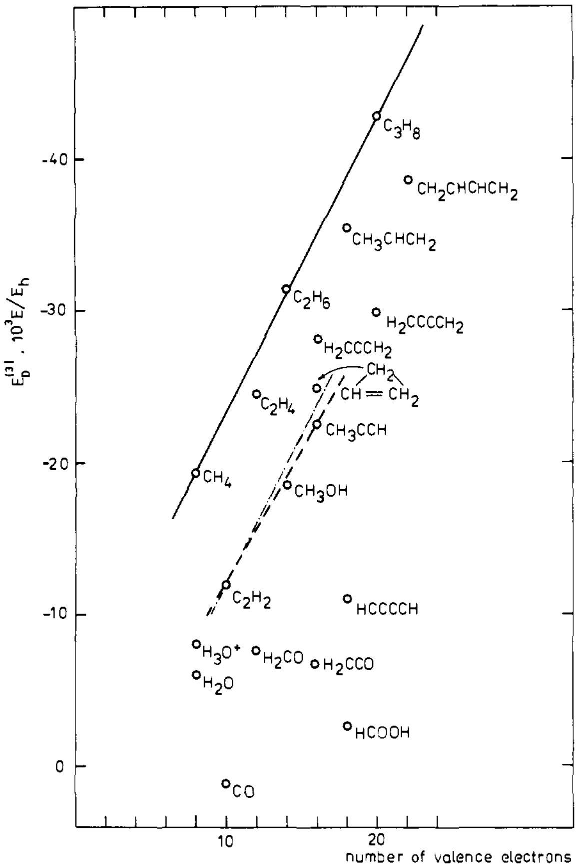

Figure 3. The third-order contribution to the correlation energy of molecules as a function of the number of electrons. The solid line connects the contributions of alkanes, and the broken line connects the contributions of molecules with one triple bond. Another broken line demonstrates that the lines of alkanes and alkynes are not parallel.

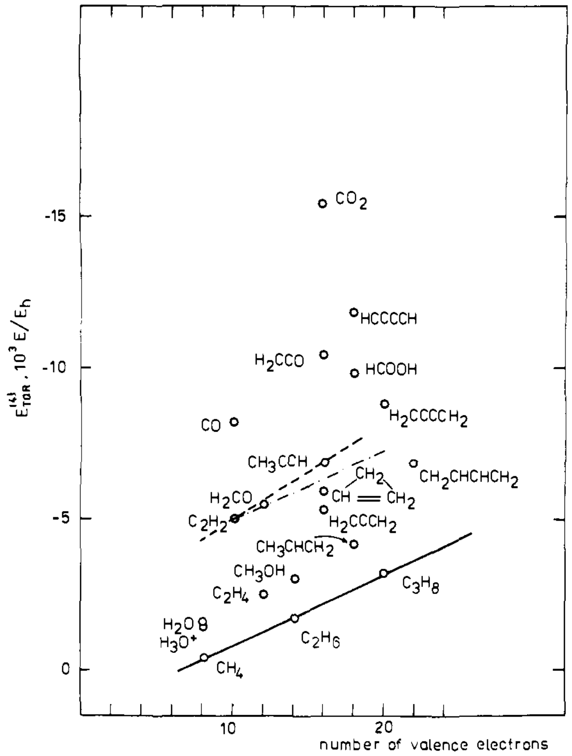

Figure 4. The contributions from the triple and quadruple excitations as a function of the number of electrons. For further comments, see Figure 3.

Table II. Valence-Shell Correlation Energy and Its Components (in 10^{-3} hartree)[a]

molecule	$-E_{\mathrm{SCF}}$	$-E_{\mathrm{SDTQR}}^{(2)-(4)}$	$-E_{\mathrm{D}}^{(2)}$	$-E_{\mathrm{D}}^{(3)}$	$-E_{\mathrm{D}}^{(4)}$	$-E_{\mathrm{D}}^{(5)}$	$-E_{\mathrm{D}}^{(6)}$	$-E_{\mathrm{S}}^{(4)}$	$-E_{\mathrm{T}}^{(4)}$	$E_{\mathrm{QR}}^{(4)}$	$-E_{\mathrm{Q}}^{(4)}$
CH_4	40.207318	185.517	160.764	19.387	4.580	1.406	0.507	0.423	2.833	2.470	1.667
$CH_3{-}CH_3$	79.248762	342.891	300.889	31.449	7.966	2.442	0.885	0.919	6.840	5.172	4.330
$CH_3{-}CH_2{-}CH_3$	118.291908	501.676	442.859	42.810	11.334	3.418	1.237	1.490	11.169	7.986	7.194
$CH_2{=}CH_2$	78.049936	310.199	273.929	24.440	7.647	2.652	1.166	1.662	8.299	5.779	4.300
$CH_3{-}CH{=}CH_2$	117.097526	468.597	415.829	35.400	11.020	3.564	1.489	2.224	12.777	8.654	7.151
$H_2C{=}C{=}CH_2$	115.883005	437.255	390.009	28.194	10.754	3.672	1.709	3.057	14.623	9.383	7.426
$H_2C{=}C{=}C{=}CH_2$	153.714200	567.803	509.662	29.802	14.724	4.807	2.503	4.880	22.604	13.869	11.849
$CH_2{=}CH{-}CH{=}CH_2$	154.951417	594.479	531.328	38.567	14.240	4.725	2.174	3.585	19.274	12.515	10.989
$CH{\equiv}CH$	76.831819	279.914	253.488	11.925	6.960	2.185	1.065	2.577	10.835	5.872	5.800
$CH_3{-}C{\equiv}CH$	115.885840	437.554	394.243	22.418	10.832	3.051	1.421	3.215	15.384	8.537	8.822
$HC{\equiv}C{-}C{\equiv}CH$	152.516855	537.012	493.009	10.945	14.767	3.387	2.129	5.559	26.038	13.307	15.890
$\overline{CH{=}CH{-}CH}_2$	115.843735	442.333	399.104	24.845	10.374	3.205	1.392	2.230	15.138	9.359	7.943
H_2O	76.046114	212.642	200.873	5.971	3.414	0.889	0.344	0.788	3.277	1.681	3.569
H_3O^+	76.328743	201.486	187.701	7.974	3.284			1.046	3.104	1.623	2.992
CO	112.760093	307.655	285.731	−1.165	9.133	1.480	0.944	5.809	12.358	4.210	7.988
CO_2	187.676946	501.497	478.267	−13.884	12.006	0.741	0.908	9.736	23.195	7.823	14.668
CH_3OH	115.073357	367.367	336.517	18.475	7.515	1.998	0.766	1.860	7.401	4.401	6.193
H_2CO	113.894796	341.157	315.385	7.520	8.599	1.820	0.945	4.283	10.299	4.928	7.312
HCOOH	188.813771	524.526	494.238	2.771	10.886	1.761	0.961	6.882	16.904	7.154	12.369
$H_2C{=}C{=}O$	151.757860	469.904	434.203	6.826	11.407	1.919	1.149	7.094	18.876	8.502	10.877

[a] E_{SCF} is the SCF energy, $E_{\mathrm{SDTQR}}^{(2)-(4)}$ is the sum of second-order ($E_{\mathrm{D}}^{(2)}$), third-order ($E_{\mathrm{D}}^{(3)}$), and fourth-order single ($E_{\mathrm{S}}^{(4)}$), double ($E_{\mathrm{D}}^{(4)}$), triple ($E_{\mathrm{T}}^{(4)}$), and quadruple ($E_{\mathrm{Q}}^{(4)}$) excitations and the renormalization term ($E_{\mathrm{R}}^{(4)}$).

Table III. Percentage of the Correlation Contributions ($E_{\mathrm{SDTQR}}^{(2)-(4)}$ is 100%)[a]

molecule	$E_{\mathrm{D}}^{(2)}$	$E_{\mathrm{D}}^{(2)-(3)}$	$E_{\mathrm{D}}^{(2)-(4)}$	$E_{\mathrm{S}}^{(4)}$	$E_{\mathrm{D}}^{(4)}$	$E_{\mathrm{T}}^{(4)}$	$-E_{\mathrm{QR}}^{(4)}$	$E_{\mathrm{Q}}^{(4)}$
CH_4	86.66	97.11	99.58	0.23	2.47	1.53	1.33	0.90
$CH_3{-}CH_3$	87.75	96.92	99.25	0.27	2.32	1.99	1.51	1.26
$CH_3{-}CH_2{-}CH_3$	88.28	96.81	99.07	0.30	2.26	2.23	1.59	1.43
$CH_2{=}CH_2$	88.31	96.19	98.65	0.54	2.47	2.68	1.86	1.39
$CH_3{-}CH{=}CH_2$	88.74	96.29	98.65	0.47	2.35	2.73	1.85	1.53
$H_2C{=}C{=}CH_2$	89.19	95.64	98.10	0.70	2.46	3.34	2.15	1.70
$H_2C{=}C{=}C{=}CH_2$	89.76	95.01	97.60	0.86	2.59	3.98	2.44	2.09
$CH_2{=}CH{-}CH{=}CH_2$	89.38	95.86	98.26	0.60	2.40	3.24	2.11	1.85
$CH{\equiv}CH$	90.56	94.82	97.31	0.92	2.49	3.87	2.10	2.07
$CH_3{-}C{\equiv}CH$	90.10	95.23	97.70	0.73	2.48	3.52	1.95	2.02
$HC{\equiv}C{-}C{\equiv}CH$	91.81	93.84	96.59	1.04	2.75	4.85	2.48	2.96
$\overline{CH{=}CH{-}CH}_2$	90.23	95.84	98.19	0.50	2.35	3.42	2.12	1.80
H_2O	94.47	97.27	98.88	0.37	1.61	1.54	0.79	1.68
H_3O^+	93.16	97.12	98.75	0.52	1.63	1.54	0.81	1.48
CO	92.87	92.50	95.46	1.89	2.97	4.02	1.37	2.60
CO_2	95.37	92.60	94.99	1.94	2.39	4.63	1.56	2.92
CH_3OH	91.60	96.63	98.68	0.51	2.05	2.01	1.20	1.69
H_2CO	92.45	94.65	97.17	1.26	2.52	3.02	1.44	2.14
HCOOH	94.23	94.75	96.83	1.31	2.08	3.22	1.36	2.36
$H_2C{=}C{=}O$	92.40	93.86	96.28	1.51	2.43	4.02	1.81	2.31

[a] The notations for the energy components are the same as in Table II.

provide once again the linear dependence. It is remarkable that for all molecules the $E_{\mathrm{D}}^{(3)}$ energies are *less* negative than that of alkanes (CO and CO_2 are positive) while the $E_{\mathrm{TQR}}^{(4)}$ energies are *more* negative than that of alkanes. The comparison of positions of various molecules on the diagrams for $E_{\mathrm{D}}^{(3)}$ and $E_{\mathrm{TQR}}^{(4)}$ energies demonstrates the cancellation of these energy components if we investigate the relative values of total fourth-order energies for individual molecules. This cancellation must be taken as very approximate, however.

Another group of molecules which need discussion form molecules with one double bond (ethylene and propene) and one triple bond (acetylene and propyne). If we connect the points which correspond to ethylene and propene we obtain a line which is almost perfectly parallel to the straight line of the alkanes. This holds for $E_{\mathrm{D}}^{(2)}$ energies as well as for $E_{\mathrm{SDTQR}}^{(2)-(4)}$ energies (see Figures 1 and 2). This parallelism indicates the little mutual influence of single and double carbon–carbon bonds. This means that for molecules with a longer alkane chain in the neighborhood of the isolated double bond we may apply the additivity of correlation energies of alkanes and estimate the correlation energy just from this additivity and the increase of its value due to the presence of a double bond. The same also holds for molecules with a triple bond. It should be stressed, however, that we only obtain parallel lines with $E_{\mathrm{D}}^{(2)}$ and $E_{\mathrm{SDTQR}}^{(2)-(4)}$ energies but not with $E_{\mathrm{D}}^{(3)}$ and $E_{\mathrm{TQR}}^{(4)}$ energies (see Figures 3 and 4) or some other individual components. Once again we may observe the compensation of effects which arise from various third- and fourth-order terms.

The Percentage Participation of Various Contributions in $E_{\mathrm{SDTQR}}^{(2)-(4)}$. An alternative view on the correlation effects in our molecules is offered by Table III with the percentage participation of individual third- and fourth-order components to $E_{\mathrm{SDTQR}}^{(2)-(4)}$. The table is self-explanatory, but the diversity in trends for various energy components requires some comment. First let us stress that the percentage contribution of triple and quadruple excitations is not negligible. It does not depend primarily on the number of valence electrons but rather on the bonding character in the molecule. Generally the triple and quadruple excitations are most important in molecules with multiple bonds, especially triple C≡C bond and adjacent double C=O and C=C bonds. The importance of triple excitations in multiple bonds is known already from previous calculations.[18,19,34]

The increasing contribution of the fourth-order triple and quadruple excitations with the number of electrons in the alkane series is difficult to interpret as significant, since the increase in each of these contributions is less than 0.7% going from CH_4 to C_3H_6. Moreover the quadruple excitations are compensated by the positive renormalization term so that the increase in the $E_{\mathrm{TQR}}^{(4)}$ term is only 0.43%.

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In establishing the percentage participation of various types of excitations in the total correlation energy the uniform convergence of the perturbation series in all molecules is important. We may estimate this property of the theory only on the basis of the convergency of double excitations, having on hand the values up to the sixth order, $E_D^{(2)}$ ... $E_D^{(6)}$. Our results suggest that the convergence is very good. The total contribution $E_D^{(5)} + E_D^{(6)}$ does not exceed 1.3% of $E_{SDTQR}^{(2)-(4)}$, and in most molecules it is about 1% or less. Very important is the third-order term, $E_D^{(3)}$. At the second order the difference between molecules with the highest and the lowest percentage contribution of $E_D^{(2)}$ is about 9%, CH_4 being the molecule with the lowest value. At the third order the difference decreases to 4.8% which does not differ much from 4.6% with $E_D^{(2)-(4)}$. With $E_D^{(2)-(4)}$ the methane molecule has the highest percentage contribution. These changes clearly demonstrate the unbalanced recovery of the correlation energy in second order. For a different set of molecules this was noticed by Bartlett.[9] From another point of view Bartlett and Purvis[14] and Pople et al.[15] demonstrated the convergence of MB-RSPT at the level which includes the double and quadruple excitations. They compared the fourth-order energy $E_{DQR}^{(2)-(4)}$ (i.e., the effect of the T_2 operator in the first four orders of MB-RSPT and that of the T_2T_2 operator in the fourth order) with the energy obtained from the coupled cluster method limited to double-excitation operators (CCD). That is, they investigated the effect of T_2 and T_2T_2 operators iteratively. Generally, for a series of closed-shell molecules at an equilibrium geometry the $E_{DQR}^{(2)-(4)}$ and the converged CCD energies agree excellently, demonstrating the good convergence of MB-RSPT.

The Correlation Energy of Ethylene—A Test Example. The ethylene molecule is a very suitable test case for the verification of the reliability of our correlation contributions since as a prototype molecule with a double bond it has been examined by various methods to which our fourth-order MB-RSPT results may be compared. For our purposes the comparison of $E_{DQR}^{(2)-(4)}$ and $E_{SDQR}^{(2)-(4)}$ with the converged values from CCD and CCSD, performed by Laidig, Purvis, and Bartlett (LPB),[35] is important. The MB-RSPT results agree with their coupled cluster counterparts to within ~1 mhartree, or 0.4%, and demonstrate once again the good convergence of MB-RSPT. Our $E_{SDTQR}^{(2)-(4)}$ result and all energy components agree with the LPB MB-RSPT results excellently. The minor differences may be explained by the different exponents of polarization functions (LPB used $\alpha_{d(C)} = 0.75$) in an otherwise identical DZ+P basis and partly perhaps also by a slightly different geometry.

Also useful is a comparison of our results with the very extended variational one million configuration CI of Saxe et al. (SFSH),[36] who used the same basis as LPB. Their final wave function denoted as CISD+SD includes single and double excitations and also the important portion of triple and quadruple excitations, yielding the correlation energy of −303.98 mhartree. Our result is 6 mhartree more negative. According to the analysis of LPB, the difference between $E_{SDTQR}^{(2)-(4)}$ and SFSH results may be explained mainly by the different selection of quadruple excitation configurations.[35] The triple excitation energy from CI calculations is −7.0 mhartree or 2.3% of the CISD+SD value, and very similar to our result. The quadruple excitation energy from CI is approximately −19.5 mhartree or 6.4%, but this value may not be directly compared to the energy due to the quadruple excitation diagrams in MB-RSPT, which has a different meaning. Usually one takes as a representative of quadruple excitations in MB-RSPT the energy given by the fourth-order connected quadruple excitation diagrams. Since these diagrams also contain the renormalization part of the energy, the resulting value is usually positive. We denote this term as $E_{QR}^{(4)}$. Using the decomposition[22,23,37] of this term into the $E_Q^{(4)}$ and $E_R^{(4)}$ components, we are able to exctract the net effect of quadruple excitations, but even this energy may not be compared to the CI value. In CI, an important part of the effect of quadruple excitations is responsible for the correction of the "size-extensivity" error of CI-SD. The corresponding MB-RSPT contribution may be estimated after decomposition of the fourth-order renormalization term $E_D^{(2)}S$ (where S is the overlap of the first-order perturbed wave function) into its disjoint and conjoint terms (DJ and CJ, respectively—these terms were introduced by Bartlett and Purvis[14]). The resulting values are $[E_D^{(2)}S]_{CJ} = -E_R^{(4)} = -10.08$ mhartree and $[E_D^{(2)}S]_{DJ} = -17.08$ mhartree. Then the quadruple excitations in CI may be approximated in the fourth-order MB-RSPT as $[E_D^{(2)}S]_{DJ} + E_Q^{(4)} = -21.38$ mhartree, which compares quite well to the value −19.5 mhartree of SFSH, bearing in mind the incomplete (and different) treatment of quadruple excitations in CI and the fourth-order MB-RSPT. Analysis of this problem was also made by Laidig et al.[35] Finally let us stress that the meaning of quadruple excitations in various approaches is often different and may considerably influence the investigations of the relative importance of various higher excitation terms.

Bond-Correlation Energies. In order to systemize the correlation effects in molecules, we decided to calculate the bond-correlation energies from which it would be possible to predict the correlation energy of the structurally related molecules. Behind this aim is, of course, the assumption of the additivity of the correlation energies, which must not be accurately valid. Consequently, use of bond-correlation energies is only approximate.

In calculations of bond-correlation energies it is usually assumed[3,4,6] that the energy of the molecule may be approximated by the sum of the group contributions $\epsilon_{corr}(xy)$ from all bonded groups and lone pairs,

$$E_{corr} \approx \sum_{\text{all } x,y} \epsilon_{corr}(xy) \qquad (1)$$

Cremer[6] used this equation with his $E_D^{(2)}$ energies as well as with experimental correlation energies. For example, using eq 1 we may obtain the correlation energy of the C–H bond from the calculated correlation energy of CH_4 simply as

$$\epsilon_{corr}(\text{C–H; CH}_4) = E_{corr}(\text{CH}_4)/4$$

Since in our MB-RSPT calculations we used canonical molecular orbitals we tried to take into account the delocalization effects and the interaction of bond-correlation contributions by using the correlation energies of larger molecules, when possible. Thus we obtain the bond contribution of the C–H bond and the C–C bond in alkanes solving the two equations

$$\begin{aligned} E_{corr}(\text{C}_2\text{H}_6) &= \epsilon_{corr}(\text{C–C}) + 6\epsilon_{corr}(\text{C–H}) \\ E_{corr}(\text{C}_3\text{H}_8) &= 2\epsilon_{corr}(\text{C–C}) + 8\epsilon_{corr}(\text{C–H}) \end{aligned} \qquad (2)$$

So obtained, ϵ_{corr}(C–H) was used in all other molecules. We are aware that ϵ_{corr}(C–H) in all molecules may not be the same as in alkanes, but we were forced to accept this oversimplification by the absence of data for lager molecules. Accepting the constant ϵ_{corr}(C–H) enables us to investigate the differences in ϵ_{corr}(C–C) and ϵ_{corr}(C=C) in different bond environments.

In oxygen-containing molecules it was first necessary to separate the correlation contribution which arises from the oxygen lone pair O(LP). We used two equations

$$\begin{aligned} E_{corr}(\text{H}_2\text{O}) &= 2\epsilon_{corr}(\text{O–H}) + 2\epsilon_{corr}(\text{O(LP)}) \\ E_{corr}(\text{H}_3\text{O}^+) &= 3\epsilon_{corr}(\text{O–H}) + \epsilon_{corr}(\text{O(LP)}) \end{aligned} \qquad (3)$$

which gives us ϵ_{corr}(O(LP)) together with the contribution from the O–H bond, ϵ_{corr}(O–H). These were used in all subsequent calculations. The resulting bond-correlation energies are presented in Table IV. Generally, they confirm the results discussed in the previous part of this paper.

Concerning the individual contributions to $E_{SDTQR}^{(2)-(4)}$, higher excitations are important in multiple bonds while in single C–H and O–H bonds and also in oxygen lone pair they are the lowest. The third-order energy is very important for a balanced description of the contribution from the double excitations. Generally the resulting difference between $\epsilon_{SDTQR}^{(2)-(4)}$ and $\epsilon_D^{(2)}$ is once again influenced by the complicated balance of various third- and fourth-order terms.

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Table IV. Bond Energy Contributions[a] (in 10^{-3} hartree)

bond[b]	source[c]	$-E^{(2)-(4)}_{SDTQR}$	$-E^{(2)}_{D}$	$E^{(3)}_{D}$	$-E^{(4)}_{D}$	$-E^{(4)}_{S}$	$-E^{(4)}_{T}$	$E^{(4)}_{QR}$	$-E^{(4)}_{Q}$
C—H	CH_4	46.38	40.19	−4.85	1.14	0.11	0.71	0.62	0.42
C—H	C_2H_6, C_3H_8	46.03	39.73	−5.02	1.15	0.09	0.63	0.59	0.37
C—C	C_2H_6, C_3H_8	66.73	62.51	−1.32	1.07	0.40	3.07	1.63	2.13
C=C	C_2H_4, C—H	126.09	115.01	−4.35	3.05	1.31	5.79	3.42	2.83
$C{\not-}C{=}C$	C_3H_6, C=C, C—H	66.35	62.44	−0.92	1.07	0.39	3.22	1.70	2.12
C≡C	C_2H_2	187.86	174.03	−1.88	4.66	2.40	9.58	4.69	5.07
$C{\not-}C{\equiv}C$	CH_3CCH, C≡C, C—H	65.59	61.29	−0.45	1.57	0.46	3.29	1.49	2.29
$C{=}C{\neq}C$	$H_2C{=}C{=}CH_2$, C—H	126.57	115.54	−4.05	3.08	1.35	6.06	3.51	2.98
$C{=}O{\neq}C{=}C$	C_4H_2, $C{=}O{\neq}C$, C—H	130.55	119.65	−1.61	3.97	1.82	7.98	4.49	4.42
O—H	H_2O, H_3O^+	47.58	43.63	−2.49	0.79	0.33	0.73	0.39	0.60
O(LP)	H_2O, H_3O^+	58.74	56.80	−0.49	0.92	0.07	0.91	0.45	1.18
C—O	CH_3OH, O—H, C—H, O(LP)	64.23	60.09	0.07	1.44	1.14	2.97	1.34	2.13
$O{=}C{\neq}O$	CO_2, O(LP)	133.27	125.52	7.92	4.17	4.73	9.79	3.01	4.97
C=O	H_2CO, C—H, O(LP)	131.63	122.32	3.51	4.46	3.97	7.23	2.85	4.22
$C{=}C{\neq}O$	H_2CCO, $C{=}O{\neq}C$, C—H, O(LP)	133.80	125.59	8.25	4.19	5.43	9.75	2.91	4.80

[a] The notations for the energy components are the same as in Table II. [b] The concerned bond is denoted by a slash, if necessary. [c] Molecules used for the calculation of the bond energy and bonds used from some of the previous rows. C–H bonds are always those for which the energies of C_2H_6 and C_3H_8 were used.

Table V. Test of the Additivity of Bond-Correlation Energies (in 10^{-3} hartree)

molecule	$-E^{(2)}_{D}$	$-\sum\epsilon^{(2)}_{D}$	diff	$-E^{(2)-(4)}_{SDTQR}$	$-\sum\epsilon^{(2)-(4)}_{SDTQR}$	diff
$CH_2{=}CH{-}CH{=}CH_2$	531.33	530.91	0.42	594.48	595.08	−0.60
HC≡C—C≡CH	493.01	490.03	2.98	537.01	534.51	2.50
HCOOH	494.24	492.98	1.26	524.53	524.42	0.11
$\overline{CH{=}CH{-}CH}_2$	399.10	398.95	0.15	442.33	443.66	−1.33
$H_2C{=}C{=}C{=}CH_2$	509.66	503.95[a]	5.71	567.80	562.39[a]	5.41
$H_2C{=}C{=}O$	434.20	430.39[a,b]	3.81	469.90	467.25[a,b]	2.65

[a] Calculated from the bond energies of the isolated C=C bond in ethylene. [b] Calculated from the bond energy of the isolated C=O bond in formaldehyde.

The most considerable environmental effects may be observed in the adjacent double bonds. The energy of the terminal double bond in allene, $\epsilon(C{=}C{\neq}C)$, still agrees quite well with the energy of the isolated double C=C bond, $\epsilon(C{=}C)$ in ethylene; but the central C=C bond in butatriene differs from it considerably (with $E^{(2)-(4)}_{SDTQR}$ the difference is 4.5 mhartree, but significant differences may be observed also in all individual contributions). This may be explained by the orientation of π orbitals in both molecules. While in allene both π bonds are mutually perpendicular and thus influence each other very little, in butatriene the terminal π bonds are obtained in the same plane, interact strongly, and influence by this interaction the central bond (this bond is much shorter than are the terminal bonds). Considerable environmental effects may also be observed in C=O bonds in the neighborhood of the C=C or another C=O double bond.

The increase of the correlation energy in the oxygen-containing molecules may be explained by the contribution from the lone pairs, which is much larger than that of the bond pairs in the simple O–H bonds. This is in accord with Cremer's observation.[6] The high value of ϵ(O(LP)) is due mainly to the second-order contribution. The total third- and fourth-order contribution to the correlation energy of the oxygen lone pairs is the least of all the group contributions investigated.

Finally let us note that our fourth-order calculations with the DZ+P basis in most cases recover about 70–74% of the "experimental" valence-shell bond-correlation energies, presented by George et al.[3] for various bonds. The most remarkable difference is found with the O–H bond, for which we obtained only 64% of the "experimental" value, in contrast to 74% for the C–H bond. It seems that the "experimental" valence-shell correlation energy of H_2O used by George et al.[3] for the calculation of the O–H bond-correlation energy is too high. They used the value −321 mhartree; the estimate published by Rosenberg and Shavitt[38] is −306 ± 8 mhartree. If they would use this last estimate, our $\epsilon^{(2)-(4)}_{SDTQR}$(O–H) is 71% of the "experimental value". The correlation of our bond contributions with that of Cremer[6] is also quite satisfactory (see Figure 5).

The trends observed in the cited papers[3,6] are similar to that found in our work. For example, the bond energy of the double C=C bond and the triple C≡C bond is slightly less than two and three times the energy of the single C–C bond. This trend also conforms to the thermodynamic bond energies.[39] Bearing in mind the quite different approach of cited authors,[3,6] the fact that they did not take into account the environmental effects, the different consideration of the oxygen lone pair contribution, and also the basis set effects, the correlation of our bond correlation energies with those inferred from the "experimental" correlation energies is satisfactory.

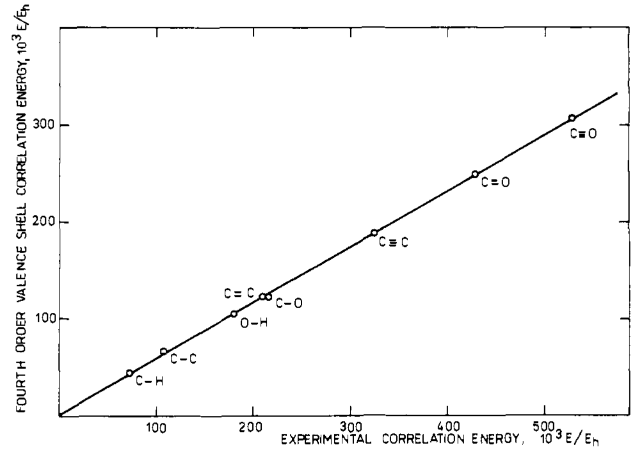

Figure 5. The correlation of our fourth-order bond-correlation energies with "experimental" correlation energies.[6] The fourth-order bond energies also include contributions from the lone pairs of oxygen.

Limitations in Using the Additivity of Bond-Correlation Contributions. In Table V we compared the correlation energies calculated from the bond-correlation contributions with those calculated accurately. Included are some molecules whose bonds do not correspond to any bonding type presented in Table IV, so that the additivity scheme may not work properly in this case. In butadiene, butadiyne, and formic acid the additivity is not expected due to resonance while cyclopropene is taken as a rep-

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resentative of a cyclic compound. Ketene and butatriene are examples of molecules with adjacent double bonds and are taken here only for a comparison. The nonadditivity in these molecules has been demonstrated in the preceding sections. Significant differences of the estimated and calculated values are observed only in CH_2CCCH_2, H_2CCO, and HCCCCH. Little difference is found in butadiene and formic acid (both with conjugated double bonds) as well as in cyclic C_3H_4. Since the bond lengths in these molecules exhibit significant changes in comparison with bonds in molecules from which the bond contributions were calculated, the conclusion about the additivity in these cases requires further study. For example, it may be the result of the mutual compensation of changes in individual bond energies in single and double bonds.

Concluding Remarks

The results presented in this paper show some interesting regularities in correlation effects in molecules. In our analysis the dependence of the correlation energy on the specific bonding character in the molecule is stressed. Systems with single C–C bonds have the lowest values of the correlation energy. The multiple bonds generally increase its value. This effect is reinforced when the adjacent double bonds are present. The conjugation leads to no substantial effect; the same also holds for the cyclic compounds. The higher (triple and quadruple) excitations are important especially in molecules with multiple bonds and with adjacent double bonds. The percentage participation of triple and quadruple excitations in alkanes exhibits an increase with the number of electrons. However, this increase is so small that it cannot be taken as significant, so that no definitive conclusions on the role of higher excitations in extended systems may be drawn (we recall the forecast of Davidson[40] on the important role of higher excitations in very extended systems; of course, also higher than quadruple excitations come into consideration). The problem of the correlation energy in extended systems is very topical in the present-day quantum chemistry. Since presently it is not possible to obtain reliable ab initio data on such systems directly, some investigations may be inferred from results of calculations for model systems, see, e.g., ref 41–44.

Since we have used the canonical orbitals, we cannot analyze the contributions to the correlation effects from individual orbitals. This requires the use of localized oribtals (within the MB-RSPT and CCSD scheme, the use of localized orbitals has been pioneered by Laidig, Purvis, and Bartlett;[45] at the semiempirical level localized orbitals have been used by Kapuy et al.[46] through the fifth order of MB-RSPT). Nevertheless, our results are useful in energy predictions. The knowledge of regularities in correlation energies may be helpful in the prediction of enthalpies of chemical reactions, relative energies of various isomers, etc.

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Registry No. CH_4, 74-82-8; C_2H_2, 74-86-2; C_2H_4, 74-85-1; $CH_3{-}CH_3$, 74-84-0; $CH_3{-}CH_2{-}CH_3$, 74-98-6; $CH_3{-}CH{=}CH_2$, 115-07-1; $H_2C{=}C{=}CH_2$, 463-49-0; $H_2C{=}C{=}C{=}CH_2$, 2873-50-9; $CH_2{=}CH{-}CH{=}CH_2$, 106-99-0; $CH_3{-}C{\equiv}CH$, 74-99-7; $HC{\equiv}C{-}C{\equiv}CH$, 460-12-8; $\overline{CH{=}CH{-}CH_2}$, 2781-85-3; H_2O, 7732-18-5; H_3O^+, 13968-08-6; CO, 630-08-0; CO_2, 124-38-9; CH_3OH, 67-56-1; H_2CO, 50-00-0; HCOOH, 64-18-6; $H_2C{=}C{=}O$, 463-51-4.

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Energy Transfer in Inverse Micelles

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Abstract: Energy transfer between several naphthalene derivatives and Tb^{3+} in inverse micelles of dodecylammonium propionate and water in cyclohexane was found to be very efficient. In the case of the micelle-bound probes, the efficiency is determined by the donor and acceptor concentrations, the distance between the chromophore and the water pool, the water concentration, and the rate of intermicellar collisions. From the results it could be deduced that the apolar tails of the probes are time-averaged nonfolded and that the probe location is dependent on the water concentration. A kinetic scheme allows the estimation of the rate of solubilizate exchange between micelles by intermicellar collisions. Because of a very rapid exchange ($k_E \approx 10^9$ M^{-1} s^{-1}), the Poisson distribution of probe and quenchers has no influence on the kinetics.

Some decades ago, mainly by the groups of Weissman[1] and Crosby[2], it was found that luminescence of rare-earth (RE) ions can be sensitized by excited aromatic ligands. They concluded that the transfer occurred from the triplet state of the sensitizer.

That the sensitizer need not to be chelated to the RE ion was indicated by Heller and Wasserman,[3] studying the transfer facilities of several aromatic aldehydes and ketones to Tb^{3+} and Eu^{3+}. Although it was originally assumed that this process was diffusion controlled, it follows from more recent work that the energy transfer is slower than for a diffusion-controlled process.[4]

Energy transfer from the triplet state of aromatic hydrocarbons to Tb^{3+} could be measured at 77 K. From these studies, Weller et al.[5] concluded that the transfer process occurred at short dis-

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