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Estimation of Binding Energies of Molecules by a Semiempirical Molecular Orbital Electron Correlation Method with Applications to Saturated and Unsaturated Hydrocarbons, Aromatics, and Heterocyclics

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Abstract: The energy of binding of atoms into a molecule (BE) is rigorously the sum of Hartree–Fock MO binding (BE_{HF}) and electron correlation binding (BE_{corr}). Approximate MO calculations are often unable to account for chemical binding because BE_{corr} is a large fraction of BE. The latter is calculated by a simple semiempirical MO correlation method based on the theory by Sinanoğlu of electron correlation in ground-state molecules (MET) in an approximation referred to as the "EPCE–F2σ" method. Input consists of LCAO–MO coefficients and a set of effective average one- and two-center pair correlation parameters. The BE_{corr} and E_{corr} of over 30 molecules of B, C, N, O, and F including saturated and unsaturated hydrocarbons, aromatics, and heterocyclics are given. The σ, σ–π, and π electron portions are shown separately. Hartree–Fock MO energy limits are estimated for some large molecules based on the method. It is found that the ratio of correlation binding to experimental binding energies is approximately constant within classes of molecules and yields predicted dissociation energies for other molecules.

The difference between the ground-state energy of a molecule and the sum of the ground-state energies of the separated atoms, which make up the molecule, represents the binding energy (BE). For a diatomic molecule, for example, this is minus the dissociation energy measured from the minimum of the potential curve. Direct measurement of this quantity is not possible. The "energy of atomization," the "total bond energy," and the "dissociation energy" are also used to describe the binding energy.[1–6] However, these do not include the zero-point energy. We shall use BE^0 for these definitions, where $BE = BE^0 + (^1/_2)\Sigma h\nu_i$. For diatomic molecules $(-D_0)$ and $(-D_e)$ are used for BE^0 and BE, respectively. (In this paper binding energy refers to BE unless otherwise specified.)

There are two basic types of experimental methods for the determination of BE^0: (i) thermochemical methods and (ii) spectroscopic methods. Determination by thermochemical methods involves the measurement or the calculation of the heats of certain reactions at temperatures at which they are best studied and controlled. Then the values are converted to a standard temperature with the aid of specific heat data. In the spectroscopic methods, first the energy levels of a molecular species are determined. Then, the energy required to take a single molecule from its lowest possible energy state to the state in which the constituent atoms can be removed to the infinite distance apart is calculated using the energy level scheme. Multiplying this by Avogadro's number, the value for a gram molecule is obtained. In some favorable cases, the spectroscopic value can be determined rather more directly and with greater accuracy than the thermochemical values.[5,6]

If the relativistic energy of a molecule is assumed

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to nearly cancel the sum of the relativistic energies of the constituent atoms, the binding energy is given by

$$\mathrm{BE}_{\mathrm{calcd}} = \mathrm{BE}_{\mathrm{HF}} + \mathrm{BE}_{\mathrm{corr}} \tag{1a}$$

where $\mathrm{BE}_{\mathrm{HF}}$ and $\mathrm{BE}_{\mathrm{corr}}$ are the *Hartree–Fock* and *correlation binding energies*, respectively. The correlation binding energy is defined as

$$\mathrm{BE}_{\mathrm{corr}} = \Delta E_{\mathrm{corr}} = \sum_{\mathrm{atoms}} E_{\mathrm{corr}}(\mathrm{atoms}) - E_{\mathrm{corr}}(\mathrm{molecule}) \tag{1b}$$

Hartree–Fock binding energies are generally smaller (in magnitude) than the experimental values. Methods like "atoms in molecules,"[7] "deformed atoms in molecules,"[8] and "intraatomic correlation corrections"[9] usually predict better binding energies because in these methods either the intraatomic correlation energy is introduced directly or experimental atomic energies which already contain the correlation are used as input data. Since two-center correlation effects are neglected, these methods do not yield the experimental binding energy. However, the improvement in the values indicates the important contribution of the electron correlation to the binding.

The theory of electron correlation in atoms and molecules has been developed by Sinanoğlu, who has shown that in an N-electron singlet ground state the E_{corr} consists mainly of $N(N-1)/2$ MO pair correlations.[10a] In excited states, *i.e.*, general nonclosed shell systems, on the other hand, there are additional effects whose calculation has led to a quantitative new atomic structure theory.[10b] This yields, *e.g.*, the optical transition probabilities to within about 5% accuracy,[10c] compared with the Hartree–Fock (orbital) methods which are often in error by factors of 2 to 10. The nonclosed shell theory also enables the nonempirical calculation of molecular potential energy surfaces for use, *e.g.*, in chemical beam kinetics.[10d] As in the atomic work, Sinanoğlu has also developed semiempirical versions of the theory for molecular correlation energies. A more approximate one of these was recently given for π-electron systems.[11] Its use for σ systems involves additional approximations, like the neglect of "cross-pair correlations" of the full theory.[10b] Nevertheless, it has been possible to parametrize this semiempirical method, referred to as "EPCE-F2σ" (effective pair correlation energy method with the "F2σ" approximations given in ref 12), quite successfully for estimates of molecular E_{corr}. Although more complete and rigorous semiempirical methods can and are being developed based on the Sinanoğlu theory "MET,"[10a] the present EPCE-F2σ has the advantage of much simplicity. Its basic equation is

$$E_{\mathrm{corr}} \underset{\mathrm{F}2\sigma}{\cong} \frac{1}{4}\sum_{p_{\mathrm{A}}q_{\mathrm{B}}}\left(\sum_k \frac{Q_{p_{\mathrm{A}}}{}^k}{N_k}\right)\left(\sum_l \frac{Q_{q_{\mathrm{B}}}{}^l}{N_l}\right)\bar{\epsilon}_{p_{\mathrm{A}}q_{\mathrm{B}}} \tag{2}$$

where $Q_{p_{\mathrm{A}}}{}^k$ is the Mulliken partial gross atomic population in the kth spinless MO and the $\mathrm{AO}_{p\mathrm{A}}$ on center A. The N_k is the number of electrons in the kth MO. For singlet ground states with all MO's doubly occupied, $N_k = 2$. The $\bar{\epsilon}_{p_{\mathrm{A}}q_{\mathrm{B}}}$ are the one-center ($\bar{\epsilon}_{p_{\mathrm{A}}p_{\mathrm{A}}}$, $\bar{\epsilon}_{p_{\mathrm{A}}q_{\mathrm{A}}}$) or two-center ($\bar{\epsilon}_{p_{\mathrm{A}}q_{\mathrm{B}}}$, A $\neq$ B) "effective pair correlation parameters" ($\bar{\epsilon}_{p_{\mathrm{A}}q_{\mathrm{B}}} \equiv \epsilon_{p_{\mathrm{A}}{}^{\alpha}q_{\mathrm{B}}{}^{\beta}} + \epsilon_{p_{\mathrm{A}}{}^{\alpha}q_{\mathrm{B}}{}^{\alpha}}$) of the EPCE-F2$\sigma$ method.

The EPCE-F2σ is closer in form to the rigorous correlation theory than the first semiempirical method that was available in the literature for molecules beyond diatomics or the simplest central hydrides. That method ("PPM," "pair population method;" *cf.* ref 23 below) also used gross populations, but by an approximation requiring only one-center pair energies, *i.e.*, the atomic total pair energies introduced by MET.[10a] Equation 2 here shows what quantitative relation this implies between the two-center $\epsilon_{p_{\mathrm{A}}q_{\mathrm{B}}}$ and the atomic ones $\epsilon_{p_{\mathrm{A}}q_{\mathrm{A}}}$. The PPM works well for the smaller molecules, but, as can be shown from eq 2, it becomes less and less accurate as the number of atoms in the molecule increases.

In this paper, we use the (EPCE-F2σ) to study the effect of electron correlation on chemical binding for several classes of molecules. The $\mathrm{BE}_{\mathrm{corr}}$ and the E_{corr} are given for over 30 molecules including saturated and unsaturated hydrocarbons, aromatics, and heterocyclics. From these we also obtain an empirical method for the estimation of the actual total binding energy, BE, or the heat of atomization. Because both nonempirical (*ab initio*) and recent semiempirical MO theories like CNDO/2 give poor results for thermochemical quantities, the present method, which uses the MO coefficients of such methods as input, should be quite useful. Binding energies of some molecules, for which the HF energies are known, are also calculated and compared with the experimental values.

In the last few years, it has become evident that good LCAO–MO–SCF wave functions can be obtained for large molecules using a contracted Gaussian basis for constructing the MO wave functions.[13-19] The resulting energies do not reach the HF limit because the basis sets are not sufficiently large. To determine the size of the basis set, and the HF wave functions, the HF limit of the energy must be known. We have estimated the HF energies for some large molecules by using the calculated correlation binding energies, experimental binding energies, and the atomic HF energies. Because of the errors involved, the pre-

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Table I. Correlation Energies of Diatomic Molecules (in eV)

Molecule		E_{corr}^{exptl}	This work (EPCE-F2σ)	S-C[c]	PPM[c]	SI
B_2[a]	$^3\Sigma_g^-$	−8.81[d]	−8.34	−8.22	−7.98	−7.03
C_2[a]	$^1\Sigma_g^-$	−14.18[d]	−11.17	−11.91	−11.59	−10.66
N_2[b]	$^1\Sigma_g^+$	−14.96[d]	−14.95	−13.44	−14.17	−15.19[e]
O_2[f]	$^3\Sigma_g^-$	−17.94[d]	−17.07	−15.43	−15.73	−16.92
F_2[a]	$^1\Sigma_g^+$	−20.69	−18.48	−19.65	−19.46	−19.40
BN[g]	$^3\Pi$		−10.56	−11.10[h]	−10.92[h]	−10.05
BF[a]	$^1\Sigma^+$	−14.31[i]	−14.18	−13.43	−13.87	−13.88[e]
CO[a]	$^1\Sigma^+$	−14.61[i]	−14.63	−13.68	−13.77	−14.50[e]

[a] Wave functions are from ref 28. [b] The values for N_2 are from ref 12. [c] These are obtained by using ΔE_{corr} of ref 23 and the atomic correlation energies, ref 26 (S-C = "shrunken-core" method; PPM =" pair population method" of ref 23). [d] These are obtained from [ΔE_{corr}^{exptl}] of ref 23 and the atomic correlation energies.[25] [e] These values are from ref 24 (SI = "separated ions" estimate). [f] Wave functions are taken from ref 29. [g] The wave function is obtained by the CNDO/2 program.[21] [h] Calculated by the present authors based on methods of ref 23. [i] HF binding energies are obtained from ref 30. Experimental binding energies are obtained from the data given in ref 31. Zero-point corrections are from ref 5.

dicted HF energies are expected to be accurate only within 0.1 au (2.7 eV).

The molecular correlation energies given here were calculated using simple LCAO–MO–SCF wave functions and the electron populations obtained from them. When these were not already available in the literature, they were calculated using the extended Hückel method (the computer program EXTHUC) of Hoffmann,[20] or the CNDO/2 program of Pople and Segal.[21] In some cases both were used to study the dependence of the calculated correlation energies on the wave function used. In addition the atomic $\bar{\epsilon}_{p_A q_A}$ values, coming from MET/NCMET, and the semiempirical two-center $\bar{\epsilon}_{p_A q_B}$ (A ≠ B), obtained from these and tested earlier,[12,22] enter as input.

Correlation Energies of Small Molecules

Correlation energies of some small molecules are tabulated in Tables I and II. The "experimental" correlation energy is defined as

$$E_{corr}^{exptl} = -(BE_{exptl} - BE_{HF}) + \sum_{atoms} E_{corr}\,(atoms) \quad (3)$$

The results were obtained using the effective pair correlation energies in set C of ref 12 as mentioned in ref 22. The "shrunken-core" (S-C) and the pair population method (PPM) results are taken from ref 23. With the exceptions of N_2, CO, and BF,[24] we have calculated the values of the separated ion (SI) approximation by using the total correlation energies of atoms and ions.[25] Others have also used the SI approximation to estimate the correlation energies of diatomic molecules.[26,27]

Table II. Correlation Energies[a] of Small Polyatomic Molecules

Molecule	$E_{corr}^{exptl\,b}$	This work (EPCE-F2σ)	PPM[c]
BH_3[d]		−5.90	
B_2H_6[d]		−14.05	
HCN[e]	−14.07[f]	−13.90	−12.75
H_2O[e]	−10.33[g]	−9.75	−9.53
NH_3[d]	−9.14[h]	−9.57	−8.67
CO_2[e]	−23.81[f]	−23.69	−22.33
N_2O[e]	−25.02[f]	−23.82	
FCN[e]		−23.67	
FCCH[e]		−22.87	
C_2N_2[e]	−27.58[f]	−27.12	
CH_4[i]	−8.61[j]	−8.64	−7.99
C_2H_2[d]	−13.15[f]	−13.17	−11.24
C_2H_4[d]	−15.34[k]	−15.46	−12.60
C_2H_6[e]	−17.07[l]	−17.47	

[a] In electron volts. [b] Experimental binding energies are taken from Table IV. [c] These correlation energies are obtained from the ΔE_{corr} given in ref 23 and from the atomic correlation energies in ref 25. [d] Wave functions are from ref 32. [e] Wave functions are obtained by using the CNDO/2 program in ref 21. [f] Hartree–Fock binding energies are obtained from the data given in ref 30. [g] HF binding energy is obtained from ref 33. [h] HF binding energy is from ref 34. [i] Wave functions are from ref 35. [j] See ref 12. [k] HF binding energy is from ref 36. [l] HF binding energy is from ref 37.

In general, correlation energies for diatomic molecules obtained by the EPCE-F2σ method are in good agreement with those predicted by other methods and experimental correlation energies.

The experimental correlation energies of C_2 and N_2O are much larger, in absolute value, than the estimated ones. The experimental correlation energy of C_2H_6 is, in absolute value, 1.73 eV larger than that of C_2H_4, which in turn is 2.19 eV larger than the absolute value of the correlation energy of C_2H_2. Then, lower and upper bound estimates for the absolute value of the correlation energy of C_2 are expected to be 10.9 and

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(20) QCPE 30. EXTHUC, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(21) QCPE 91. CNDO/2, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(22) Pamuk[12] has obtained and tested three sets of two-center $\epsilon_{p_A q_B}$'s (sets A, B, and C in ref 12). All of these give quite similar results. Set C is the most refined one. Therefore, only set C is used in the present paper.

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11.5 eV, respectively. If we assume that C–H and π bonds have almost constant correlation energies, the lower bound estimate seems reasonable because a π bond is broken and two C–H bonds are formed during the hydrogenation of C_2H_2 or C_2H_4, but the number of π bonds did not change from C_2 to C_2H_2. However, most of the estimates for the correlation energy of C_2 are closer to the higher limit. This indicates that the C–H $\leftrightarrow$ C–H interbond correlation energy is almost as large as half of the π bond correlation energy.[12,38] Comparison of the correlation energies of the 22-electron isoelectronic series shows that $E_{corr} = -23.75 \pm 0.25$ eV is a reasonable value for the N_2O molecule. From the above arguments, one might conclude that either experimental binding energies or HF energies of C_2 and N_2O may be in error.

As the charge on the central atom is decreased in the Ne, HF, H_2O, NH_3, and CH_4 isoelectronic series, the expected gradual decrease in correlation energies can be observed.[39,40] It is also interesting to see a similar change in the correlation energies of the 14-electron isoelectronic series: N_2, CO, BF, HCN, and C_2H_2.

The absolute value of the experimental correlation energy of the C_2H_4 molecule is given in ref 36 as 0.678 au or 18.45 eV. This is 2.99 eV larger than the value estimated using the EPCE-F2σ method. This difference is much greater than the error that we were expecting in our calculations. Recalculation of the experimental binding energy from the data given in ref 31 and 41 yields 24.37 eV, which is 2.97 eV less than the one given in ref 23. With this new value, we obtain $E_{corr}{}^{exptl} = -15.34$ eV.

Recent *ab initio* calculations of the correlation energies of H_2O, NH_3, and CH_4 give only 50–80% of the correlation energy contribution by the valence electrons.[42,43]

Contribution of Electron Correlation to the Binding Energy of Small Molecules

As was noted earlier, the binding energies are useful in chemical calculations but their experimental determination is sometimes very difficult or even impossible. We can calculate the binding energies of molecules if good Hartree–Fock (HF) calculations are available. In fact, for many small molecules, HF energies are available.[26,30,33,34,36,40] From these energies, HF binding energies are found and listed in Tables III and IV. From correlation energies given in ref 12, Tables I and II, and from atomic correlation energies,[25] correlation binding energies are calculated. They are also given in Tables III and IV. According to eq 1, the sum of the HF binding energy and the correlation binding energy is the calculated binding energy.

The Hartree–Fock binding energies of diatomic hydrides are from ref 26. With the exception of BH, the calculated binding energies of the diatomic hydrides agree very well with the experimental ones. All experimental values for the binding energy of BH are less than 3.66 eV,[5,6,26,44,45] which shows that the EPCE-F2σ method overestimates the correlation energy of this molecule.

Table III. Binding Energies[a] of Diatomic Molecules (in eV)

Molecule	BE_{HF}	This work $BE_{corr\text{-}(EPCE\text{-}F2\sigma)}$[b]	This work BE_{calcd}	BE_{exptl}[c]
BH	2.78	1.41	4.19	3.58
CH	2.47	1.39	3.86	3.65
NH	2.10	1.81	3.91	3.80
OH	3.03	1.58	4.61	4.63
HF	4.38	1.30	5.68	6.12
B_2	0.89	1.54	2.73 (*Cf.* text)	2.90[d]
C_2	0.79	2.57	(3.36)	6.31
N_2	5.27	4.72	9.99	9.91
O_2	1.28	3.03	4.31	5.18
F_2	−1.37	0.84	(*Cf.* text)	1.69
BF	6.24	1.96	8.20	8.33
CO	7.93	3.31	11.24	11.22

[a] In this paper BE's (binding energy) are defined so as to be positive for stable molecules. [b] BE_{corr}'s for hydrides are obtained from ref 12. [c] Experimental binding energies of hydrides are from ref 26. Others are obtained from the data given in ref 31 and 5. [d] This value is from ref 46.

Table IV. Binding Energies[a] of Small Polyatomic Molecules

Molecule	BE_{HF}	This work $BE_{corr\text{-}(EPCE\text{-}F2\sigma)}$	This work BE_{calcd}	BE_{exptl}[b]
HCN	8.89[c]	4.48	13.37	13.54
H_2O	6.77[d]	2.73	9.50	10.08
NH_3	8.87[e]	4.45	13.32	12.89
CO_2	11.39[c]	5.36	16.75	16.86
N_2O	3.97[c]	6.57	10.54	11.73
C_2H_2	13.01[c]	8.29	21.30	21.75
CH_4	13.87[f]	4.34	18.21	18.18
C_2H_2	12.98[c]	4.57	17.55	17.53
C_2H_4	17.63[g]	6.86	24.29	24.37
C_2H_6	22.35[h]	8.87	31.22	30.82
FCN	7.66[c]	5.44	13.10	
FCCH	11.91[c]	5.45	17.36	

[a] In electron volts. [b] Experimental binding energies are obtained from the data given in ref 31. Zero-point corrections are from ref 41. [c] HF binding energies are obtained from the data given in ref 30. [d] HF binding energy from ref 33. [e] HF binding energy from ref 34. [f] HF binding energy from ref 40. [g] This value from ref 36. [h] HF binding energy is from ref 37.

Comparison of calculated and experimental binding energies of homonuclear diatomic molecules is not entirely satisfactory. In some of these, specific "internal" and "semiinternal" correlations of the full nonclosed shell theory[10b] play a particularly important role, while EPCE-F2σ is too crude to take these into account properly. The uncertainty in the experimental binding energy of the B_2 molecule is 0.24 eV,[46] and so $BE_{exptl} = 2.66$ eV is in the range of calculated values. In ref 47, the experimental binding energy ($-\Delta E_{corr}$ in eq 2) for C_2 is reported as 1.80 eV, which is much smaller than the earlier values.[23,26] Although the new value is closer to those obtained by the EPCE-F2σ method, it differs by approximately

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1.0 eV which is more than the usual error in this method. For further discussion on this, we have to know the BE_{HF} and BE_{exptl} values from which $BE_{corr}^{exptl} = 1.80$ eV is obtained.[48]

Since B_2 and O_2 are in the triplet state, the correlation energy calculations for these molecules are much less accurate than those for the others, since EPCE-F2σ approximations are well studied only for singlet ground states.[11]

The F_2 case has been a very anomalous one, previous methods and calculations either giving no binding or at most about one-third of it (~0.5–0.6 eV).[50] Only after the suggestion[10d] of Sinanoğlu, at the Argonne Laboratory, that the new "semiinternal" correlations of his NCMET should be included to account for binding, a proper binding energy (~1.53 eV) could be obtained in nonempirical calculations.[51]

The present EPCE-F2σ method is not based on NCMET[10b,d] but uses the simpler treatment MET applicable to quasi-closed shells only. Thus, not including a treatment of the semiinternal correlation fully, it is not expected to work for F_2 and does not.

The results for heteronuclear diatomic and polyatomic small molecules are much better. From the data presented in Tables III and IV, we conclude that if the ratio of the HF binding energy to the experimental binding energy is less than 0.35, the total binding energy can be predicted to only within 1.0 eV as for the B_2, C_2, O_2, F_2, and N_2O molecules.

The Hartree–Fock binding energies for BF, CO, HCN, CO_2, N_2O, C_2N_2, C_2H_2, FCN, and FCCH are obtained from the data given in ref 30. These authors estimate the largest error in their calculations to be 0.01 au or 0.27 eV. The accuracy in the experimental binding energy of C_2N_2 is about 0.35 eV.[6] For similar reasons, the calculated and experimental binding energies of other molecules generally agree to within 0.5 eV.

We also calculated the binding energies for the FCN and FCCH molecules for which the experimental values are not available in the literature. We expect that the actual binding energies of these molecules are very close to 13.22 ± 0.25 eV for FCN and to 17.86 ± 0.25 eV for FCCH. These values are comparable with the binding energies of HCN, $BE_{exptl} = 13.54$ eV, and C_2H_2, $BE_{exptl} = 17.53$ eV.

Dependence of Estimated Correlation Energies on the Approximate MO Wave Functions

In the EPCE-F2σ method, the total correlation energy is expressed in terms of effective pair energies and electron populations. To find out the dependence on the wave functions, we have calculated the correlation energies of some small molecules by using different LCAO–MO wave functions. The results are tabulated in Table V. The maximum error is 0.59 eV and the standard deviation is 0.26 eV.

In ref 37, the authors have not reached the HF limit for C_2H_6. Present correlation energy calculations for this molecule indicate that the error in the HF energy is less than 1.0 eV. If we compare the difference between estimated correlation energies for the same molecules obtained by using different LCAO–MO wave functions, we find the largest differences among the results for C_2H_6 is 0.99 eV. These differences are only 5–6% of the total correlation energy. Thus we conclude that estimated correlation energies are not sensitive to the approximate nature of the MO's used. This is convenient since few actual HF MO's are likely to be available on larger molecules.

Table V. Correlation Energies[a] of Some Small Molecules Obtained by Using Different LCAO–MO Wave Functions

Molecule	This work E_{corr}^{calcd}	Δ
HF[b]	−10.46	−0.10
HF[c]	−10.12	−0.44
BF[b]	−14.20	−0.11
BF[d]	−14.18	−0.13
CO[b]	−14.49	−0.12
CO[d]	−14.63	0.02
HCN[e]	−13.65	−0.42
HCN[b]	−13.90	−0.17
CH_4[c]	−8.85	0.24
CH_4[f]	−8.64	0.03
CH_4[g]	−8.60	−0.01
C_2H_2[b]	−12.98	−0.17
C_2H_2[e]	−13.17	0.02
C_2H_2[g]	−12.96	−0.19
C_2H_4[b]	−14.89	−0.45
C_2H_4[e]	−15.46	0.12
C_2H_4[g]	−15.14	−0.20
C_2H_6[e]	−16.48	−0.59
C_2H_6[b]	−17.47	0.40
C_2H_6[g]	−17.11	0.04

[a] In electron volts. The difference is $E_{corr}^{exptl} - E_{corr}^{calcd} \equiv \Delta$. [b] Wave functions are obtained by the CNDO/2 program in ref 21. [c] Wave functions are from ref 52. [d] Wave functions are from ref 28. [e] Wave functions are from ref 32. [f] Wave functions are from ref 35. [g] Wave functions are obtained by the EXTHUC program in ref 20.

Correlation Energies of Hydrocarbons and Some Related Compounds

The correlation energies of large molecules were calculated using the EPCE-F2σ method. Since no other calculations or predictions of the correlation energies were available for these molecules, we have also calculated them using the PPM of Hollister and Sinanoğlu.[23] In these calculations the PPM is slightly modified as follows: (i) eq 43 of ref 10 is used with $(K_{p_A}) = 1$; (ii) ϵ_{2s^2} pair correlation energies are obtained from the polynomials (eq 4) fitted to the curves

$$\epsilon_{2s}^2(\mathrm{A}) = an^2 + bn + c \qquad (4)$$

in ref 23; (iii) all other pair correlation energies are obtained by the "weighted average method" given in ref 12. In eq 4, n denotes the 2p population on the atom A.[53] The coefficients for the polynomials are listed in Table VI.

The wave functions needed for the calculation of the correlation energies are generally obtained by the EXTHUC program of Hoffmann.[20] Exceptions are the heterocyclic molecules and benzene, for which

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(48) Several values are reported for the experimental dissociation energy of C_2, from 3.5[5] to 6.25[49] eV. Assuming the accuracy of the HF binding energy, the present estimation suggests the first value as the BE_{exptl} of C_2 although the second is generally accepted.[31,49]

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(53) In the random spin approximation $n/2$, 2p electrons are assumed to have α spin if the molecule is in a singlet state.

Table VI. Coefficients for the Polynomials Given in Eq 4

Atom	a	b	c
B	0.00	0.207	−0.854
C	−0.019	0.418	−1.828
N	−0.041	0.602	−2.309
O	−0.021	0.538	−2.472

gross populations are taken from ref 13 and 14, respectively.

The correlation energies obtained by the PPM and the EPCE-F2σ methods are tabulated in the second and third columns of Table VII. Comparison of these results shows that the PPM values are always smaller in absolute value than the EPCE-F2σ results and that the difference between them increases with the size of the molecule. This was expected because K_{p_A} is set equal to 1 although it is generally larger. Therefore, the PPM results may be assumed to be lower limits of the correlation energies (in absolute value).

Table VII. Correlation Energies[a] of Large Molecules

Molecule[b]	PPM	E_{corr}[c]	E_{corr}^{σ}	$E_{\text{corr}}^{\sigma-\pi}$	E_{corr}^{π}
Methane	−7.87	−8.60			
Ethane	−14.77	−17.11			
Propane	−21.03	−24.69			
Butane	−27.77	−33.11			
Acetylene	−12.47	−12.96	−6.90	−3.61	−2.45
Methylacetylene	−19.18	−21.25	−13.41	−5.33	−2.51
Dimethylacetylene	−25.61	−29.14	−19.19	−6.68	−2.55
Ethylene	−13.35	−15.14	−11.66	−2.63	−0.85
trans-Butadiene	−25.64	−29.62	−22.35	−5.30	−1.97
trans-Butene-2	−26.64	−31.14	−24.58	−5.68	−0.88
cis-Butene-2	−26.74	−31.48	−24.92	−5.68	−0.88
Isobutylene	−26.72	−31.80	−25.31	−5.61	−0.88
Pyrrole[d]	−32.11	−39.13	−27.70	−8.92	−2.52
Pyridine[d]	−37.74	−46.24	−34.32	−8.46	−3.41
Pyrazine[d]	−38.69	−46.24	−34.59	−8.63	−3.03
Benzene[e]	−37.47	−46.29	−34.13	−8.42	−3.74
Naphthalene	−60.64	−75.44	−55.10	−13.68	−6.66

[a] In electron volts. [b] The MO wave functions are obtained by the EXTHUC program in ref 20, unless otherwise indicated. [c] This and σ, $\sigma-\pi$, and π electron correlations are obtained by the EPCE-F2σ method. [d] The MO wave functions used are from ref 13. [e] The MO wave functions used are from ref 14.

In the EPCE-F2σ method, the absolute value of the correlation energy increases approximately 8.0 ± 0.5 eV with the addition of every CH_2 group. This can be seen in the series from methane to butane and from acetylene to dimethylacetylene. The increase from ethylene to the C_4H_8 isomers is also approximately 16 eV.

The EPCE-F2σ method predicts that the correlation energy of the C_4H_8 isomers increases in absolute value from *trans*-butene-2 to isobutylene as electrons are confined into a smaller volume. This may be interpreted as electrons seeing each other more often and interacting more strongly when they are restricted to a smaller volume.

In the benzene, pyridine, and pyrazine series, the differences are small, and, therefore, the distinction is not very clear.

In the acetylene, ethylene, and ethane series and in the dimethylacetylene, *trans*-butene-2, and butane series, the absolute value of the correlation energy increases approximately 2.0 ± 0.5 eV. Along these series, a π bond is broken and two CH bonds are formed with each increase of H_2. If we neglect the interbond correlation energies, we would expect approximately a 1.0-eV increase. Therefore, we conclude once more that the interbond correlations are also important as first shown by Sinanoǧlu and Skutnik[38] and predicted by MET.[10a,b]

Comparison of the known correlation energies may help to find the correlation energies of other related molecules. For example, the average of the correlation energies of acetylene and ethane is approximately equal to the correlation energy of ethylene. The average of the correlation energies of dimethylacetylene and butane is approximately equal to the correlation energy of *trans*-butene-2. Similarly, we assume that the average of the correlation energies of methylacetylene and propane should give approximately the correlation energy of propylene. From earlier conclusions, correlation energies of other molecules can be estimated. For example, the addition of −8.0 eV to the correlation energy of butane should yield approximately the correlation energy of pentane. Subtracting −2.0 and −4.0 eV from the correlation energy of pentane, we obtain approximately the correlation energies of pentane and pentadiene, respectively.[54]

If we assume that the average correlation energy per σ bond is approximately constant, the difference

$$\Delta E_{\text{corr}} = 2E_{\text{corr}}(C_2H_4) - E_{\text{corr}}(C_4H_6) \qquad (5)$$

gives the correlation energy of a CH bond of −0.66 eV. This result is close to the calculated correlation energy of a CH bond in ethylene.[55]

σ, $\sigma-\pi$, and π Electron Correlation Energies

In ref 10a and 11, we have discussed the rigorous separation of the total correlation energies into the correlation energy of σ electrons only, E_{corr}^{σ}, the correlation energy due to the interactions between the σ and π electrons, $E_{\text{corr}}^{\sigma-\pi}$, and the correlation energy of the π electrons only, E_{corr}^{π}. In this work, we have carried out the partitioning of the correlation energies obtained by the EPCE-F2σ. The results are listed in the last three columns of Table VII. In general, the σ correlation energy is the major contributor to the total correlation energy, and the smallest contribution comes from the π-electron correlation. The π-electron correlation energies of benzene, naphthalene, and anthracene are −3.74, −6.66, and −9.62 eV,[55] respectively. These values are comparable with the AMO results[56] of −3.70 eV for benzene, −6.73 eV for naphthalene, and −9.65 eV for anthracene, which are the best values obtained by *ab initio* calculations.

The π-electron correlation energy of acetylene is −2.45 eV. Configuration interaction (CI) yields −2.83 eV.[57] The agreement between the two results is

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Table VIII. Contribution of the Electron Correlation to the Binding, Predicted Binding,[b] and HF Energies of Some Noncyclic Hydrocarbons

Molecule	BE_{corr}	BE_{exptl}[d]	BE_{corr}/BE_{exptl}[a]	This work: BE_{pred}[b]	This work: E_{HF}^{pred}
Propane	0.4333	1.5994[e]	27.1	1.5469	−118.2320
Butane	0.5847	2.0798[f]	28.1	2.0875	−157.2496
Methylacetylene	0.3072	1.1205[e]	27.4	1.0968	−115.8792
Dimethylacetylene	0.4392	1.5957[e]	27.5	1.5680	−154.9110
trans-Butadiene	0.4564	1.6090[f]	28.4	1.6294	−154.9071
trans-Butene-2	0.5123	1.8398[f]	27.8	1.8290	−156.0820
cis-Butene-2	0.5252	1.8379[f]	28.6	1.8750	−156.0672
Isobutylene	0.5369	1.8420[f]	29.1	1.9168	−156.0596

[a] × 100 [b] BE in this paper is defined so as to be positive for a stable molecule. [c] All energies are in atomic units: 1 au = 27.21 eV. [d] Dissociation energies are obtained from the data given in ref 59. [e] Zero-point energies are from ref 41. [f] Zero-point energies are approximated by using the group equivalents taken from ref 60.

Table IX. Contribution of the Electron Correlation to the Binding, Predicted Binding,[a] and HF Energies of Some Aromatic Compounds

Molecule	BE_{corr}	BE_{exptl}[c]	BE_{corr}/BE_{exptl}[b]	BE_{pred}	E_{HF}^{pred}
Pyrrole	0.6182	1.7758[d]	34.8	1.7836	−208.793
Pyridine	0.7233	2.0533[d]	35.2	2.0868	−246.674
Pyrazine	0.6917	1.9[e]	36.4	1.9957	−262.765
Benzene	0.7530	2.2448[f]	33.5	2.1725	−230.624
Naphthalene	1.1926	3.472[g]	34.3	3.441	−383.17

[a] BE is defined in this paper so as to be positive for a stable molecule (eq 6 in text). All energies are in atomic units; 1 au = 27.21 eV. [b] × 100. [c] Dissociation energies are obtained from the data given in ref 61. [d] See ref 62. [e] This value is obtained by extrapolation with respect to the number of N atoms from the experimental binding energies of benzene and pyridine. [f] Zero-point energy is from ref 41. [g] Zero-point energies are approximated by using the group equivalents taken from ref 60.

excellent. The AMO value[58] is only 70% of the "full CI" result.

The π-electron correlation energy decreases along the benzene, pyridine, and pyrazine series as the number of nitrogen atoms increases. The σ and σ–π correlation energies, on the other hand, increase with the number of N atoms. The opposite charges cancel each other and the resulting correlation energies are approximately equal.

Predicted Binding and Hartree–Fock Energies of Some Large Molecules

From the correlation energies given in Table VII, and from the ground-state correlation energies of atoms,[25] we have calculated the correlation binding energies of some large molecules. The results are listed in the second columns of Tables VIII and IX. We have also calculated the experimental binding energies from the data given in ref 41 and 58–60. They are tabulated in the third columns of the same tables. The value for pyrazine is found by extrapolation from the experimental binding energies of benzene and pyridine and, therefore, may be very inaccurate. The accuracy in the experimental binding energy of naphthalene may be on the order of 0.1 au.

The ratios of the correlation binding energies to the experimental binding energies are listed in the fourth columns of Tables VIII and IX. The contribution of the electron correlation to the binding energy is different for noncyclic and for aromatic compounds, but it is approximately constant in each group. The average value of the ratios is 0.2801 in the first group of molecules and 0.3466 in the second one. Using these constants and the estimated correlation binding energies, we have predicted the binding energies given in the fifth columns of the Tables VII and IX. The maximum error and the standard deviation for the noncyclic molecules are 2.04 and 1.06 eV, respectively. Both quantities are larger than the desirable chemical accuracy. However, in the case of aromatic compounds, all predicted binding energies are in the experimental error range (*i.e.*, 0.1 au $\cong$ 2.7 eV). Further, these estimates are closer to actual values than those possible by approximate MO theories and other quantum mechanical means in the literature.

The exact binding energy (defined here + for a stable molecule) of a molecule is the sum of the exact energy of the molecule

$$BE = \sum_{\text{atoms}} E(\text{atoms}) - E(\text{molecule}) \tag{6}$$

The exact energies can be represented by the sum of the Hartree–Fock, correlation, and relativistic energies Since, throughout this work, the relativistic energy of a molecule is assumed to be roughly equal to the sum of the relativistic energies of the constituent atoms, the HF energy of a molecule can be obtained from

$$E_{HF}^{\text{predict}} = \sum_{\text{atoms}} E_{HF}(\text{atoms}) - BE_{\text{exptl}} + BE_{\text{corr}} \tag{7}$$

We have predicted the HF energies of some molecules and tabulated their values in the last columns of Tables VIII and IX.[63]

The predicted HF energies may be used as a guide to find better wave functions and energies by direct calculations. In ref 13, 14, and 18, the SCF energies of *trans*-butadiene, benzene, pyrrole, pyridine, and pyrazine are reported as −154.7103, −230.463, −207.931, −245.622, and −261.554 au, respectively. These SCF energies are approximately 0.197 au or 5.35 eV, 0.161 au or 4.38 eV, 0.862 au or 23.46 eV, 1.052 au or 28.62 eV, and 1.211 au or 32.95 eV higher than the predicted values. The SCF energies of butadiene and benzene are very close to the HF limits. However, the others are too high and better SCF wave functions must be found to reach the HF limit and chemical accuracy. It is very difficult presently to obtain the actual Hartree–Fock wave functions of sizable molecules.

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Conclusion

Binding energies of small molecules can be predicted by the EPCE-F2σ method within the ± 0.5-eV error range if accurate Hartree–Fock energies are available.

It was expected that the calculated correlation energies would depend on the choice of the molecular wave functions. Calculations have demonstrated that any molecular wave function yields a correlation energy which is within 5–6% of the experimental value. Generally, results are better than this range and we may conclude that the EPCE-F2σ method can predict the correlation energies of small molecules with an accuracy of usually less than 0.5 eV, although the discrepancies in C_2 and F_2, which many authors encountered, remain.

We have also investigated the correlation energies of some hydrocarbons, aromatics, and heterocyclic compounds. The results indicate that: (i) the absolute value of the correlation energy increases approximately 8.0 eV by addition of a CH_2 group; (ii) the absolute increase in correlation energy is approximately 2.0 eV after a π bond is broken and two CH bonds are formed; (iii) the correlation energy of a CH bond is approximately -0.66 eV; (iv) the interbond correlation is also very important.

The ratio of the correlation binding energy to the experimental value is approximately constant for noncyclic hydrocarbons and for aromatic compounds. Especially for very large molecules, the average value of the ratios can be used for predicting binding energies within an error range of 2–3 eV, which is considerably better than those possible say by approximate MO methods.

The HF energies of some large molecules are predicted by using the experimental binding energies, calculated correlation binding energies, and atomic HF energies. The errors in these calculations may be of the order of 0.1 au (*i.e.*, 2.7 eV). However, they would be a useful guide in finding better wave functions and energies by *ab initio* calculations.

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Estimation of Atomic Charges by an Electronegativity Equalization Procedure Calibrated with Core Binding Energies

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Abstract: A simple procedure, based on the equalization of orbital electronegativities, has been devised for calculating atomic charges in molecules. The calculation involves four empirical parameters (only two of which are needed for most molecules), which have been evaluated by application of the potential model equation for calculating core binding energies to 126 experimental 1s binding energies for 66 gaseous compounds. The method yields standard deviations in the binding energies of carbon, nitrogen, oxygen, and fluorine of ± 0.69, ± 0.53, ± 0.74, and ± 0.36 eV, respectively. The calculated and experimental binding energies are used to test the expected correlation between the ligancy of an ionizing atom and the electronic relaxation energy and to test the "transition state" method of providing for relaxation energy.

Most of the chemical properties of molecular systems are explicable in terms of the distribution of electron density within the molecules. Consequently methods for describing molecular electron distribution are of considerable interest to chemists.[1–11] For simple molecules, it is possible to calculate accurate electron densities by SCF–MO techniques and to display the data in the form of electron density contour maps.[1,2] In favorable cases, X-ray and neutron diffraction data can yield similar plots.[12] However, such plots, or even *tabulations*, of electron density are not easily used except for making qualitative comparisons. The favorite and most practical method for quantitatively describing electron distribution in a molecule is the assignment of partial charges to the atoms. A wide variety of theoretical and empirical methods have been used for evaluating atomic charges, and most of these have

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