# Variation of Parameters in Becke-3 Hybrid Exchange-Correlation Functional

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**ABSTRACT:** We have investigated the consequences of varying the three parameters in Becke's hybrid exchange-correlation functional, which includes five contributions: Hartree–Fock exchange, local exchange, Becke's gradient exchange correction, local correlation, and some form of gradient correlation correction. Our primary focus was upon obtaining orbital energies with magnitudes that are reasonable approximations to the electronic ionization potentials; however, we also looked at the effects on molecular geometries and atomization enthalpies. A total of 12 parameter combinations was considered for each of three different gradient correlation corrections: the Lee–Yang–Parr, the Perdew-86, and the Perdew–Wang 91. Five molecules were included in the study: HCN, $N_2$, $N_2O$, $F_2O$, and $H_2O$. For comparison, a Hartree–Fock calculation was also carried out for each of these. The 6-31+G** basis set was used throughout this work. We found that the ionization potential estimates can be greatly improved (to much better than Hartree–Fock levels) by increasing the Hartree–Fock exchange contribution at the expense of local exchange. In itself, this also introduces major errors in the atomization enthalpies. However, this can be largely or even completely counteracted by reducing or eliminating the role of the gradient exchange correction. © 2000 John Wiley & Sons, Inc. J Comput Chem 21: 227–238, 2000

**Keywords:** Becke three-parameter hybrid functional; ionization potentials; Kohn–Sham orbital energies

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## Introduction

The Kohn–Sham version of density functional theory is in principle exact for the ground-state electron density and total energy.[1–3] In practice, however, it requires an approximation to the exchange-correlation functional. A number of these have been proposed in recent years, and several are encoded in the Gaussian 94[4] and Gaussian 98[5] systems of programs. Particularly widely used is Becke's three-parameter hybrid functional (B3[6]), which combines, in variable proportions, local and nonlocal treatments of exchange and correlation with Hartree–Fock exchange. (Gaussian 98 also offers Becke's recent one-parameter expression;[7] however, our present interest is in the earlier, more flexible one.)

As implemented in Gaussian 94 and Gaussian 98,[4,5] Becke's three parameter hybrid has the form,

$$E_{xc} = \alpha E_x^{\text{Slater}} + (1-\alpha)E_x^{\text{HF}} + \beta \Delta E_x^{\text{Becke}} + E_c^{\text{VWN}} + \gamma \Delta E_c^{\text{nonlocal}} \quad (1)$$

The exchange energy is written as a sum of Hartree–Fock (HF) and local (Slater[8]) contributions plus Becke's gradient correction;[9] the correlation energy is given by a local Vosko–Wilk–Nusair formula (VWN III, based on the RPA uniform electron gas[10]), supplemented by some form of nonlocal (gradient) correction. The possibilities for the latter are those in the Lee–Yang–Parr (LYP[11]), the Perdew-86 (P86[12]), and the Perdew–Wang 91 (PW91[13]) functionals.

Becke determined the values of the parameters $\alpha$, $\beta$, and $\gamma$ by a linear least-squares fit to 56 atomization energies, 42 ionization potentials, 8 proton affinities, and 10 atomic energies,[6] taken from the G1 database.[14,15] Using the Perdew–Wang gradient correction and their electron-gas parametrization for the local term in eq. (1), he obtained $\alpha = 0.80$, $\beta = 0.72$, and $\gamma = 0.81$. Gaussian 94 and Gaussian 98 employ these values of $\alpha$, $\beta$, and $\gamma$ for the LYP and P86 nonlocal corrections, as well as the PW91, and introduce the VWN III for the local contribution.

These B3 procedures (B3LYP, B3PW91, and B3P86) have been overall quite successful.[16–21] For example, the average absolute error in 28 B3P86/6-31+G(d,p) dissociation energies was 1.9 kcal/mol,[19] and in 148 B3LYP/6-311+G(3df,2p) enthalpies of formation, 3.11 kcal/mol.[16] For molecules containing third-row atoms, the average absolute error in B3PW91/6-311+G(3df,2p) atomization energies, ionization potentials, electron affinities and proton affinities was 2.03 kcal/mol.[18]

Nevertheless, it is interesting to consider the possibility of improving the results for a particular property or class of molecules by appropriately changing the values of $\alpha$, $\beta$, and $\gamma$ in eq. (1), an option that is available in both Gaussian 94 and Gaussian 98.[4,5] For example, the poor descriptions of $Cr_2$ that have been obtained with eq. (1) have led to suggestions that it be reparametrized in terms of a database that includes molecules containing transition metal atoms.[22,23]

A property that might usefully be the target of reparametrization are the orbital energies, $\varepsilon_i$. The interpretation of these continues to be the focus of considerable attention.[24–37] It is tempting to view their magnitudes as approximations to electronic ionization potentials, $I_i$, as is frequently done for their Hartree–Fock counterparts; however, the B3 values differ by greater amounts from the experimental data, typically being too low by at least 2 ev and often much more.[34] For a given exchange-correlation functional, however, the differences tend to be roughly similar, even for different molecules. (This is not the case at the Hartree–Fock level.[34]) Thus, B3 orbital energies can be quite satisfactory for applications that depend upon trends in ionization potentials.[35,36]

Our objective in this work has been to find a set or sets of parameters $\alpha$, $\beta$, and $\gamma$ for eq. (1) that produce $|\varepsilon_i|$ that are in good agreement with measured electronic ionization potentials. We assess possible negative consequences for other molecular properties by comparing the various calculated geometries and atomization enthalpies with experimental data. Because atomization energies were one of the properties originally used by Becke to determine the parameters,[6] any change in the latter can be expected to produce poorer results for the former. It is the degree that will be of interest.

## Procedure

We computed optimized geometries and energies for five different molecules, using the LYP, PW91, and P86 correlation corrections and various combinations of selected $\alpha$, $\beta$, and $\gamma$ values in eq. (1). Because it has been shown that actual electronic ionization potentials lie between the B3 and the Hartree–Fock $|\varepsilon_i|$,[26,34] an obvious first step was to increase the contribution of the Hartree–Fock exchange in eq. (1), i.e., decrease $\alpha$, which we did in several stages, going from $\alpha = 0.80$ to $\alpha =$

0.30 while keeping $\beta$ and $\gamma$ constant. By eq. (1), this simultaneously diminishes the role of Slater's local exchange term. For $\alpha = 0.40$, we also incrementally reduced Becke's nonlocal exchange. As a limiting case, we eliminated both local and nonlocal exchange, and kept only the Hartree–Fock ($\alpha = \beta = 0$). We also assessed the effect of correlation, by both increasing and decreasing $\gamma$. For comparison purposes, we carried out a Hartree–Fock calculation for each molecule. The 6-31+G** basis set and Gaussian 94[4] were used throughout this work.

For each $\alpha$, $\beta$, $\gamma$ combination, we computed $\Delta H$ (298 K) for the separation of the molecule into its ground-state atoms. We have shown earlier that the zero-point plus thermal corrections in going from $E_{\min}$ (0 K) to $H$ (298 K) are very nearly the same for the B3LYP, B3PW91, and B3P86 functionals, for several different basis sets.[38] We found now that the consequences of changing the parameters are somewhat greater, but usually not more than about 1 kcal/mol, and often much less. Because our purpose in calculating the enthalpies of atomization is simply to monitor the effects of varying the parameters, we used an average value for the correction term for each molecule, rather than computing it separately for each of the total of 180 cases considered. The resulting error should generally be less than 0.5 kcal/mol.

## Results

The molecules included in this study are HCN, $N_2$, $N_2O$, $F_2O$, and $H_2O$. Our results are presented in Tables I–V. Each table includes the optimized geometries and total energies, the B3 $|\varepsilon_i|$ and the enthalpies of atomization at 298 K obtained for a given molecule using the LYP, PW91, and P86 correlation corrections and 12 different $\alpha$, $\beta$, $\gamma$ combinations. Experimental and Hartree–Fock values are also given. The $|\varepsilon_i|$ are to be compared to measured vertical ionization potentials determined by means of photoelectron spectroscopy,[39] the level of agreement being indicated by the root-mean-square (rms) error.

For each functional, the first $\alpha$, $\beta$, $\gamma$ set is the standard one used in Gaussian 94 and Gaussian 98: $\alpha = 0.80$, $\beta = 0.72$, $\gamma = 0.81$. The next eight $\alpha$, $\beta$, $\gamma$ combinations explore various treatments of exchange. First, $\alpha$ is decreased incrementally to 0.30, holding $\beta$ and $\gamma$ constant. This gradually increases the Hartree–Fock contribution at the expense of the local (Slater). Next, the effect of reducing the nonlocal (Becke) exchange is examined, by setting $\beta$ to 0.50, 0.25, and 0.00 (with $\alpha = 0.40$, $\gamma = 0.81$). This is followed by eliminating both the local and nonlocal terms ($\alpha = \beta = 0$) and keeping only Hartree–Fock exchange. (Some of the calculations for $N_2$ and $F_2O$ produce orbital orderings that differ from the experimental; this is consistently observed for the Hartree–Fock and the B3 with $\alpha = \beta = 0$.) Finally, the last three $\alpha$, $\beta$, $\gamma$ combinations investigate the consequences of both increasing and decreasing the role of nonlocal correlation ($\gamma = 1.00$ and $\gamma = 0.60$, respectively). The results for the various properties will be summarized in turn.

### IONIZATION POTENTIALS

Confirming earlier findings,[34] the experimental ionization potentials are overestimated by the Hartree–Fock $|\varepsilon_i|$ (rms errors between 1.26 and 2.75 ev) and underestimated by the B3 with standard $\alpha$, $\beta$, $\gamma$ (rms errors between 2.49 and 3.91 ev). As expected, however, the B3 $|\varepsilon_i|$ can be increased dramatically by enlarging the Hartree–Fock exchange contribution, i.e., reducing $\alpha$ while holding $\beta$ and $\gamma$ constant. Already for $\alpha = 0.40$, the rms errors are less than 1.00 ev for all three correlation functionals (LYP, PW91, and P86), and they range as low as 0.18 ev (for $H_2O$, P86). On the other hand, the combination of only Hartree–Fock exchange with local and nonlocal correlation ($\alpha = \beta = 0$) is not desirable in the present context; the $|\varepsilon_i|$ and the rms errors actually become considerably higher than the Hartree–Fock values. Decreasing the nonlocal exchange correction (by reducing $\beta$) and modifying the extent of nonlocal correlation (via $\gamma$) have variable but usually relatively small effects upon the rms error, although there are some exceptions.

### GEOMETRIES

The bond lengths all show basically the same pattern, and the results are usually similar for the LYP, PW91, and P86 calculations (except for the N—O and F—O bonds, for which the LYP distances are consistently somewhat longer). The Hartree–Fock tend to be too short; as anticipated, this is largely remedied by the introduction of correlation,[43] so that the B3 with standard hybrid parameters ($\alpha = 0.80$, $\beta = 0.72$, $\gamma = 0.81$) are quite accurate. Increasing the role of Hartree–Fock exchange by reducing $\alpha$ progressively shortens the bonds, most markedly in $F_2O$, and in the limit of no density functional exchange ($\alpha = \beta = 0$), they are actually worse than the pure Hartree–Fock. Varying the contributions of nonlocal exchange and correlation (by changing $\beta$

**TABLE I.**
**Experimental and Computed Data for HCN.**

| | Distances, Å | | | | | rms error, | $E_{tot}$, | $\Delta H_{atomiz.}$, |
|---|---|---|---|---|---|---|---|---|
| Method[a] | H—C | C—N | | $I_i$ or $\lvert\varepsilon_i\rvert$, ev | | ev | hartrees | kcal/mol |
| Experiment[b] | 1.065 | 1.153 | 13.80 | 14.15 | 19.68 | — | — | 304.1 |
| Hartree–Fock | 1.060 | 1.133 | 13.70 | 15.80 | 22.14 | 1.71 | −92.88066 | 187 |
| B3LYP: | | | | | | | | |
| 0.80, 0.72, 0.81 | 1.071 | 1.158 | 10.10 | 10.70 | 16.78 | 3.37 | −93.43061 | 300 |
| 0.60, 0.72, 0.81 | 1.063 | 1.148 | 11.28 | 12.28 | 18.50 | 1.94 | −93.66497 | 280 |
| 0.50, 0.72, 0.81 | 1.059 | 1.144 | 11.88 | 13.08 | 19.37 | 1.28 | −93.78295 | 271 |
| 0.40, 0.72, 0.81 | 1.055 | 1.140 | 12.48 | 13.89 | 20.24 | 0.84 | −93.90144 | 262 |
| 0.30, 0.72, 0.81 | 1.052 | 1.136 | 13.08 | 14.70 | 21.12 | 0.98 | −94.02043 | 252 |
| 0.40, 0.50, 0.81 | 1.058 | 1.139 | 12.46 | 13.79 | 20.10 | 0.84 | −93.62756 | 272 |
| 0.40, 0.25, 0.81 | 1.061 | 1.139 | 12.45 | 13.69 | 19.94 | 0.84 | −93.31669 | 283 |
| 0.40, 0.00, 0.81 | 1.064 | 1.138 | 12.43 | 13.58 | 19.78 | 0.86 | −93.00619 | 295 |
| 0.00, 0.00, 0.81 | 1.051 | 1.124 | 14.85 | 16.85 | 23.26 | 2.66 | −93.48260 | 259 |
| 0.40, 0.72, 1.00 | 1.056 | 1.141 | 12.29 | 13.70 | 20.04 | 0.93 | −93.76413 | 261 |
| 0.30, 0.72, 1.00 | 1.053 | 1.137 | 12.89 | 14.51 | 20.91 | 0.91 | −93.88306 | 252 |
| 0.30, 0.72, 0.60 | 1.050 | 1.135 | 13.28 | 14.91 | 21.36 | 1.11 | −94.17230 | 253 |
| B3PW91: | | | | | | | | |
| 0.80, 0.72, 0.81 | 1.071 | 1.157 | 10.13 | 10.68 | 16.78 | 3.36 | −93.38740 | 298 |
| 0.60, 0.72, 0.81 | 1.063 | 1.148 | 11.33 | 12.26 | 18.51 | 1.92 | −93.62217 | 279 |
| 0.50, 0.72, 0.81 | 1.060 | 1.144 | 11.93 | 13.06 | 19.37 | 1.26 | −93.74034 | 269 |
| 0.40, 0.72, 0.81 | 1.056 | 1.140 | 12.53 | 13.87 | 20.25 | 0.82 | −93.85902 | 260 |
| 0.30, 0.72, 0.81 | 1.052 | 1.136 | 13.14 | 14.69 | 21.13 | 0.97 | −93.97819 | 251 |
| 0.40, 0.50, 0.81 | 1.059 | 1.139 | 12.52 | 13.78 | 20.10 | 0.81 | −93.58515 | 270 |
| 0.40, 0.25, 0.81 | 1.061 | 1.139 | 12.50 | 13.68 | 19.94 | 0.81 | −93.27428 | 282 |
| 0.40, 0.00, 0.81 | 1.064 | 1.138 | 12.49 | 13.57 | 19.78 | 0.83 | −92.96379 | 293 |
| 0.00, 0.00, 0.81 | 1.052 | 1.124 | 14.92 | 16.84 | 23.27 | 2.67 | −93.44089 | 258 |
| 0.40, 0.72, 1.00 | 1.057 | 1.140 | 12.48 | 13.80 | 20.16 | 0.84 | −93.77647 | 261 |
| 0.30, 0.72, 1.00 | 1.053 | 1.136 | 13.09 | 14.61 | 21.04 | 0.92 | −93.89564 | 252 |
| 0.30, 0.72, 0.60 | 1.051 | 1.136 | 13.20 | 14.77 | 21.23 | 1.02 | −94.06947 | 250 |
| B3P86: | | | | | | | | |
| 0.80, 0.72, 0.81 | 1.071 | 1.157 | 10.70 | 11.25 | 17.35 | 2.80 | −93.67108 | 308 |
| 0.60, 0.72, 0.81 | 1.063 | 1.148 | 11.89 | 12.83 | 19.07 | 1.39 | −93.90594 | 288 |
| 0.50, 0.72, 0.81 | 1.059 | 1.143 | 12.49 | 13.64 | 19.94 | 0.83 | −94.02416 | 279 |
| 0.40, 0.72, 0.81 | 1.055 | 1.139 | 13.10 | 14.44 | 20.82 | 0.79 | −94.14288 | 270 |
| 0.30, 0.72, 0.81 | 1.052 | 1.135 | 13.70 | 15.26 | 21.70 | 1.33 | −94.26210 | 261 |
| 0.40, 0.50, 0.81 | 1.058 | 1.139 | 13.08 | 14.35 | 20.67 | 0.72 | −93.86901 | 280 |
| 0.40, 0.25, 0.81 | 1.061 | 1.138 | 13.07 | 14.25 | 20.51 | 0.64 | −93.55814 | 291 |
| 0.40, 0.00, 0.81 | 1.064 | 1.138 | 13.05 | 14.14 | 20.35 | 0.58 | −93.24764 | 303 |
| 0.00, 0.00, 0.81 | 1.051 | 1.123 | 15.48 | 17.41 | 23.84 | 3.20 | −93.72490 | 267 |
| 0.40, 0.72, 1.00 | 1.057 | 1.140 | 13.06 | 14.38 | 20.74 | 0.76 | −94.06221 | 271 |
| 0.30, 0.72, 1.00 | 1.053 | 1.136 | 13.66 | 15.20 | 21.62 | 1.28 | −94.18143 | 262 |
| 0.30, 0.72, 0.60 | 1.051 | 1.135 | 13.74 | 15.32 | 21.78 | 1.39 | −94.35131 | 259 |

[a] All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

[b] Distances: ref. 39; ionization potentials: ref. 40; atomization energies: ref. 41.

**TABLE II.**

**Experimental and Computed Data for $N_2$.**

| Method[a] | Distances, Å | $I_i$ or $\lvert\varepsilon_i\rvert$, ev | | | rms error, ev | $E_{tot}$, hartrees | $\Delta H_{atomiz.}$, kcal/mol |
|---|---|---|---|---|---|---|---|
| Experiment[b] | 1.098 | 15.60 | 16.98 | 18.78 | — | — | 226.0 |
| Hartree–Fock | 1.078 | 17.31 | 17.02 | 21.08 | 1.65 | −108.94702 | 106 |
| B3LYP: | | | | | | | |
| 0.80, 0.72, 0.81 | 1.105 | 11.95 | 12.87 | 15.35 | 3.74 | −109.52978 | 220 |
| 0.60, 0.72, 0.81 | 1.096 | 13.61 | 14.20 | 17.12 | 2.19 | −109.77762 | 200 |
| 0.50, 0.72, 0.81 | 1.091 | 14.45 | 14.87 | 18.01 | 1.46 | −109.90230 | 190 |
| 0.40, 0.72, 0.81 | 1.087 | 15.30 | 15.54 | 18.91 | 0.85 | −110.02746 | 181 |
| 0.30, 0.72, 0.81 | 1.083 | 16.15 | 16.21 | 19.80 | 0.80 | −110.15310 | 171 |
| 0.40, 0.50, 0.81 | 1.086 | 15.21 | 15.54 | 18.78 | 0.86 | −109.73372 | 188 |
| 0.40, 0.25, 0.81 | 1.085 | 15.12 | 15.54 | 18.65 | 0.88 | −109.40017 | 197 |
| 0.40, 0.00, 0.81 | 1.085 | 15.02 | 15.54 | 18.51 | 0.91 | −109.06690 | 205 |
| 0.00, 0.00, 0.81 | 1.070 | 18.44 | 18.23 | 22.11 | 2.63 | −109.57060 | 169 |
| 0.40, 0.72, 1.00 | 1.088 | 15.10 | 15.36 | 18.71 | 0.98 | −109.88749 | 181 |
| 0.30, 0.72, 1.00 | 1.084 | 15.95 | 16.03 | 19.61 | 0.76 | −110.01308 | 171 |
| 0.30, 0.72, 0.60 | 1.083 | 16.37 | 16.42 | 20.02 | 0.90 | −110.30789 | 171 |
| B3PW91: | | | | | | | |
| 0.80, 0.72, 0.81 | 1.104 | 11.90 | 12.91 | 15.37 | 3.74 | −109.48157 | 216 |
| 0.60, 0.72, 0.81 | 1.095 | 13.56 | 14.25 | 17.15 | 2.18 | −109.72987 | 196 |
| 0.50, 0.72, 0.81 | 1.091 | 14.40 | 14.93 | 18.04 | 1.44 | −109.85477 | 187 |
| 0.40, 0.72, 0.81 | 1.086 | 15.25 | 15.60 | 18.94 | 0.83 | −109.98015 | 177 |
| 0.30, 0.72, 0.81 | 1.083 | 16.10 | 16.28 | 19.84 | 0.79 | −110.10598 | 168 |
| 0.40, 0.50, 0.81 | 1.086 | 15.17 | 15.60 | 18.82 | 0.83 | −109.68641 | 185 |
| 0.40, 0.25, 0.81 | 1.085 | 15.07 | 15.60 | 18.68 | 0.86 | −109.35288 | 193 |
| 0.40, 0.00, 0.81 | 1.084 | 14.98 | 15.60 | 18.55 | 0.88 | −109.01962 | 202 |
| 0.00, 0.00, 0.81 | 1.070 | 18.40 | 18.31 | 22.15 | 2.64 | −109.52408 | 166 |
| 0.40, 0.72, 1.00 | 1.086 | 15.16 | 15.55 | 18.87 | 0.87 | −109.89444 | 178 |
| 0.30, 0.72, 1.00 | 1.083 | 16.02 | 16.23 | 19.77 | 0.76 | −110.02030 | 169 |
| 0.30, 0.72, 0.60 | 1.082 | 16.20 | 16.34 | 19.92 | 0.83 | −110.20071 | 167 |
| B3P86: | | | | | | | |
| 0.80, 0.72, 0.81 | 1.104 | 12.48 | 13.49 | 15.95 | 3.16 | −109.76926 | 224 |
| 0.60, 0.72, 0.81 | 1.094 | 14.14 | 14.83 | 17.72 | 1.62 | −110.01765 | 204 |
| 0.50, 0.72, 0.81 | 1.090 | 14.98 | 15.50 | 18.62 | 0.93 | −110.14258 | 195 |
| 0.40, 0.72, 0.81 | 1.086 | 15.83 | 16.18 | 19.52 | 0.64 | −110.26800 | 185 |
| 0.30, 0.72, 0.81 | 1.082 | 16.69 | 16.85 | 20.42 | 1.14 | −110.39387 | 176 |
| 0.40, 0.50, 0.81 | 1.085 | 15.75 | 16.18 | 19.39 | 0.59 | −109.97426 | 193 |
| 0.40, 0.25, 0.81 | 1.084 | 15.65 | 16.17 | 19.26 | 0.54 | −109.64072 | 201 |
| 0.40, 0.00, 0.81 | 1.083 | 15.56 | 16.17 | 19.12 | 0.51 | −109.30745 | 210 |
| 0.00, 0.00, 0.81 | 1.069 | 18.98 | 18.88 | 22.73 | 3.20 | −109.81206 | 174 |
| 0.40, 0.72, 1.00 | 1.086 | 15.76 | 16.14 | 19.46 | 0.63 | −110.18445 | 186 |
| 0.30, 0.72, 1.00 | 1.082 | 16.62 | 16.81 | 20.36 | 1.09 | −110.31034 | 177 |
| 0.30, 0.72, 0.60 | 1.082 | 16.76 | 16.89 | 20.48 | 1.19 | −110.48624 | 175 |

[a] All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

[b] Distances: ref. 39; ionization potentials: ref. 40; atomization energies: ref. 41.

**TABLE III.**
**Experimental and Computed Data for $N_2O$.**

| Method[a] | Distances, Å |  | $I_i$ or $\lvert\varepsilon_i\rvert$, ev |  |  |  | rms error, ev | $E_{tot}$, hartrees | $\Delta H_{atomiz.}$, kcal/mol |
|---|---|---|---|---|---|---|---|---|---|
|  | N—N | N—O |  |  |  |  |  |  |  |
| Experiment[b] | 1.128 | 1.184 | 12.89 | 16.38 | 18.23 | 20.11 | — | — | 266.0 |
| Hartree–Fock | 1.091 | 1.181 | 13.54 | 19.05 | 21.15 | 22.51 | 2.34 | −183.68528 | 73 |
| B3LYP: |  |  |  |  |  |  |  |  |  |
| 0.80, 0.72, 0.81 | 1.133 | 1.195 | 9.64 | 13.32 | 15.56 | 16.75 | 3.10 | −184.66830 | 261 |
| 0.60, 0.72, 0.81 | 1.119 | 1.189 | 10.88 | 15.08 | 17.29 | 18.51 | 1.51 | −185.04660 | 220 |
| 0.50, 0.72, 0.81 | 1.112 | 1.187 | 11.52 | 15.97 | 18.14 | 19.39 | 0.80 | −185.23746 | 200 |
| 0.40, 0.72, 0.81 | 1.106 | 1.186 | 12.16 | 16.87 | 18.99 | 20.28 | 0.59 | −185.42940 | 181 |
| 0.30, 0.72, 0.81 | 1.100 | 1.185 | 12.82 | 17.78 | 19.84 | 21.16 | 1.19 | −185.62239 | 162 |
| 0.40, 0.50, 0.81 | 1.106 | 1.181 | 12.12 | 16.76 | 19.03 | 20.21 | 0.59 | −184.96728 | 198 |
| 0.40, 0.25, 0.81 | 1.105 | 1.175 | 12.08 | 16.64 | 19.08 | 20.14 | 0.60 | −184.44267 | 218 |
| 0.40, 0.00, 0.81 | 1.104 | 1.171 | 12.04 | 16.51 | 19.12 | 20.07 | 0.62 | −183.91859 | 238 |
| 0.00, 0.00, 0.81 | 1.083 | 1.166 | 14.69 | 20.15 | 22.49 | 23.66 | 3.47 | −184.69391 | 165 |
| 0.40, 0.72, 1.00 | 1.107 | 1.186 | 11.97 | 16.67 | 18.81 | 20.08 | 0.56 | −185.20893 | 182 |
| 0.30, 0.72, 1.00 | 1.101 | 1.185 | 12.63 | 17.58 | 19.65 | 20.97 | 1.03 | −185.40185 | 163 |
| 0.30, 0.72. 0.60 | 1.100 | 1.185 | 13.03 | 18.00 | 20.05 | 21.38 | 1.38 | −185.86620 | 161 |
| B3PW91: |  |  |  |  |  |  |  |  |  |
| 0.80, 0.72, 0.81 | 1.132 | 1.189 | 9.65 | 13.30 | 15.65 | 16.80 | 3.07 | −184.59574 | 262 |
| 0.60, 0.72, 0.81 | 1.118 | 1.183 | 10.89 | 15.05 | 17.39 | 18.57 | 1.49 | −184.97495 | 221 |
| 0.50, 0.72, 0.81 | 1.112 | 1.181 | 11.53 | 15.94 | 18.25 | 19.46 | 0.79 | −185.16622 | 201 |
| 0.40, 0.72, 0.81 | 1.106 | 1.179 | 12.18 | 16.84 | 19.10 | 20.35 | 0.62 | −185.35855 | 182 |
| 0.30, 0.72, 0.81 | 1.100 | 1.178 | 12.84 | 17.75 | 19.95 | 21.25 | 1.24 | −185.55191 | 162 |
| 0.40, 0.50, 0.81 | 1.105 | 1.175 | 12.14 | 16.73 | 19.14 | 20.29 | 0.62 | −184.89658 | 199 |
| 0.40, 0.25, 0.81 | 1.104 | 1.170 | 12.10 | 16.61 | 19.18 | 20.22 | 0.63 | −184.37212 | 219 |
| 0.40, 0.00, 0.81 | 1.104 | 1.165 | 12.06 | 16.49 | 19.22 | 20.15 | 0.65 | −183.84819 | 239 |
| 0.00, 0.00, 0.81 | 1.083 | 1.160 | 14.71 | 20.12 | 22.62 | 23.77 | 3.53 | −184.62487 | 166 |
| 0.40, 0.72, 1.00 | 1.106 | 1.177 | 12.11 | 16.76 | 19.06 | 20.30 | 0.61 | −185.22492 | 185 |
| 0.30, 0.72, 1.00 | 1.100 | 1.176 | 12.77 | 17.66 | 19.92 | 21.20 | 1.19 | −185.41831 | 166 |
| 0.30, 0.72, 0.60 | 1.100 | 1.180 | 12.91 | 17.84 | 20.00 | 21.31 | 1.29 | −185.69962 | 159 |
| B3P86: |  |  |  |  |  |  |  |  |  |
| 0.80, 0.72, 0.81 | 1.131 | 1.188 | 10.23 | 13.88 | 16.23 | 17.38 | 2.49 | −185.05242 | 274 |
| 0.60, 0.72, 0.81 | 1.118 | 1.182 | 11.47 | 15.63 | 17.97 | 19.15 | 0.94 | −185.43175 | 233 |
| 0.50, 0.72, 0.81 | 1.111 | 1.180 | 12.11 | 16.52 | 18.83 | 20.04 | 0.50 | −185.62307 | 213 |
| 0.40, 0.72, 0.81 | 1.105 | 1.179 | 12.76 | 17.42 | 19.69 | 20.94 | 0.99 | −185.81545 | 193 |
| 0.30, 0.72, 0.81 | 1.099 | 1.178 | 13.41 | 18.33 | 20.54 | 21.83 | 1.76 | −186.00885 | 174 |
| 0.40, 0.50, 0.81 | 1.105 | 1.174 | 12.72 | 17.32 | 19.72 | 20.87 | 0.96 | −185.35347 | 211 |
| 0.40, 0.25, 0.81 | 1.104 | 1.170 | 12.68 | 17.19 | 19.76 | 20.80 | 0.94 | −184.82901 | 231 |
| 0.40, 0.00, 0.81 | 1.103 | 1.165 | 12.63 | 17.07 | 19.80 | 20.73 | 0.92 | −184.30507 | 251 |
| 0.00, 0.00, 0.81 | 1.083 | 1.160 | 15.29 | 20.70 | 23.20 | 24.35 | 4.10 | −185.08193 | 178 |
| 0.40, 0.72, 1.00 | 1.106 | 1.177 | 12.71 | 17.36 | 19.66 | 20.90 | 0.96 | −185.68558 | 197 |
| 0.30, 0.72, 1.00 | 1.100 | 1.176 | 13.36 | 18.26 | 20.51 | 21.80 | 1.72 | −185.87901 | 178 |
| 0.30, 0.72, 0.60 | 1.099 | 1.179 | 13.47 | 18.41 | 20.56 | 21.87 | 1.80 | −186.15243 | 170 |

[a] All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

[b] Distances: ref. 39; ionization potentials: ref. 40; atomization energies: ref. 41.

**TABLE IV.**
**Experimental and Computed Data for $OF_2$.**

| Method[a] | Distance, Å | Angle, deg. | $I_i$ or $\lvert\varepsilon_i\rvert$, ev | | | | | | | rms error, ev | $E_{tot}$, hartrees | $\Delta H_{atomiz.}$, kcal/mol |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Experiment[b] | 1.412 | 103.2 | 13.26 | 16.17 | 16.32 | 16.47 | 18.68 | 19.50 | 20.90 | — | — | 91.7 |
| Hartree–Fock | 1.3477 | 103.3 | 15.42 | 17.91 | 18.63 | 19.87 | 22.96 | 22.55 | 22.54 | 2.80 | −273.46365 | −44 |
| B3LYP: | | | | | | | | | | | | |
| 0.80, 0.72, 0.81 | 1.413 | 104.0 | 9.74 | 12.69 | 12.53 | 12.99 | 15.30 | 15.99 | 17.26 | 3.55 | −274.67284 | 88 |
| 0.60, 0.72, 0.81 | 1.395 | 103.6 | 11.53 | 14.34 | 14.37 | 15.03 | 17.52 | 17.82 | 18.80 | 1.72 | −275.15491 | 51 |
| 0.50, 0.72, 0.81 | 1.387 | 103.5 | 12.44 | 15.16 | 15.31 | 16.06 | 18.64 | 18.77 | 19.58 | 0.86 | −275.39789 | 33 |
| 0.40, 0.72, 0.81 | 1.380 | 103.4 | 13.35 | 15.98 | 16.25 | 17.10 | 19.76 | 19.74 | 20.37 | 0.53 | −275.64204 | 16 |
| 0.30, 0.72, 0.81 | 1.373 | 103.4 | 14.28 | 16.80 | 17.20 | 18.14 | 20.89 | 20.72 | 21.17 | 1.28 | −275.88728 | −1 |
| 0.40, 0.50, 0.81 | 1.370 | 103.4 | 13.18 | 15.93 | 16.19 | 17.05 | 19.80 | 19.82 | 20.49 | 0.53 | −275.05476 | 32 |
| 0.40, 0.25, 0.81 | 1.359 | 103.2 | 12.98 | 15.87 | 16.13 | 17.00 | 19.86 | 19.92 | 20.62 | 0.55 | −274.38835 | 50 |
| 0.40, 0.00, 0.81 | 1.349 | 103.1 | 12.78 | 15.81 | 16.06 | 16.96 | 19.91 | 20.01 | 20.75 | 0.59 | −273.72293 | 68 |
| 0.00, 0.00, 0.81 | 1.328 | 103.1 | 16.46 | 19.14 | 19.88 | 21.14 | 24.40 | 24.02 | 24.04 | 4.08 | −274.70837 | 3 |
| 0.40, 0.72, 1.00 | 1.379 | 103.4 | 13.15 | 15.79 | 16.05 | 16.90 | 19.58 | 19.56 | 20.19 | 0.50 | −275.37420 | 18 |
| 0.30, 0.72, 1.00 | 1.373 | 103.4 | 14.07 | 16.61 | 17.00 | 17.94 | 20.70 | 20.54 | 20.99 | 1.11 | −275.61934 | 1 |
| 0.30, 0.72, 0.60 | 1.374 | 103.5 | 14.51 | 17.02 | 17.42 | 18.36 | 21.09 | 20.92 | 21.37 | 1.47 | −276.18348 | −3 |
| B3PW91: | | | | | | | | | | | | |
| 0.80, 0.72, 0.81 | 1.401 | 104.0 | 9.57 | 12.64 | 12.48 | 12.96 | 15.34 | 16.07 | 17.39 | 3.55 | −274.56710 | 88 |
| 0.60, 0.72, 0.81 | 1.384 | 103.6 | 11.37 | 14.30 | 14.33 | 15.01 | 17.58 | 17.92 | 18.95 | 1.72 | −275.05061 | 51 |
| 0.50, 0.72, 0.81 | 1.376 | 103.6 | 12.28 | 15.13 | 15.28 | 16.04 | 18.70 | 18.88 | 19.75 | 0.85 | −275.29426 | 34 |
| 0.40, 0.72, 0.81 | 1.369 | 103.5 | 13.19 | 15.96 | 16.23 | 17.09 | 19.83 | 19.85 | 20.54 | 0.54 | −275.53904 | 16 |
| 0.30, 0.72, 0.81 | 1.363 | 103.5 | 14.12 | 16.79 | 17.19 | 18.13 | 20.95 | 20.84 | 21.35 | 1.30 | −275.78489 | −1 |
| 0.40, 0.50, 0.81 | 1.360 | 103.4 | 13.02 | 15.90 | 16.17 | 17.04 | 19.87 | 19.93 | 20.66 | 0.55 | −274.95222 | 32 |
| 0.40, 0.25, 0.81 | 1.349 | 103.3 | 12.82 | 15.84 | 16.11 | 17.00 | 19.93 | 20.03 | 20.79 | 0.60 | −274.28631 | 51 |
| 0.40, 0.00, 0.81 | 1.340 | 103.2 | 12.62 | 15.78 | 16.04 | 16.95 | 19.98 | 20.12 | 20.91 | 0.67 | −273.62140 | 70 |
| 0.00, 0.00, 0.81 | 1.320 | 103.2 | 16.31 | 19.14 | 19.88 | 21.15 | 24.48 | 24.15 | 24.23 | 4.12 | −274.60899 | 4 |
| 0.40, 0.72, 1.00 | 1.366 | 103.5 | 13.06 | 15.88 | 16.15 | 17.01 | 19.78 | 19.82 | 20.53 | 0.52 | −275.37097 | 19 |
| 0.30, 0.72, 1.00 | 1.360 | 103.5 | 13.99 | 16.71 | 17.10 | 18.06 | 20.90 | 20.81 | 21.34 | 1.24 | −275.61689 | 2 |
| 0.30, 0.72, 0.60 | 1.367 | 103.5 | 14.26 | 16.88 | 17.28 | 18.22 | 21.00 | 20.87 | 21.36 | 1.36 | −275.97068 | −4 |

**TABLE IV.**
**(Continued)**

| Method[a] | Distance, Å | Angle, deg. | $I_i$ or $\lvert\varepsilon_i\rvert$, ev | | | | | | | rms error, ev | $E_{tot}$, hartrees | $\Delta H_{atomiz.}$, kcal/mol |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B3P86: | | | | | | | | | | | | |
| 0.80, 0.72, 0.81 | 1.399 | 103.9 | 10.14 | 13.23 | 13.06 | 13.54 | 15.95 | 16.67 | 18.00 | 2.96 | −275.11862 | 96 |
| 0.60, 0.72, 0.81 | 1.382 | 103.6 | 11.94 | 14.88 | 14.92 | 15.60 | 18.19 | 18.53 | 19.56 | 1.29 | −275.60228 | 59 |
| 0.50, 0.72, 0.81 | 1.374 | 103.5 | 12.85 | 15.71 | 15.86 | 16.63 | 19.31 | 19.49 | 20.35 | 0.43 | −275.84599 | 41 |
| 0.40, 0.72, 0.81 | 1.368 | 103.5 | 13.76 | 16.54 | 16.81 | 17.67 | 20.43 | 20.46 | 21.15 | 0.93 | −276.09084 | 24 |
| 0.30, 0.72, 0.81 | 1.362 | 103.5 | 14.69 | 17.37 | 17.77 | 18.72 | 21.56 | 21.45 | 21.95 | 1.85 | −276.33674 | 7 |
| 0.40, 0.50, 0.81 | 1.358 | 103.4 | 13.59 | 16.49 | 16.75 | 17.63 | 20.48 | 20.54 | 21.26 | 0.94 | −275.50407 | 40 |
| 0.40, 0.25, 0.81 | 1.348 | 103.3 | 13.39 | 16.43 | 16.69 | 17.58 | 20.53 | 20.63 | 21.39 | 0.96 | −274.83823 | 59 |
| 0.40, 0.00, 0.81 | 1.338 | 103.2 | 13.19 | 16.37 | 16.62 | 17.54 | 20.59 | 20.72 | 21.51 | 0.98 | −274.17337 | 77 |
| 0.00, 0.00, 0.81 | 1.318 | 103.1 | 16.88 | 19.73 | 20.46 | 21.74 | 25.09 | 24.76 | 24.83 | 4.70 | −275.16114 | 12 |
| 0.40, 0.72, 1.00 | 1.365 | 103.4 | 13.65 | 16.48 | 16.74 | 17.61 | 20.41 | 20.45 | 21.15 | 0.90 | −275.92843 | 28 |
| 0.30, 0.72, 1.00 | 1.359 | 103.4 | 14.58 | 17.31 | 17.70 | 18.66 | 21.53 | 21.43 | 21.95 | 1.80 | −276.17438 | 11 |
| 0.30, 0.72, 0.60 | 1.365 | 103.5 | 14.81 | 17.44 | 17.84 | 18.79 | 21.59 | 21.46 | 21.95 | 1.89 | −276.51632 | 3 |

[a] All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

[b] Distance and angle: ref. 42; ionization potentials: ref. 40; atomization energies: ref. 41.

**TABLE V.**
**Experimental and Computed Data for $H_2O$.**

| Method[a] | Distance, Å | Angle, deg. | $I_i$ or $\lvert\varepsilon_i\rvert$, ev | | | rms error, ev | $E_{tot}$, hartrees | $\Delta H_{atomiz.}$, kcal/mol |
|---|---|---|---|---|---|---|---|---|
| Experiment[b] | 0.958 | 104.5 | 12.62 | 14.74 | 18.51 | — | — | 221.6 |
| Hartree–Fock | 0.943 | 107.1 | 13.87 | 15.81 | 19.94 | 1.26 | −76.03123 | 143 |
| B3LYP: | | | | | | | | |
| 0.80, 0.72, 0.81 | 0.965 | 105.7 | 8.74 | 10.73 | 14.75 | 3.88 | −76.43405 | 217 |
| 0.60, 0.72, 0.81 | 0.956 | 106.1 | 10.33 | 12.31 | 16.40 | 2.28 | −76.59810 | 206 |
| 0.50, 0.72, 0.81 | 0.951 | 106.3 | 11.13 | 13.11 | 17.22 | 1.48 | −76.68061 | 200 |
| 0.40, 0.72, 0.81 | 0.947 | 106.4 | 11.95 | 13.92 | 18.06 | 0.66 | −76.76342 | 195 |
| 0.30, 0.72, 0.81 | 0.943 | 106.5 | 12.77 | 14.74 | 18.90 | 0.24 | −76.84653 | 189 |
| 0.40, 0.50, 0.81 | 0.948 | 106.6 | 11.87 | 13.83 | 17.98 | 0.75 | −76.57214 | 202 |
| 0.40, 0.25, 0.81 | 0.949 | 106.8 | 11.77 | 13.72 | 17.89 | 0.85 | −76.35502 | 210 |
| 0.40, 0.00, 0.81 | 0.950 | 107.0 | 11.68 | 13.61 | 17.79 | 0.94 | −76.13814 | 218 |
| 0.00, 0.00, 0.81 | 0.935 | 107.4 | 14.98 | 16.92 | 21.17 | 2.41 | −76.47088 | 197 |
| 0.40, 0.72, 1.00 | 0.948 | 106.4 | 11.76 | 13.73 | 17.85 | 0.86 | −76.66486 | 194 |
| 0.30, 0.72, 1.00 | 0.944 | 106.5 | 12.58 | 14.55 | 18.69 | 0.15 | −76.74791 | 188 |
| 0.30, 0.72, 0.60 | 0.942 | 106.5 | 12.98 | 14.96 | 19.13 | 0.43 | −76.95558 | 190 |
| B3PW91: | | | | | | | | |
| 0.80, 0.72, 0.81 | 0.963 | 105.6 | 8.69 | 10.71 | 14.76 | 3.91 | −76.40460 | 216 |
| 0.60, 0.72, 0.81 | 0.953 | 106.0 | 10.29 | 12.30 | 16.41 | 2.29 | −76.56922 | 204 |
| 0.50, 0.72, 0.81 | 0.949 | 106.2 | 11.10 | 13.11 | 17.24 | 1.48 | −76.65199 | 199 |
| 0.40, 0.72, 0.81 | 0.945 | 106.3 | 11.92 | 13.93 | 18.08 | 0.67 | −76.73507 | 193 |
| 0.30, 0.72, 0.81 | 0.941 | 106.4 | 12.75 | 14.76 | 18.93 | 0.25 | −76.81843 | 188 |
| 0.40, 0.50, 0.81 | 0.946 | 106.5 | 11.84 | 13.84 | 18.00 | 0.75 | −76.54380 | 201 |
| 0.40, 0.25, 0.81 | 0.947 | 106.7 | 11.75 | 13.73 | 17.91 | 0.84 | −76.32668 | 209 |
| 0.40, 0.00, 0.81 | 0.948 | 106.9 | 11.66 | 13.62 | 17.82 | 0.94 | −76.10981 | 217 |
| 0.00, 0.00, 0.81 | 0.933 | 107.3 | 14.97 | 16.95 | 21.22 | 2.43 | −76.44351 | 196 |
| 0.40, 0.72, 1.00 | 0.945 | 106.3 | 11.84 | 13.85 | 18.00 | 0.74 | −76.67632 | 193 |
| 0.30, 0.72, 1.00 | 0.941 | 106.4 | 12.67 | 14.68 | 18.85 | 0.20 | −76.75969 | 187 |
| 0.30, 0.72, 0.60 | 0.941 | 106.4 | 12.84 | 14.84 | 19.01 | 0.32 | −76.88338 | 188 |
| B3P86: | | | | | | | | |
| 0.80, 0.72, 0.81 | 0.963 | 105.7 | 9.26 | 11.28 | 15.32 | 3.34 | −76.61055 | 224 |
| 0.60, 0.72, 0.81 | 0.953 | 106.0 | 10.86 | 12.87 | 16.97 | 1.73 | −76.77521 | 213 |
| 0.50, 0.72, 0.81 | 0.949 | 106.2 | 11.67 | 13.68 | 17.81 | 0.92 | −76.85800 | 208 |
| 0.40, 0.72, 0.81 | 0.945 | 106.4 | 12.49 | 14.49 | 18.65 | 0.18 | −76.94109 | 202 |
| 0.30, 0.72, 0.81 | 0.941 | 106.5 | 13.32 | 15.32 | 19.49 | 0.77 | −77.02447 | 197 |
| 0.40, 0.50, 0.81 | 0.946 | 106.6 | 12.41 | 14.40 | 18.56 | 0.23 | −76.74983 | 209 |
| 0.40, 0.25, 0.81 | 0.947 | 106.8 | 12.32 | 14.29 | 18.47 | 0.31 | −76.53274 | 217 |
| 0.40, 0.00, 0.81 | 0.948 | 107.0 | 12.23 | 14.18 | 18.38 | 0.40 | −76.31589 | 226 |
| 0.00, 0.00, 0.81 | 0.933 | 107.4 | 15.54 | 17.51 | 21.78 | 2.99 | −76.64964 | 205 |
| 0.40, 0.72, 1.00 | 0.945 | 106.4 | 12.43 | 14.43 | 18.58 | 0.21 | −76.88420 | 203 |
| 0.30, 0.72, 1.00 | 0.941 | 106.5 | 13.25 | 15.26 | 19.42 | 0.71 | −76.96758 | 197 |
| 0.30, 0.72, 0.60 | 0.941 | 106.5 | 13.39 | 15.39 | 19.57 | 0.84 | −77.08738 | 196 |

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[a] All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

[b] Distance and angle: ref. 39; ionization potentials: ref. 40; atomization energies: ref. 41.

and $\gamma$) generally has only minor consequences, most notable for the N—O and F—O bonds. Particularly striking is the shortening of the latter with decreasing $\beta$ (about 0.03 A when $\beta$ goes from 0.72 to 0.00). Finally, the angles in $F_2O$ and $H_2O$ tend to be relatively little affected by changing the $\alpha$, $\beta$, $\gamma$ combination. The primary exceptions to this are when $\alpha = \beta = 0$ for $H_2O$.

### TOTAL ENERGIES AND ATOMIZATION ENTHALPIES

As expected, the standard Becke parameters give the most accurate atomization enthalpy in most instances, although the corresponding total energies are among the least negative. As $\alpha$ is decreased, with $\beta = 0.72$, $\gamma = 0.81$, the total energies become more negative but $\Delta H_{\text{atomiz.}}$ drops rapidly; for $\alpha = 0.40$, the changes relative to $\alpha = 0.80$ are about 39 kcal/mol for HCN and $N_2$, 80 for $N_2O$, 72 for $F_2O$, and 22 for $H_2O$. In fact, the LYP and PW91 calculations with $\alpha = 0.30$, $\beta = 0.72$, $\gamma = 0.81$ predict $F_2O$ to be unbound! Lowering $\beta$ (nonlocal exchange) makes the total energy more positive, but markedly improves the $\Delta H_{\text{atomiz.}}$. Thus, $\alpha = 0.40$, $\beta = 0.00$, $\gamma = 0.81$ yields more positive total energies than any other combination, but the atomization enthalpies are actually more accurate than for the standard parameters in three cases. Increasing and decreasing $\gamma$ (nonlocal correlation) respectively raises and lowers the total energy, but has little effect upon $\Delta H_{\text{atomiz.}}$ for HCN, $N_2$, and $H_2O$; for $N_2O$ and $F_2O$, the consquences for $\Delta H_{\text{atomiz.}}$ are slightly greater—3 or 4 kcal/mol. For each molecule and each functional, the parameter combination producing the most negative total energy (of those tested), but one of the least accurate $\Delta H_{\text{atomiz.}}$, was $\alpha = 0.30$, $\beta = 0.72$, $\gamma = 0.60$.

## Discussion

There is no single $\alpha$, $\beta$, $\gamma$ combination that can be identified as the optimum one for predicting electronic ionization potentials. However the results in Tables I–V indicate that $\alpha$ is the most important determinant of B3 orbital energies, and that $\alpha = 0.40$ is overall the most effective of the values investigated. Thus, the rms error obtained for all five molecules with the five $\alpha = 0.40$ combinations tested in this work is about 0.74 ev. This is considerably better than the best of the Hartree–Fock (1.26 ev, for $H_2O$). Of course, there are some notable special cases. For example, the $\alpha = 0.30$, $\beta = 0.72$, $\gamma = 1.00$ combination produced rms errors $\leq 0.20$ ev for $H_2O$ (LYP and PW91), and $\alpha = 0.50$, $\beta = 0.72$, $\gamma = 0.81$ gave rms errors $\leq 0.50$ ev for $N_2O$ and $F_2O$ (P86).

Hartree–Fock orbital energies tend to give better approximations to the ionization potentials of the highest occupied orbitals than the lower ones.[34] For the molecules in Tables I–V, the Hartree–Fock rms error for the highest orbital is 1.38 ev compared to 2.22 overall. For the $\alpha = 0.40$ combinations, the rms error for the highest orbital is 0.71 ev.

The trends shown by the atomization enthalpies in Tables I–V are interesting and suggestive. Equation (1) contains three types of terms: local density approximations, nonlocal corrections to these, and Hartree–Fock. It is well known that local density procedures considerably overestimate binding energies.[44–48] Becke demonstrated that the error can be substantially reduced by introducing his gradient correction;[9] for a group of 55 molecules, the average absolute deviation dropped from 36.2 to 3.7 kcal/mol.[49] On the other hand, Hartree–Fock calculations greatly underestimate binding energies,[43] as is confirmed again in Tables I–V. Becke's standard $\alpha$, $\beta$, $\gamma$ represents an optimum balance between these various tendencies. When $\alpha$ is decreased (so as to increase the magnitudes of the B3 orbital energies), then the role of local exchange is diminished and that of Hartree–Fock expanded, and the atomization enthalpies consequently become smaller. This can be reversed, however, by lessening the reducing effect of Becke's nonlocal exchange correction. As $\beta$ is decreased (with $\alpha = 0.40$, $\gamma = 0.81$), the $\Delta H_{\text{atomiz.}}$ increase until they are very similar to the values obtained with the standard parameters for HCN and $H_2O$, and approaching them for the other three molecules.

One can accordingly speculate that it may often be possible to obtain B3 $|\varepsilon_i|$ that are reasonable approximations to the electronic ionization potentials while maintaining satisfactory accuracy for other properties. This might be done, for example, by setting $\alpha = 0.40$, $\beta = 0.00$. The molecules that may pose a problem, based on the data in Tables I–V, are those having several linked "electron-rich" atoms, such as N, O, and F, which have high outer-shell electron densities.[50] Computational challenges associated with such molecules have been noted earlier,[43, 51–55] although the focus has been upon the treatment of correlation.

## Conclusions

It is certainly feasible, by suitable modification of the parameters in eq. (1), to achieve $|\varepsilon_i|$ that are good approximations to the experimental electronic ionization potentials. The primary determinant is $\alpha$, which governs the proportions of Slater local and Hartree–Fock exchange to be included. he parameter $\gamma$ can be adjusted to further improve the agreement. The particular $\alpha$, $\gamma$ combination that should be selected in any given case depends upon the correlation function being used and the general class of compounds to which the molecule of interest belongs; the data in Tables I–V provide some guidelines, and additional tests could, of course, be made for specific types of molecules. In general, $\alpha = 0.40$ appears to be a good starting point.

Our results suggest that for many organic molecules and others that do not involve bonds between N, O, and/or F atoms, setting $\beta = 0.00$ in conjunction with $\alpha = 0.40$ may produce acceptable approximations to electronic ionization potentials without an undue sacrifice of accuracy in other properties. This speculation will, of course, require considerable further investigation. In those instances in which this approach is not successful (e.g., $N_2O$ and $F_2O$), it may be necessary to determine ionization potentials and other properties in separate runs.

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