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# Parametrization of the Becke3-LYP Hybrid Functional for a Series of Small Molecules Using Quantum Molecular Similarity Techniques

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**ABSTRACT:** The  $a_0$ ,  $a_x$ , and  $a_c$  semiempirical parameters of the original Becke three-parameter method have been optimized by minimizing the difference between the density given by this method and the singles and doubles quadratic configuration interaction (QCISD) generalized density using quantum molecular similarity measures. The optimization is performed including the hybrid energy functional in a self-consistent fashion and employing the relaxed geometry at each set of  $a_0$ ,  $a_x$ , and  $a_c$  parameters. This method has been applied to a series of 16 small molecules with different bonding patterns. Results show that, at least in diatomic molecules, it is possible to obtain a set of parameters that reproduces almost exactly the QCISD electron density. The optimized parameters for the studied molecules follow two main general trends: (a) the parameters governing the amount of gradient corrections for exchange and correlation have similar values ( $a_c \approx a_x$ ); and (b) the larger the exact exchange included, the smaller the gradient correction for exchange needed ( $a_0 \approx 1 - a_x$ ). Especially interesting are the values obtained for the  $a_0$  parameter, which reflect how much exact exchange should be included in the description of a particular system. Finally, for  $H_2$  and  $LiH$ , we have carried out a search for other possible local minima on the quadratic error integral surface concluding that for these molecules there is not a unique set of parameters that produces a B3LYP density of QCISD quality.

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**Keywords:** density functional theory; hybrid functionals; B3LYP parametrization; quantum molecular similarity measures

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## Introduction

In the last decade, density functional theory (DFT)<sup>1–5</sup> has been gradually more employed for the prediction of molecular properties and for the study of chemical reactivity in many areas of chemistry, especially in the field of organometallic and bioinorganic chemistry.<sup>6</sup> The use of density gradients in exchange and correlation corrections [the so-called generalized gradient approximation (GGA)<sup>7–9</sup>] has led to significant improvements in the computed molecular structures and properties compared to those obtained from the earlier local spin-density approximation (LSDA), in particular the molecular bond energies.<sup>10</sup> Because DFT errors often arise from an unsatisfactory description of the exchange energy,<sup>4,11</sup> it is not surprising that even more accurate results can be usually achieved using hybrid functionals. These hybrid methods combine, in variable proportions, local and GGA treatments of exchange and correlation with Hartree–Fock exchange and are based on the adiabatic connection formula.<sup>12</sup>

Certainly the most used hybrid scheme for the exchange–correlation functional is Becke three-parameter method (B3), which was originally formulated as:<sup>13</sup>

$$E_{XC} = E_{XC}^{\text{LSDA}} + a_0(E_X^{\text{exact}} - E_X^{\text{LSDA}}) + a_x \Delta E_X^{\text{B88}} + a_c \Delta E_C^{\text{PW91}} \quad (1)$$

Here, the  $E_X^{\text{exact}}$  term corresponds to the Hartree–Fock exchange energy based on Kohn–Sham orbitals, while  $E_{XC}^{\text{LSDA}}$  is the uniform electron gas exchange–correlation energy,  $E_X^{\text{B88}}$  is the Becke 1988 gradient correction for exchange,<sup>7</sup> and  $E_C^{\text{PW91}}$  is the Perdew and Wang gradient correction for correlation.<sup>14</sup> Commonly, this procedure is referred to as the B3PW91 method. The coefficients  $a_0$ ,  $a_x$ , and  $a_c$  were determined by Becke<sup>13</sup> by a linear least-squares fit to 56 atomization energies, 42 ionization potentials, and 8 proton affinities. The values thus obtained, which are in some sense semiempirical, were  $a_0 = 0.20$ ,  $a_x = 0.72$ , and  $a_c = 0.81$ .

The so-called B3LYP functional is probably even more popular than the B3PW91 method. In the Gaussian 94<sup>15</sup> implementation, the expression used is similar to eq. (1) with some minor differences:<sup>16</sup>

$$E_{XC} = E_X^{\text{LSDA}} + a_0(E_X^{\text{exact}} - E_X^{\text{LSDA}}) + a_x \Delta E_X^{\text{B88}} + E_C^{\text{VWN}} + a_c(\Delta E_C^{\text{LYP}} - E_C^{\text{VWN}}) \quad (2)$$

In this equation, the Perdew and Wang correlation functional originally used by Becke is replaced

by the Lee–Yang–Parr (LYP)<sup>8</sup> one. Because the LYP functional already contains a local part and a gradient correction, one has to remove the local part to obtain a coherent implementation. This can be done in an approximate way by subtracting  $E_C^{\text{VWN}}$  to  $E_C^{\text{LYP}}$ . The method has been normally used with the same three parameters derived originally for the B3PW91 functional. Note that in the Gaussian 94 implementation the VWN functional is the one obtained by Vosko et al. from a fit to results obtained by the random phase approximation.<sup>17</sup> Other common hybrid schemes are Becke half-and-half (BhandH)<sup>18</sup> linear interpolation of the adiabatic connection integral, which takes the values of  $a_0 = 0.5$ , and  $a_x = a_c = 0$  in eq. (1), and the more recent B1 simplification<sup>19</sup> that takes  $a_x = 1 - a_0$  with  $a_c = 1$  and  $a_0 = 0.16$  or 0.28, depending on the choice of the GGA. Other hybrid methods, containing a predefined amount of exact exchange and the same number of adjustable parameters as their GGA constituents, have been explored recently by Adamo and Barone<sup>20</sup> based on the suggestion by Perdew et al., who found that  $a_0 \approx 0.25$  is to be expected for atomization energies of most molecules.<sup>21</sup> Finally, a new set of promising hybrid functionals involving a large number of parameters have been recently developed by Becke<sup>22</sup> and by Handy and collaborators<sup>23</sup> (the so-called B97 and HCTH, respectively).

The B3 procedures have been overall quite successful.<sup>24</sup> For instance, in a test on 55 atomization energies of the G2 set, it was found that B3LYP yields atomization energies superior to CCSD(T) for smaller basis sets, whereas for larger basis sets, CCSD(T) is superior.<sup>25</sup> Further, Bertran et al.<sup>26</sup> and Fonseca Guerra et al.<sup>27,28</sup> showed that the B3LYP and BP86 functionals perform remarkably well for the hydrogen bonds in Watson–Crick pairs. However, it is also true that, in general, for very weak interactions the accuracy of current functionals is not as impressive as for strong interactions. Indeed, the B3LYP method yields, in general, erroneous results for charge transfer and van der Waals complexes.<sup>29</sup>

Despite the undeniable success of the B3-based methods, some authors have considered the possibility of changing the values originally derived by Becke to improve the results for a particular property or class of molecules. Latajka and coworkers<sup>30</sup> were the first who proposed to change the  $a_0$  parameter from 0.20 to 0.35 in B3P86 calculations to better describe the structural properties of hydrogen-bonded complexes. Later on, it was reported<sup>31</sup> that a more accurate infrared signature of these hydrogen-bonded systems can be achieved by using the parameters  $a_0 = 0.322$ ,  $a_x = 1$ , and  $a_c = 0.67$ . On

the other hand, Chermette et al.<sup>32</sup> carried out a specific parametrization of the B3LYP functional for  $H_{2n+1}^+$  clusters using the  $H_5^+$  system as a reference. The optimization of the  $a_0$  and  $a_x$  parameters in eq. (1), which gives the B3LYP geometry that better matches the CCSD(T) structure of this  $H_5^+$  cluster, leads to values of  $a_0 = 0.559$  and  $a_x = 0.493$  ( $a_c$  was fixed to 1.0). More recently, Abu-Awwad and Politzer<sup>33</sup> have analyzed 12 parameter combinations of the B3LYP coefficients to find a set of parameters that provides orbital energies that can be taken as reasonable approximations to the ionization potentials. They have concluded that, despite there is no single parameter combination that can be identified as the optimum,  $a_0 = 0.4$  seems to be the best option to get accurate ionization potentials. Finally, we have to refer to the work carried out by Csonka and coworkers,<sup>34</sup> who analyzed the influence of the three parameters of the B3LYP method on the H—H equilibrium bond length. They concluded that the experimental H—H distance can be reproduced with appropriate selection of these parameters, although an infinite number of solutions exist.

Most of the suggestions made above<sup>30–34</sup> represent a substantial change compared to the original B3-parameters. Further, it is worth noting that, in the original fitting of the B3LYP parameters by Becke,<sup>13</sup> single-point energy calculations were performed at experimental geometries. Furthermore, the exact exchange and the gradient corrections were added in the evaluation of energies in a nonself-consistent fashion using converged LSDA densities. Finally, the parameters were optimized for the B3PW91 functional and not for the B3LYP method. Therefore, one can wonder whether a more precise parameterization of the B3LYP method may lead to a significant improvement of the method. The purpose of this work is to check such a hypothesis optimizing the  $a_0$ ,  $a_x$ , and  $a_c$  semiempirical parameters of the B3LYP method for a series of small molecules by minimizing the differences between the density furnished by the B3LYP method and the singles and doubles quadratic configuration interaction (QCISD)<sup>35</sup> generalized density, which is used as the reference density. Ideally, the reference density should be taken from experimental results. In practice, however, it is very difficult to obtain a reliable electron density from a direct experimental measurement. In this case, the best choice is to use an electron density obtained from a full configuration interaction calculation. Owing to computational limitations, here the QCISD generalized density is taken as the reference density, because

it is expected to be quite close to the exact density distribution. The optimization of the  $a_0$ ,  $a_x$ , and  $a_c$  parameters is then performed by minimizing the quadratic error integral between the B3LYP and the QCISD densities, including the GGA energy functional in a self-consistent fashion, and reoptimizing the geometry for each set of  $a_0$ ,  $a_x$ , and  $a_c$  parameters. Preliminary results on this work were published in ref. 36.

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## Method of Calculation

Let us define the function difference:

$$P(\vec{r}) = \rho_{\text{B3LYP}}(\vec{r}) - \rho_{\text{QCISD}}(\vec{r}) \quad (3)$$

If the  $a_0$ ,  $a_x$ , and  $a_c$  Becke parameters are allowed to change, the function difference  $P(\mathbf{r})$  will depend on these three parameters. Then, one can obtain the set of parameters that yields the B3LYP density closest to the QCISD density by minimizing the quadratic error integral:

$$D = \int P^2(\vec{r}) d\vec{r} \quad (4)$$

which is obtained as a function of  $a_0$ ,  $a_x$ , and  $a_c$ . The substitution of eq. (3) into eq. (4) leads to:

$$\begin{aligned} D = & \int \rho_{\text{B3LYP}}(\vec{r})\rho_{\text{B3LYP}}(\vec{r}) d\vec{r} \\ & - 2 \int \rho_{\text{B3LYP}}(\vec{r})\rho_{\text{QCISD}}(\vec{r}) d\vec{r} \\ & + \int \rho_{\text{QCISD}}(\vec{r})\rho_{\text{QCISD}}(\vec{r}) d\vec{r} \end{aligned} \quad (5)$$

Given the definition of quantum molecular similarity measure (QMSM) as:<sup>37,38</sup>

$$Z_{IJ} = \int \rho_I(\vec{r}) \cdot \rho_J(\vec{r}) d\vec{r} \quad (6)$$

one can see that the integrals appearing in eq. (5) are QMSMs. In particular, the second integral is the QMSM between the B3LYP and the QCISD densities, whereas the first and the third are the self-QMSM<sup>39</sup> of B3LYP and QCISD densities, respectively.

In this work, we have used the Gaussian 94 program<sup>15</sup> to perform QCISD and B3LYP calculations. B3LYP calculations with  $a_0$ ,  $a_x$ , and  $a_c$  coefficients different from the standard coefficients provided by Becke can be performed with Gaussian 94 using internal options.<sup>40</sup> The 6-311++G\*\* basis set<sup>40</sup> have been used throughout. This basis set is not really large enough for having converged results, but for QMSM differences such as those found in eqs.

(3)–(5) the particular choice of a basis set is less relevant. All calculations have been done within the restricted formalism except for open-shell systems that have been calculated using the unrestricted approach.

QMSM have been obtained from the Gaussian 94 electron densities using the Messem program<sup>42</sup> developed in our group. QCISD generalized densities<sup>43</sup> and B3LYP electron densities calculated from self-consistently converged Kohn–Sham orbitals have been used throughout. Gradients of the  $D$  function in eq. (5) with respect to the  $a_0$ ,  $a_x$ , and  $a_c$  parameters have been computed numerically, and the optimization of this function has been performed using the quasi-Newton Davidon–Fletcher–Powell (DFP) algorithm.<sup>44</sup>

Thus, starting from the initial set of  $a_0$ ,  $a_x$ , and  $a_c$  parameters given by Becke,<sup>13</sup> the QCISD and B3LYP electron densities are computed allowing complete electronic and nuclear relaxation of the system. With these two densities and using the Messem program one can obtain the value for the  $D$  function through eq. (5). After that, the gradients of the  $D$  function with respect to the  $a_0$ ,  $a_x$ , and  $a_c$  coefficients are computed numerically using the central difference approximation, i.e.:

$$\frac{\partial D}{\partial a_k} = \frac{D(a_k + \delta) - D(a_k - \delta)}{2\delta} \quad (7)$$

with  $\delta = 10^{-3}$ . Finally, and after checking the convergence of the process, a DFP optimization step is performed. We have considered that the optimization has been converged when the norm of the gradient vector was below  $2 \times 10^{-3}$  a.u. Throughout this contribution, the final converged  $a_0$ ,  $a_x$ , and  $a_c$  parameters will be referred to as the QCISD-density optimized parameters.

## Results and Discussion

The algorithm described in the previous section has been applied to the ground state of a series of 16 small molecules with different bonding patterns. Table I collects the QCISD-density optimized parameters for these species together with the initial quadratic error integral obtained when using the original Becke parameters ( $D_0$ ), the final  $D$  value obtained with the optimized parameters, the self-QMSM for the QCISD density, and the total delocalization index<sup>45–47</sup> computed using the AIMPAC series of programs.<sup>48</sup> Remarkably, the final  $D$  value in Table I is always much smaller than  $D_0$ , and smaller than 0.015 a.u. for all molecules. For diatomic molecules, the QCSID density and the B3LYP density calculated with the optimized parameters are almost identical with  $D$  values of about  $10^3$ – $10^{-4}$  a.u. As one can see in the  $D_0$  values of Table I,

**TABLE I.** 6-311++G\*\* Optimized Three Becke's Parameters, Initial and Final Quadratic Integral Error (a.u.) Obtained from eq. (5), Self-QMSM for QCISD, and Total Delocalization Index (Electrons).

Molecule	$a_0$	$a_x$	$a_c$	$D_0$	$D$	$Z_{\text{qcisdqcisd}}$	$\delta^a$
H <sub>2</sub>	0.260	0.540	0.490	0.0000	0.0000	2.6391	1.000
LiH	0.109	0.626	0.884	0.0031	0.0004	11.2373	0.225
BH	0.240	0.441	0.648	0.0025	0.0010	28.0567	0.780
Li <sub>2</sub>	0.398	0.772	0.506	0.0060	0.0007	20.0841	0.749
CH <sub>2</sub>	0.101	0.727	0.655	0.0061	0.0026	49.3282	—
H <sub>2</sub> O	0.305	0.654	1.080	0.0137	0.0009	93.2441	1.445
HF	0.340	0.731	0.688	0.0984	0.0014	111.4526	0.525
C <sub>2</sub>	0.018	0.935	0.925	0.0292	0.0010	101.1334	3.356
LiF	0.029	1.003	0.730	0.0210	0.0011	123.0299	0.219
HCN	0.169	0.580	1.150	0.1442	0.0150	135.7653	3.556
N <sub>2</sub>	0.021	0.761	0.704	0.0600	0.0010	149.5945	3.046
CO	0.099	0.857	0.935	0.7459	0.0007	113.4132	1.829
NO	0.050	0.876	0.833	0.1566	0.0010	174.5276	—
O <sub>2</sub>	0.222	0.725	0.807	0.0039	0.0006	200.6081	—
F <sub>2</sub>	0.151	0.763	0.804	0.1245	0.0008	258.2817	1.252
CO <sub>2</sub>	0.154	0.739	0.813	0.0264	0.0132	295.6002	3.243

<sup>a</sup> Computed at the B3LYP/6-311++G\*\* level using the original B3 parameters. Unrestricted open-shell calculations are not available in the current version of the AIMPAC program.

$D$  depends on the size of the system. In general, the larger the system, the larger the QCISD self-QMSM ( $Z_{\text{qcisdqcisd}}$ ) and the larger the  $D$  value. Scaling the  $D$  value by  $Z_{\text{qcisdqcisd}}$  will give a  $D$  function more size independent. However, we have not scaled the  $D$  value by  $Z_{\text{qcisdqcisd}}$  in eq. (5) for two reasons: first, because we perform the optimization for each molecule independently of the rest of species; and second, because most molecules studied here have a similar size.

The value of the  $a_0$  parameter is especially interesting because it reflects how much exact exchange should be included in the description of a particular system. The values for this parameter in Table I fit into the interval 0.018–0.398, a range of values that is broader but not essentially different from that obtained by Burke and coworkers<sup>49</sup> for a similar set of molecules ( $0.13 \leq a_0 \leq 0.29$ ) using a different approach. In the same work,<sup>49</sup> the authors also reported that they found  $a_0$  usually being higher for single bonds than for multiple bonds. Here, we get a similar trend for most of the systems studied. This is likely due to the too weak nature of the Fermi hole around the reference electron and its static nature, which are deficiencies that make the HF model deficient in the description of the chemical bond, more so in weaker bonds and when there are multiple bonds.<sup>50</sup> Therefore, in multiple bonds the need of HF exchange becomes smaller and the optimum  $a_0$  value is reduced. For instance, all species having  $a_0$  values larger than 0.22 possess single bonds ( $\text{H}_2$ ,  $\text{Li}_2$ ,  $\text{BH}$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$ ) while most of the species with  $a_0 \leq 0.22$  have multiple bonds ( $\text{C}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{HCN}$ , and  $\text{CO}_2$ ). Remarkably, all systems with multiple bonds have  $a_0 \leq 0.22$ . The low  $a_0$  value for  $\text{NO}$  can also be related to the fact that, according to Perdew et al.,<sup>21</sup> small  $a_0$  values are more appropriate for molecules with degenerate ground states. We also find that for isoelectronic systems with similar bonding patterns, such as  $\text{N}_2$  and  $\text{CO}$  or  $\text{H}_2\text{O}$  and  $\text{HF}$ , the larger the delocalization (see  $\delta$  values<sup>45–47</sup> in Table I) the smaller the amount of pure exchange. This can be probably attributed to the fact that localized systems are usually better described by Hartree–Fock methods than delocalized ones.<sup>46</sup>

We found in most cases that the common  $a_x = 1 - a_0$  relation used in some hybrid functionals<sup>19, 49</sup> roughly holds ( $0.681 \leq a_0 + a_x \leq 1.170$ ). This indicates that the presence of the  $E_X^{\text{exact}}$  term reduces the need for the GGA correction  $E_X^{\text{B88}}$  to approximately the same extent. For the same reason, because  $a_0 > 0$ , in all molecules  $a_x < 1.0$ ,<sup>13</sup> with the exception of  $\text{LiF}$ , for which  $a_0$  is almost zero

and  $a_x$  is slightly larger than 1.0. In a recent article, Perdew et al.<sup>21</sup> have provided a qualitative physical explanation for this relationship and have indicated that the  $a_0$  parameter must have a value of ca. 0.25 for most molecules. Our result reinforces the existence of this simple correlation between  $a_x$  and  $a_0$  parameters. With the exception of  $\text{HCN}$  and  $\text{H}_2\text{O}$ , the parameters governing the amount of gradient corrections for exchange and correlation have similar values ( $a_c \approx a_x$ ), indicating that  $a_c = a_x$  could be a better approximation in B1-like methods than  $a_c = 1$ .

The average QCISD-density optimized  $a_0$ ,  $a_x$ , and  $a_c$  parameters obtained from Table I are 0.167, 0.733, and 0.791. These values do not differ much from the original Becke parameters (0.20, 0.72, and 0.81). However, it is worth noting that the differences found for the optimized parameters of the different molecules are relevant and stresses the nonuniversal nature of these parameters, a point that has been already noted by Burke et al.<sup>49</sup> and by Baerends and coworkers<sup>51</sup> in previous works. As a whole, there is no single  $a_0$ ,  $a_x$ , and  $a_c$  combination of parameters that can be identified as the optimum one for getting good densities in all systems. However, the combination  $a_x = 1 - a_0$  and  $a_c = a_x$  with  $a_0$  in the interval 0.1–0.3 seems to be the most appropriate for most systems.

Because all molecular properties are related, directly or indirectly, to the electron density, one may expect that the set of parameters that leads to a B3LYP density of QCISD quality should overall improve the computed molecular properties. However, it is also true that, frequently, energy functionals turn out to be relatively insensitive toward small changes in the density. For instance, energy differences computed at the GGA and LSDA levels at the LSDA optimized geometries are quite similar.<sup>4, 5</sup> Table II lists some molecular properties for the systems studied that have been obtained using the QCISD methodology and the B3LYP functional with the original Becke parameters (B3LYPBE) and with the QCISD-density optimized parameters given in Table I (B3LYPNP). In all cases, the B3LYPNP optimized molecular structure is closer to the QCISD geometry than to the B3LYPBE one. This is not surprising if one considers that we have optimized the parameters to get a density as close as possible to the QCISD density. Because most of the electron density accumulates around nuclei, this is accomplished when the two molecular structures match as perfectly as possible. Thus, normally the set of parameters that produces a geometry closest to the QCISD structure is also the set of para-

**TABLE II.** **B3LYP<sup>a</sup> and QCISD 6-311++G\*\* Optimized Bond Lengths,<sup>b</sup> Harmonic Frequencies,<sup>c</sup> Ionization Potentials,<sup>d</sup> Electron Affinity,<sup>e</sup> Dipole Moments,<sup>f</sup> and Electronic Polarizability.<sup>g</sup>**

H <sub>2</sub>						
	$r(\text{H—H})$	$\nu(\text{H—H})$	IP	EA	$\mu$	$\alpha$
QCISD	0.743	4421.3	16.30	−1.89		2.884
B3LYPBE <sup>a</sup>	0.744	4418.4	16.53	−1.48		3.035
B3LYPNP <sup>a</sup>	0.743	4447.3	16.86	−1.30		3.005
Exp.	0.741	4401 <sup>i</sup>	15.43			
LiH						
	$r(\text{Li—H})$	$\nu(\text{Li—H})$	IP	EA	$\mu$	$\alpha$
QCISD	1.601	1405.9	7.84	0.27	5.793	27.295
B3LYPBE <sup>a</sup>	1.593	1408.7	8.29	0.42	5.725	28.044
B3LYPNP <sup>a</sup>	1.600	1386.8	8.12	0.34	5.655	30.529
Exp.	1.595	1406 <sup>i</sup>	7.7	0.34	5.884	
BH						
	$r(\text{B—H})$	$\nu(\text{B—H})$	IP	EA	$\mu$	$\alpha$
QCISD	1.238	2347.5	9.60	−0.23	1.323	19.037
B3LYPBE <sup>a</sup>	1.235	2331.1	9.70	0.32	1.582	21.364
B3LYPNP <sup>a</sup>	1.238	2332.2	9.75	0.40	1.602	21.374
Exp.	1.233		9.77			
Li <sub>2</sub>						
	$r(\text{Li—Li})$	$\nu(\text{Li—Li})$	IP	EA	$\mu$	$\alpha$
QCISD	2.692	348.4	5.18	−0.24		212.259
B3LYPBE <sup>a</sup>	2.703	342.3	5.32	−0.06		197.527
B3LYPNP <sup>a</sup>	2.692	354.2	5.58	0.11		192.283
Exp.	2.673	351 <sup>i</sup>	5.11			229
CH <sub>2</sub>						
	$r(\text{C—H})$ $\angle\text{HCH}$	$\nu(\text{C—H})$	IP	EA	$\mu$	$\alpha$
QCISD	1.083 133.0	1122.5 3142.2 3364.7	10.21	−0.30	0.654	10.322
B3LYPBE <sup>a</sup>	1.080 135.3	1042.3 3116.5 3357.7	10.45	0.24	0.690	11.140
B3LYPNP <sup>a</sup>	1.083 135.6	1020.6 3085.4 3327.6	10.60	0.43	0.694	15.000
Exp.	1.078 136.0 <sup>i</sup>		10.40	0.65		

TABLE II.  
(Continued)

H <sub>2</sub> O						
	$r(\text{O—H})$ $\angle\text{HOH}$	$\nu(\text{O—H})$	IP	EA	$\mu$	$\alpha$
QCISD	0.959 103.5	1657.2 3887.1 3989.5	12.35	-0.97	2.159	7.074
B3LYPBE <sup>a</sup>	0.962 105.0	1602.9 3815.3 3920.3	12.78	-0.71	2.159	7.382
B3LYPNP <sup>a</sup>	0.959 105.3	1614.7 3866.9 3971.5	12.47	-0.92	2.170	7.224
Exp.	0.958 104.5	1595 3657 3756	12.61		1.854	9.79
HF						
	$r(\text{H—F})$	$\nu(\text{H—F})$	IP	EA	$\mu$	$\alpha$
QCISD	0.915	4215.1	15.84	-1.04	1.947	3.409
B3LYPBE <sup>a</sup>	0.922	4097.4	16.35	-0.75	1.982	3.592
B3LYPNP <sup>a</sup>	0.915	4196.3	16.40	-0.67	1.981	3.427
Exp.	0.917	4139 <sup>i</sup>	16.04		1.826	5.40
C <sub>2</sub>						
	$r(\text{C—C})$	$\nu(\text{C—C})$	IP	EA	$\mu$	$\alpha$
QCISD	1.259	1828.0	14.97	3.14		29.755
B3LYPBE <sup>a</sup>	1.252	1866.7	14.54	4.37		50.166
B3LYPNP <sup>a</sup>	1.259	1827.1	12.40	4.05		35.439
Exp.	1.243		12.11	3.27		
LiF						
	$r(\text{Li—F})$	$\nu(\text{Li—F})$	IP	EA	$\mu$	$\alpha$
QCISD	1.595	886.8	11.55	0.35	6.539	7.735
B3LYPBE <sup>a</sup>	1.582	903.9	12.24	0.49	6.355	8.385
B3LYPNP <sup>a</sup>	1.595	880.6	12.48	0.58	6.317	9.560
Exp.	1.564	914 <sup>i</sup>			6.326	
HCN						
	$r(\text{H—C})$ $r(\text{C—N})$	$\nu(\text{H—C—N})$	IP	EA	$\mu$	$\alpha$
QCISD	1.071 1.159	705.4 2142.3 3452.0	13.63	-0.89	3.024	14.099

TABLE II.  
(Continued)

HCN						
	$r(\text{H—C})$ $r(\text{C—N})$	$\nu(\text{H—C—N})$	IP	EA	$\mu$	$\alpha$
B3LYPBE <sup>a</sup>	1.068 1.149	758.4 2196.1 3444.9	14.12	-0.72	3.055	14.513
B3LYPNP <sup>a</sup>	1.073 1.151	746.7 2184.9 3409.2	13.74	-0.98	3.063	14.753
Exp.	1.066 1.153	712 2097 3311	13.6		2.984	17.5
N <sub>2</sub>						
	$r(\text{N—N})$	$\nu(\text{N—N})$	IP	EA		$\alpha$
QCISD	1.104	2387.4	15.37	-2.73		10.141
B3LYPBE <sup>a</sup>	1.095	2441.4	15.88	-1.99		10.332
B3LYPNP <sup>a</sup>	1.104	2353.7	15.68	-1.82		10.644
Exp.	1.098	2360 <sup>i</sup>	15.58 <sup>j</sup>			11.7
CO						
	$r(\text{C—O})$	$\nu(\text{C—O})$	IP	EA	$\mu$	$\alpha$
QCISD	1.1326	2177.2	13.71	-2.01	0.090	11.557
B3LYPBE <sup>a</sup>	1.1268	2210.3	14.21	-1.33	0.072	11.791
B3LYPNP <sup>a</sup>	1.1326	2162.1	14.04	-1.36	0.104	12.071
Exp.	1.1283	2170 <sup>i</sup>	14.01		0.110	13.2
NO						
	$r(\text{N—O})$	$\nu(\text{N—O})$	IP	EA	$\mu$	$\alpha$
QCISD	1.159	1851.476	9.52	-0.68	0.106	9.259
B3LYPBE <sup>a</sup>	1.148	1976.464	10.30	-0.12	0.099	9.415
B3LYPNP <sup>a</sup>	1.159	1887.081	10.22	-0.07	0.144	9.714
Exp.	1.151	1904 <sup>i</sup>	9.26	0.03	0.159	11.5
O <sub>2</sub>						
	$r(\text{O—O})$	$\nu(\text{O—O})$	IP	EA		$\alpha$
QCISD	1.205	1645.7	12.27	-0.52		8.589
B3LYPBE <sup>a</sup>	1.206	1631.4	13.13	0.05		8.382
B3LYPNP <sup>a</sup>	1.201	1654.5	13.26	0.10		8.296
Exp.	1.207	1580 <sup>i</sup>	12.07	0.45		10.7



**TABLE II.**  
(Continued)

F <sub>2</sub>					
	<i>r</i> (F—F)	<i>ν</i> (F—F)	IP	EA	<i>α</i>
QCISD	1.416	874.5	15.81	0.25	5.814
B3LYPBE <sup>a</sup>	1.408	982.6	16.09	0.78	6.008
B3LYPNP <sup>a</sup>	1.416	962.7	16.02	0.90	6.063
Exp.	1.412	891 <sup>i</sup>	15.70	3.08	
CO <sub>2</sub>					
	<i>r</i> (C—O)	<i>ν</i> (C—O)	IP	EA	<i>α</i>
QCISD	1.163	637.7 1365.4 2386.3	13.39	−4.36	14.812
B3LYPBE <sup>a</sup>	1.161	656.2 1371.8 2406.1	13.87	−0.91	14.659
B3LYPNP <sup>a</sup>	1.163	648.6 1360.5 2393.1	13.85	−0.90	14.806
Exp.	1.160	667 1333 2349	13.77		19.6

Experimental data are also included.<sup>h</sup>

<sup>a</sup> B3LYPBE refers to the standard B3LYP procedure, while B3LYPNP indicates the B3LYP method with the  $a_0$ ,  $a_x$ , and  $a_c$  QCISD density-optimized parameters.

<sup>b</sup>  $r$  in Å.

<sup>c</sup> All frequencies are harmonic and are reported in cm<sup>−1</sup>.

<sup>d</sup> IP in eV.

<sup>e</sup> EA in eV.

<sup>f</sup>  $\mu$  in Debyes.

<sup>g</sup>  $\alpha$  in a.u.

<sup>h</sup> Unless otherwise noted, experimental data have been obtained from Lide, D. R., Ed. CRC Handbook of Chemistry and Physics, 76th ed.; CRC Press: Boca Raton, FL, 1995.

<sup>i</sup> Experimental data obtained from Johnson, B. G.; Gill, P. W.; Pople, J. A. J Chem Phys 1993, 98, 5612.

<sup>j</sup> N<sub>2</sub><sup>+</sup> cation in <sup>2</sup>Σ state.

eters that minimizes the differences between the B3LYP and QCISD electron densities. With only a few exceptions, the harmonic frequency, which also has a large dependence on molecular structure, is improved with the optimized parameters. Values in Tables I and II show that the B3LYPNP frequency is larger than the B3LYPBE when  $a_0$  is larger than 0.20 (the original  $a_0$  Becke parameter) and smaller otherwise. This effect can be probably related to the well-known Hartree–Fock overestimation of harmonic frequencies.<sup>52</sup> In this case, it is reasonable to expect that the inclusion of a large

amount of Hartree–Fock exchange produces higher frequencies. This finding suggests a simple way to improve B3LYP frequencies by calculating them with an appropriate  $a_0$  value instead of using scaling factors.<sup>52,53</sup>

The other properties are in some cases improved and in other cases worsened. In particular, poorer ionization potentials (IPs) and electron affinities (EAs) are obtained in most cases. This result is not completely unexpected if one considers that the Becke original parameters were optimized so as to reproduce experimental IPs and EAs. In gen-

eral,  $a_0$  coefficients larger than 0.2 leads to larger IPs and larger EAs when compared to those found with the original parameters. In contrast to the results reported by Abu-Awwad and Politzer,<sup>33</sup> here we found that, in general, IPs become better with smaller  $a_0$  coefficients. The  $a_c$  seems to play also a key role in the calculation of IPs and EAs. In general, systems with  $a_c < 0.81$  have larger IPs and larger EAs than the B3LYP ones computed with the standard parameters. Finally, the dipole moments and polarizabilities are less sensitive to a change in the parameters. In particular, the dipole moments for CH<sub>2</sub>, HF, and HCN remain almost unchanged with the new parameters. For the rest of the systems, it is found that the dipole moment enlarges when  $a_0$  increases. Thus, a larger contribution of the HF exchange leads to larger dipole moments. This behavior may be attributed to the well-known Hartree–Fock overestimation of the ionic character of the chemical bond.<sup>54</sup> It is worth noting that the CO and NO molecules do not follow this trend and we obtain larger dipole moments with reduced  $a_0$  values. However, in these two cases, the C—O and N—O bond lengths increase significantly with the new parameters, thus explaining the increase of the dipole moment.

In summary, despite the density becoming better with the new parameters, the calculated molecular properties are not always improved, some of them being improved and others worsened depending on the molecule.

In an earlier work<sup>36</sup> we found that, in the case of CO, the  $D = D(a_0, a_x, a_c)$  surface has a single minimum provided that B3LYP calculations were performed at the frozen QCISD geometry. We also detected the presence of flat regions on the surface that slow the process of optimization. One may wonder whether we still have a single minimum on the  $D$  surface when complete electron and nuclear relaxation is allowed in B3LYP calculations. To answer this point we have taken the smallest molecules, H<sub>2</sub> and LiH, and have optimized Becke parameters starting from different initial sets of coefficients (Table III). For any different initial set of parameters we have found different local minima. In fact, the combination of parameters that yield a lowest  $D$  value is not the one obtained starting the optimization from the original Becke parameters. The main conclusion is that there is not a unique set of parameters that minimizes the quadratic error integral in H<sub>2</sub> and LiH, a conclusion that, most probably, can be applied to the rest of the molecules. Because we find a number of local minima on this relatively simple surface that depends only on

three parameters, it is quite possible that the functionals that depend on 15<sup>23</sup> or 21<sup>55</sup> parameters will have even more complicated surfaces. Therefore, these functionals may suffer not only the problem of overparametrization, that can introduce physically meaningless parameters,<sup>22, 56</sup> but also the problem of multiple minima and the dependence of the optimization process on the starting set of parameters used. It is worth noting, however, that the problem of multiple minima may disappear if the optimization of the three parameters is performed over a sum of  $D$  values obtained from a statistically significant number of molecules.

Finally, Table III gathers the molecular properties of H<sub>2</sub> and LiH, computed with the different QCISD-density optimized parameters. The values in Table III show that properties, like the polarizability and the dipole moment, are rather insensitive to a change in the parameters, at least, whenever these parameters provide B3LYP densities of QCISD-like quality. For the H<sub>2</sub> molecule, when the weight of the exact exchange is increased, the bond length is slightly shortened. This is in agreement with the tendency already observed by Csonka et al.<sup>34</sup> for the same molecule. In both systems we find that a small  $a_0$  parameter leads to smaller energies. Also, it is worth noting the good correlation found between the  $a_0$  value and the computed harmonic frequency, which becomes larger with the increase of the  $a_0$  parameter. Other properties like the IP and the EA change by as much as 1.31 and 0.80 eV, respectively. Remarkably, the value of the IP and EA obtained is quite dependent on the  $a_c$  parameter. Thus, the lower the  $a_c$  parameter, the larger the IPs and the larger the EAs. Large  $a_c$  parameters yield IPs closer to the experimental ones.

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## Conclusions

In this work, we have analyzed a procedure that allows to obtain a set of  $a_0$ ,  $a_x$ , and  $a_c$  parameters that reproduces properly, for small molecules, any reference density. In particular, the QCISD density has been chosen as the reference density, because it yields reliable geometries and energetic parameters, although in principle any density could be used.

For the molecules studied, the values of the QCISD-density optimized parameters follow approximately the simple rules  $a_x = 1 - a_0$  and  $a_c = a_x$  with  $a_0$  about 0.1–0.3. Larger values of  $a_0$  are found for systems with single bonds, while species containing multiple bonds give in general small values of  $a_0$ . For N<sub>2</sub> and CO and for H<sub>2</sub>O and HF, which are

**TABLE III.** The Different Starting Parameters Taken for the Optimization Process in the H<sub>2</sub> and LiH Molecules, Together with the Final QCISD-Density Optimized Parameters and the Molecular Properties Obtained with These Optimized Parameters.

H <sub>2</sub>													
Starting Parameters			Optimized Parameters				Molecular Properties						
a <sub>0</sub>	a <sub>x</sub>	a <sub>c</sub>	a <sub>0</sub>	a <sub>x</sub>	a <sub>c</sub>	D <sup>a</sup>	Energy <sup>a</sup>	r(H—H) <sup>b</sup>	ν(H—H) <sup>c</sup>	IP <sup>d</sup>	EA <sup>d</sup>	α <sup>a</sup>	
0.200	0.720	0.810	0.260	0.540	0.490	0.000028	-1.199170	0.743	4447.3	16.86	-1.30	3.005	
0.900	0.100	0.100	0.268 <sup>e</sup>	0.327 <sup>e</sup>	0.001 <sup>e</sup>	0.000016	-1.225114	0.743	4449.4	17.28	-1.02	2.998	
0.900	0.100	0.900	0.225	0.490	0.226	0.000021	-1.215041	0.743	4438.3	17.11	-1.13	3.007	
0.900	0.900	0.100	0.301	0.327	0.126	0.000020	-1.216594	0.743	4451.5	17.15	-1.11	2.997	
0.100	0.100	0.100	0.232 <sup>e</sup>	0.381 <sup>e</sup>	0.001 <sup>e</sup>	0.000015	-1.226667	0.743	4444.6	17.30	-1.00	3.002	
0.900	0.900	0.900	0.315	0.700	1.010	0.000047	-1.169773	0.741	4459.3	16.39	-1.63	3.002	
0.100	0.100	0.900	0.392	0.693	1.244	0.000059	-1.154587	0.741	4476.3	16.15	-1.80	2.991	
0.100	0.900	0.100	0.184	0.472	0.052	0.000021	-1.225746	0.743	4437.2	17.28	-1.01	3.010	
0.100	0.900	0.900	0.310	0.698	1.024	0.000049	-1.167854	0.742	4454.2	16.36	-1.64	3.007	

<sup>a</sup> In a.u. Exp. value for the energy is -1.1744 a.u. (ref. 30) and for α is 5.43 a.u.

<sup>b</sup> r in Å. Exp. value 0.741 Å.

<sup>c</sup> All frequencies are harmonic and are reported in cm<sup>-1</sup>. Exp. value is 4401 cm<sup>-1</sup>.

<sup>d</sup> IPs and EAs in eV. IP exp. value is 15.43 eV.

<sup>e</sup> These two sets parameters most probably correspond to the same minimum.

LiH														
Starting Parameters			Optimized Parameters				Molecular Properties							
a <sub>0</sub>	a <sub>x</sub>	a <sub>c</sub>	a <sub>0</sub>	a <sub>x</sub>	a <sub>c</sub>	D <sup>a</sup>	Energy <sup>a</sup>	r(H—H) <sup>b</sup>	ν(H—H) <sup>c</sup>	IP <sup>d</sup>	EA <sup>d</sup>	μ <sup>e</sup>	α <sup>a</sup>	
0.200	0.720	0.810	0.107	0.625	0.884	0.000353	-8.017969	1.600	1386.8	8.12	0.34	5.655	30.529	
0.900	0.100	0.100	0.009	0.236	0.013	0.000675	-8.056243	1.600	1384.1	8.75	0.80	5.675	30.402	
0.900 <sup>f</sup>	0.100 <sup>f</sup>	0.900 <sup>f</sup>	—	—	—	—	—	—	—	—	—	—	—	
0.900	0.900	0.100	0.123	0.349	0.626	0.000609	-7.996768	1.600	1388.8	8.24	0.45	5.668	29.998	
0.100	0.100	0.100	0.071	0.105	0.109	0.000895	-8.017711	1.600	1387.9	8.60	0.72	5.682	29.815	
0.900	0.900	0.900	0.372	0.297	1.488	0.000893	-7.879164	1.600	1401.9	7.44	0.06	5.681	28.405	
0.100	0.100	0.900	0.040	0.674	0.672	0.000287	-8.055538	1.600	1382.9	8.33	0.47	5.651	31.055	
0.100	0.900	0.100	0.026	0.469	0.375	0.000426	-8.053623	1.600	1383.3	8.52	0.62	5.661	30.788	
0.100	0.900	0.900	0.034	0.838	0.912	0.000210	-8.051785	1.601	1378.0	8.18	0.35	5.633	31.693	

<sup>a</sup> In a.u. Exp. value for α is 25.9 a.u.

<sup>b</sup> r in Å. Exp. value is 1.595 Å.

<sup>c</sup> All frequencies are harmonic and are reported in cm<sup>-1</sup>. Exp. value is 1406 cm<sup>-1</sup>.

<sup>d</sup> IPS and EAs in eV. IP exp. value is 7.7 eV and EA exp. value is 0.34 eV.

<sup>e</sup> μ in Debyes. Exp. value is 5.884 Debyes.

<sup>f</sup> It was not possible to converge to a minimum starting from these three parameters.

two isoelectronic species with similar bonding patterns, we found that the a<sub>0</sub> is smaller for the more delocalized systems.

The comparison of the molecular properties obtained at the B3LYP level with the original Becke parameters and our optimized parameters shows that the expected improvement in the molecular proper-

ties does not occur in all cases, although properties that have a large dependence on the molecular structure are usually improved with the new parameters. The harmonic frequencies are quite sensitive to the a<sub>0</sub> parameter, increasing when a<sub>0</sub> becomes larger. Larger a<sub>0</sub> and smaller a<sub>c</sub> parameters leads to larger IPs and larger Eas.

For H<sub>2</sub> and LiH, we have showed that the quadratic error integral surface has multiple local minima, a conclusion that most likely applies to the rest of the systems. The calculation of some molecular properties of H<sub>2</sub> and LiH in these minima reveals that the IP and EA are quite dependent on the  $a_c$  parameter. Smaller IPs and smaller EAs are obtained when the  $a_c$  parameter increases.

As a whole, our results fully support the nonuniversal nature of the three Becke parameters in B3-like methods. First, we have found that different molecules require quite different parameters. Second, we have shown that the dependence of the molecular properties on the parameters is diverse, and that parameters optimized for one property may yield erroneous values for other different properties.

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40. In this case, the route must contain the following keywords: #B3LYP IOP(5/45 =  $P_1P_2$ ) IOP(5/46 =  $P_3P_4$ ) IOP(5/47 =  $P_5P_6$ ). The values:  $P_1 = 1000$ ,  $P_2 = 0200$ ,  $P_3 = 0720$ ,  $P_4 = 0800$ ,  $P_5 = 0810$ , and  $P_6 = 1000$ , reproduce the B3LYP results. The formula for the  $E_{B3LYP}$  energy is:  $E_{B3LYP} = p_1(p_4E_X^{LDA} + p_3E_X^{B88}) + p_2E_X^{HF} + p_5(E_C^{LYP} - E_C^{VWN}) + p_6E_C^{VWN}$ , where  $p_i = P_i/1000$ , for  $i = 1$  to 6. So, the Becke three parameters  $a_0$ ,  $a_x$ , and  $a_c$  are  $p_2$  or  $1 - p_1p_4$ ,  $p_1p_3$ , and  $p_5$ , respectively. The  $p_1$  and  $p_6$  parameter have been always set to 1.
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