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Estimating Molecular Electronic Chemical Potential and Hardness from Fragments' Addition Schemes

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A new scheme for the estimation of aggregate chemical potential and hardness is introduced and compared with the results of ab initio calculations for the aggregates as well as with the results obtained by employing various other combination schemes. Numerical results show that this new scheme provides better estimates of electronic chemical potential as well as comparable results for hardness with other addition schemes.

1. Introduction

Within the purview of the density functional theory,[1−3] the electronegativity χ of an atom has been identified[4] with the negative of the chemical potential μ of the electronic distribution, and the chemical hardness η has been defined as the partial derivative of the chemical potential with respect to the total number of electrons at constant external potential.[5] The establishment of a rigorous foundation for the popular concepts of electronegativity and hardness allows for the introduction of various combination schemes relating the global properties of the constituent fragments to the global properties of the resultant aggregate molecule.

Sanderson's geometric mean equalization principle for electronegativity has been used to approximate the reactivity parameter electronegativity of an aggregate from the corresponding properties of the constituent fragments.[6−8] The Sanderson scheme was later extended to determine the molecular hardness.[9] The other related methods for calculating aggregate hardness from fragment values are that of the average softness method introduced by Ghosh et al.[10] and the geometric mean principle of hardness introduced by Datta[11] and later extended by Chattaraj et al.[11]

Recently, an additivity scheme for the chemical potential and hardness has been introduced,[12] and the novelty of that scheme is that it involves the fukui function of component fragments for the estimation of the global properties of the aggregates. In the present work, we have obtained workable expressions for the calculation of the hardness parameter from the relevant theoretical expression and have compared the reactivity parameters viz. chemical potential and hardness so obtained with the reference ab initio results and computed from the other additivity schemes currently available.[10,11]

2. Theoretical Background

As mentioned, within the density functional theory (DFT) formalism, the chemical potential and the hardness for an N-particle system with total energy E and external potential $\upsilon(\mathbf{r})$ are defined as

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\upsilon(\mathbf{r})} = -\chi \tag{1}$$

and

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\mathbf{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{\upsilon(\mathbf{r})} \tag{2}$$

Using Koopman's theorem[2] and first-order finite difference approximation of eqs 1 and 2, we have

$$\mu \approx \frac{1}{2}(I + A) \approx \frac{1}{2}(\epsilon_L + \epsilon_H) \tag{3}$$

and

$$\eta \approx \frac{1}{2}(I - A) \approx \frac{1}{2}(\epsilon_L - \epsilon_H) \tag{4}$$

where I is the ionization potential and A is the electron affinity and ϵ_H and ϵ_L are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

Sanderson's Additivity Scheme for μ and η. Sanderson's equalization principle states that the electronegativity of a molecule is given by the geometric mean of the electronegativities of the constituent isolated atoms or fragments. Accordingly, Sanderson's expression for the aggregate chemical potential is expressed as

$$\mu_n^s = -(\prod_i^n |\mu_i|)^{1/n} \tag{5}$$

where μ_i is the chemical potential of the ith fragment. Differentiating Sanderson's expression for the aggregate μ_n^s with respect to N,[9,12] we obtain an expression for chemical hardness henceforth referred to as the Sanderson's relation for aggregate hardness:

$$\eta_n^s = \frac{\mu_n^s}{n}\sum_i^n \frac{\eta_i}{\mu_i} \tag{6}$$

where η_i is the hardness of the ith fragment. Note that the numerical factor $^1/_2$ has been dropped from the original definitions.

Ghosh Additivity Scheme for η. The combination scheme proposed by Ghosh et al.[10] expresses the aggregate hardness as

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the reciprocal of the aggregrate softness computed as the average of the softness of the constituent fragments. Accordingly, it is calculated as

$$\frac{1}{\eta_n^g} = \frac{1}{n}\sum_i^n \frac{1}{\eta_i} \tag{7}$$

Datta Additivity Scheme for $\boldsymbol{\eta}$. Another aggregation scheme has been introduced by Datta[11] which expresses the hardness of the aggregate molecule as the geometric mean of the respective hardness of the constituent fragments as follows:

$$\eta_n^d = (\prod_i^n \eta_i)^{1/n} \tag{8}$$

New Additivity Scheme for $\boldsymbol{\mu}$ and $\boldsymbol{\eta}$. A new additivity scheme for μ and η was recently proposed,[12] it comes out from the Sanderson's expression for the chemical potential (see eq 5). The chemical potential is a function of N and a functional of the external potential $v(\mathbf{r})$, and differentiation of μ_n^s with respect to N led to eq 6, whereas differentiation with respect to $v(\mathbf{r})$ leads to

$$F_n^\circ = \int \left(\frac{\delta \mu_n^s}{\delta v}\right)_N \mathrm{d}\mathbf{r} \approx \frac{\mu_n^s}{n}\sum_i^n \left(\frac{f_i}{\mu_i}\right) \tag{9}$$

where F_n° is a dimensionless quantity that contains the fragment reactivities through the condensed fukui function f_i associated with the ith constituent fragment of the molecule.[12] The Fukui function is a local property that has been defined as[2]

$$f(\mathbf{r}) = \left(\frac{\delta \rho(\mathbf{r})}{\delta N}\right)_v \tag{10}$$

which clearly integrates to unity. For removal or addition of charge from or to a neutral atom or molecule to obtain another ground state, it has been proved that[13]

$$f^-(\mathbf{r}) \approx [\rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})] \tag{11}$$

measures the reactivity toward a electrophilic attack, in this case it has been assumed that one electron was removed by the electrophile from our reference N electron system. On the other hand

$$f^+(\mathbf{r}) \approx [\rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r})] \tag{12}$$

measures the reactivity toward a nucleophilic attack, here the assumption is that one electron is transferred from the nucleophile to the reference N electron system. Using the local density approximation (LDA)[14] for assuming uniform removal or addition of charge, the Fukui function can be approximated as

$$f^-(\mathbf{r}) \approx f^+(\mathbf{r}) \approx f(\mathbf{r}) \approx \frac{\rho(\mathbf{r})}{N} \tag{13}$$

After integration over, say, the ith fragment volume, we obtain a condensed Fukui function as

$$f_i = \frac{N_i}{N} \tag{14}$$

with $\sum_i N_i = N$ as the total number of electrons in the aggregate and N_i is the number of electrons in the ith fragment. In the context of the formation of a molecular aggregate from the constituent fragments, the Fukui function as defined in eq 14 will play the role of a weighting factor instead of a reactivity parameter.

Because F_n° and f_i are dimensionless quantities, the dimensional analysis of the right-hand side of eq 9 shows that the sum containing the f_i/μ_i terms should be of dimension (1/chemical potential). Therefore, we propose the chemical potential for a composite system be defined as

$$\frac{1}{\mu_n^t} = \sum_i^n \left(\frac{f_i}{\mu_i}\right) \tag{15}$$

The corresponding hardness is obtained by differentiating eq 15 with respect to N at constant external potential, which leads to

$$\eta_n^t = \left(\frac{\partial \mu_n^t}{\partial N}\right)_{v(\mathbf{r})} = (\mu_n^t)^2 \sum_i^n \frac{1}{(\mu_\mathrm{i})^2}[f_i\eta_i - h_i\mu_i] \tag{16}$$

where

$$h_i = \left(\frac{\partial f_i}{\partial N}\right)_{v(\mathbf{r})} \tag{17}$$

h_i is a measure of the change in the fragment fukui function because of the change in the total number of electrons. It is not possible to obtain an explicit evaluation of this reactivity descriptor. So, in the present work, for two component aggregates, we obtain an approximation by rewriting eq 17 as follows:

$$\begin{aligned} h_1 &\approx \frac{\Delta f_1}{\Delta N} \\ &\approx \frac{f_1(\text{product}) - f_1(\text{reactant})}{N(\text{product}) - N(\text{reactant})} \\ &\approx \frac{N_1/N(\text{product}) - 1}{N(\text{product}) - N_1} \\ &\approx -\frac{1}{N} \end{aligned} \tag{18}$$

where $N(\text{product}) = N_1 + N_2$, so that for bicomponent aggregates, the expression for hardness as given by eq 16 can be approximated as

$$\eta_2^t = \left(\frac{\partial \mu_2^t}{\partial N}\right)_{v(\mathbf{r})} \approx \frac{(\mu_2^t)^2}{N}\sum_{i=1}^{2} \frac{1}{(\mu_i)^2}[N_i\eta_i + \mu_i] \tag{19}$$

We have also approximated eq 16 assuming f_i to remain constant as a fragment aggregates so that $h_i = 0$; accordingly, we have

$$\eta_2^{t_0} = \left(\frac{\partial \mu_2^t}{\partial N}\right)_{v(\mathbf{r})} \approx \frac{(\mu_2^t)^2}{N}\sum_{i=1}^{2} \frac{1}{(\mu_i)^2}[N_i\eta_i] \tag{20}$$

3. Computational Details

All calculations were performed at the RHF level of theory with the standard 6-311G** basis set using the Gaussian 98 package.[15] Radical fragments calculations were carried out applying the UHF theory. The electronic chemical potential and

TABLE 1: Electronic Chemical Potential at the HF/6-311G Level of Calculation for 46 Molecular Aggregates ($\mu°$) and the Corresponding Approximate Values Determined through the Use of Various Combinations Schemes**[a]

no.	fragments	aggregate	$\mu°$	μ_2^s	μ_2^t
1	CHO + CHO	CHOCHO	−0.1852	−0.1324	−0.1324
2	CHO + OCl	CHOOCl	−0.1891	−0.1567	−0.1613
3	CHO + OH	HCOOH	−0.1554	−0.1588	−0.1495
4	CHO + SH	HCOSH	−0.1391	−0.1589	−0.1581
5	CN + CHO	CNCHO	−0.2223	−0.1896	−0.1737
6	H + CHO	HCHO	−0.1493	−0.0999	−0.1264
7	H + HS	H_2S	−0.1267	−0.1120	−0.1758
8	H + CN	HCN	−0.1677	−0.1431	−0.2290
9	H + OCl	HOCl	−0.1733	−0.1183	−0.1757
10	HS + OH	HSOH	−0.1317	−0.1907	−0.1907
11	HS + NO	HSNO	−0.1571	−0.1697	0.1697
12	SN + OH	SNOH	−0.1746	−0.1846	−0.1819
13	CH_3 + CHO	CH_3CHO	−0.1326	−0.1283	−0.1292
14	CH_3 + CHS	CH_3CHS	−0.1397	−0.1362	−0.1413
15	CH_3 + HS	CH_3SH	−0.1125	−0.1540	−0.1610
16	CH_3 + CH_3	CH_3CH_3	−0.1644	−0.1243	−0.1243
17	CH_3 + CN	CH_3CN	−0.1662	−0.1837	−0.1829
18	CH_3 + OH	CH_3OH	−0.1447	−0.1539	−0.1505
19	CH_2 + CH_2	C_2H_4	−0.1064	−0.1657	−0.1657
20	CH_3 + C_2H_5	C_3H_8	−0.1560	−0.1124	−0.1085
21	CH_2 + C_2H_6	C_3H_8	−0.1560	−0.1651	−0.1648
22	C_2H_5 + CHO	C_2H_5CHO	−0.1379	−0.1160	−0.1141
23	CH_2 + C_2H_4O	C_2H_5CHO	−0.1379	−0.1482	−0.1396
24	C_2H_5 + OH	C_2H_5OH	−0.1414	−0.1392	−0.1213
25	CH_2 + CH_3OH	C_2H_5OH	−0.1414	−0.1549	−0.1506
26	C_2H_5 + CHS	C_2H_5CHS	−0.1367	−0.1232	−0.1245
27	CH_2 + CH_3CHS	C_2H_5CHS	−0.1367	−0.1522	−0.1442
28	C_2H_5 + CN	C_2H_5CN	−0.1652	−0.1662	−0.1395
29	CH_3 + CH_2CN	C_2H_5CN	−0.1652	−0.1660	−0.1610
30	C_3H_7 + CHO	C_3H_7CHO	−0.1318	−0.1203	−0.1170
31	CH_3CN + C_2H_4	C_3H_7CN	−0.1612	0.1357	−0.1342
32	CH_2CN + C_2H_5	C_3H_7CN	−0.1612	−0.1330	−0.1344
33	C_2H_5 + C_2H_5	C_4H_{10}	−0.1490	−0.1017	−0.1017
34	C_2H_4 + C_2H_6	C_4H_{10}	−0.1490	−0.1323	−0.1309
35	CH_3CHS + CH_3CHCH_2	C_4H_9CHS	−0.1372	−0.1174	−0.1185
36	C_2H_5CHS + C_2H_4	C_4H_9CHS	−0.1372	−0.1206	−0.1264
37	C_2H_4 + C_2H_4	$CH_3CH=CHCH_3$	−0.0941	−0.1064	−0.1064
38	CH_2CH_3 + $CHCH_3$	$CH_3CH=CHCH_3$	−0.0941	−0.1278	−0.1097
39	CH_2 + C_2H_4	CH_3CHCH_2	−0.0986	−0.1328	−0.1208
40	CH_2 + C_3H_7CHO	$C_2H_5CHCHOCH_3$	−0.1348	−0.1478	−0.1365
41	C_2H_4 + C_2H_5CHO	$C_2H_5CHCHOCH_3$	−0.1348	−0.1211	−0.1255
42	CH_3CHCH_2 + CH_3CHCH_2	C_6H_{12}	−0.0850	−0.0986	−0.0986
43	C_2H_4 + $CH_2C(CH_3)_2$	C_6H_{12}	−0.0850	−0.1019	−0.1004
44	CH_2 + C_3H_8	$CH(CH_3)_3$	−0.1529	−0.1608	−0.1582
45	CH_3 + C_3H_7	$CH(CH_3)_3$	−0.1529	−0.1166	−0.1130
46	CH_2 + CH_2CHCHO	$CH_3CHCHCHO$	−0.1399	−0.1601	−0.1569
	σ^b			0.0278	0.0283

[a] All values are in au. [b] σ is the root-mean-squared deviation from ab initio values.

the molecular hardness were computed using eqs 3 and 4, respectively. We have studied a total of 46 unique combinations to yield 34 aggregates composed from pairs of 37 fragments in all.

The chemical potentials of the aggregates were determined using Sanderson's and our own expressions that are given in eqs 5 and 15, respectively. For a comparative study of the relative merits of the various estimation schemes for the hardness parameter, calculations have been carried out using eq 6 (Sanderson) and methods of arithmetic average of softness[10] (eq 7) and the geometric mean principle of hardness[11] (eq 8). These results are compared to those determined using eqs 19 and 20.

4. Results and Discussion

The estimated chemical potential and hardness values in atomic units are compared with the corresponding ab initio results for the aggregates denoted as $\mu°$ and $\eta°$ given in Tables 1 and 2, respectively. The root-mean-squared deviations of chemical potentials and hardness parameters calculated as per the schemes discussed here from the corresponding ab initio values for the aggregates are also quoted in Tables 1 and 2. Evidently, for the systems studied in this work, the new combination scheme for the hardness introduced here as well as the chemical potential yields results very much comparable to those obtained from other relevant schemes.

The results quoted in Table 1 show that in most of the cases the chemical potential μ_2^t as introduced by Gutiérrez-Oliva et al.[12] yields values closer to the ab initio results as compared to the estimates obtained from eq 5 as proposed by Sanderson. The main reason for this marked improvement may be due to the introduction of f_i in the calculation of aggregate property effectively reflecting the local electronic population within that aggregate. We note that for lighter aggregates composed by a few atoms the Sanderson's expression for chemical potential μ_2^s yields closer agreement with the ab initio results. This may be due to the fact that for smaller constituents with fewer atoms the local properties and charge rearrangements play a relatively minor role, and in such cases the LDA fukui function used in μ_2^t may overestimate the local effects. In fact, this view is borne out further by the observation that for heavier aggregates composed of more atoms μ_2^t consistently yields better agreement with the ab initio results for the aggregates.

TABLE 2: Molecular Hardness at the HF/6-311G Level of Calculation for 46 Molecular Aggregates ($\eta°$) and the Corresponding Approximate Values Determined through the Use of Various Combinations Schemes[a]**

no.	$\eta°$	η_2^s	η_2^g	η_2^d	η_2^t	$\eta_2^{t_0}$
1	0.2396	0.2453	0.2453	0.2453	0.2365	0.2453
2	0.2737	0.2563	0.2538	0.2540	0.2523	0.2607
3	0.3138	0.2785	0.2759	0.2781	0.2563	0.2683
4	0.2608	0.2249	0.2119	0.2138	0.2220	0.2317
5	0.2793	0.2636	0.2486	0.2487	0.2620	0.2741
6	0.2866	0.3736	0.3109	0.3226	0.2634	0.2841
7	0.2582	0.3960	0.2591	0.2813	0.2458	0.2776
8	0.3160	0.4689	0.3163	0.3271	0.3822	0.4456
9	0.2700	0.4166	0.3248	0.3341	0.2931	0.3152
10	0.2431	0.2509	0.2343	0.2424	0.2164	0.2311
11	0.2465	0.2276	0.2162	0.2190	0.2204	0.2311
12	0.2019	0.2474	0.2320	0.2405	0.2062	0.2174
13	0.2878	0.2530	0.2524	0.2525	0.2406	0.2515
14	0.2023	0.2270	0.2163	0.2195	0.2046	0.2138
15	0.2448	0.2363	0.2172	0.2202	0.2245	0.2377
16	0.3236	0.2600	0.2600	0.2600	0.2462	0.2600
17	0.3024	0.2774	0.2560	0.2560	0.2800	0.2979
18	0.3002	0.2883	0.2850	0.2863	0.2720	0.2888
19	0.2725	0.2243	0.2243	0.2243	0.2036	0.2243
20	0.3131	0.2562	0.2553	0.2553	0.2472	0.2553
21	0.3131	0.2742	0.2650	0.2694	0.2808	0.2934
22	0.2757	0.2505	0.2480	0.2480	0.2460	0.2531
23	0.2757	0.2612	0.2521	0.2541	0.2707	0.2790
24	0.2961	0.2868	0.2793	0.2812	0.2688	0.2774
25	0.2961	0.2654	0.2568	0.2595	0.2708	0.2820
26	0.2031	0.2283	0.2131	0.2155	0.2274	0.2339
27	0.2031	0.2132	0.2128	0.2130	0.1997	0.2065
28	0.2980	0.2820	0.2514	0.2514	0.2874	0.2962
29	0.2980	0.2633	0.2576	0.2605	0.2704	0.2815
30	0.2820	0.2448	0.2438	0.2438	0.2394	0.2452
31	0.2959	0.2575	0.2457	0.2458	0.2611	0.2684
32	0.2959	0.2913	0.2867	0.2871	0.2903	0.2976
33	0.3078	0.2508	0.2508	0.2508	0.2448	0.2508
34	0.3078	0.2996	0.2959	0.2970	0.2950	0.3025
35	0.2008	0.2411	0.2285	0.2304	0.2414	0.2457
36	0.2008	0.2440	0.2328	0.2353	0.2292	0.2340
37	0.2504	0.2725	0.2725	0.2725	0.2660	0.2725
38	0.2531	0.2566	0.2419	0.2426	0.2621	0.2682
39	0.2624	0.2600	0.2461	0.2473	0.2646	0.2740
40	0.2732	0.2581	0.2499	0.2515	0.2719	0.2772
41	0.2732	0.2762	0.2741	0.2741	0.2732	0.2787
42	0.2370	0.2624	0.2624	0.2624	0.2583	0.2624
43	0.2370	0.2910	0.2883	0.2888	0.2930	0.2988
44	0.3060	0.2701	0.2614	0.2650	0.2851	0.2943
45	0.3060	0.2511	0.2506	0.2510	0.2405	0.2469
46	0.2430	0.2361	0.2350	0.2353	0.2346	0.2427
	σ^b	0.0491	0.0338	0.0340	0.0344	0.0340

[a] All values are in au. [b] σ is the root-mean-squared deviation from *ab initio* values.

In Table 2 are quoted the values of molecular hardness estimated following different schemes along with the corresponding ab initio results. It can be noticed that the expression η_2^t gives consistently better results than η_2^s and η_2^d and compares favorably with η_2^g. As before, the incorporation of the local fukui function appears to be the primary reason for this significant improvement in the estimated values. It should be mentioned that in general the estimates of the chemical potentials are better compared to the hardness estimates, with the fundamental reason for this being the second order differential involved in the expression for hardness.

Although overall numerical results obtained using eqs 15 and 16 are quite comparable to those determined through other additivity schemes, the merit of μ_n^t and η_n^t is basically that they involve local quantities that act as weighting factors in the combination of the fragments to form the molecule.

Concluding Remarks

In the present work, we have established that the proposed chemical potential additivity scheme incorporating the fragment condensed fukui function yields consistently better results for the estimation of aggregate chemical potential compared to those obtained following Sanderson's scheme. In fact, this brings out the vital importance of the *weight* of the constituent fragments within the composite system. Also, two new related schemes for the estimation of hardness have been introduced which are comparable with the results from Ghosh's scheme using the inverse of softness average. Most importantly, the explicit albeit approximate evaluation of the fragment hardness response function to the change in the external potential during bifragment aggregation has enabled the incorporation of the local fukui function in the expression for hardness thus adding fragments' weighing factors not considered in other schemes. The consequent encouraging results open up the possibility that better approximations of the fukui function can enhance the quality of prediction of global aggregate properties from the constituent fragment properties.

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References and Notes

(1) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 834.

(2) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(3) Parr, R. G.; Yang, W. *Annu. Rev. Phys. Chem.* **1995**, *46*, 701. Bartolotti, L. J.; Flurichick, K. *Rev. Comput. Chem.* **1996**, *7*, 187. Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(4) Parr, R. G. *Annu. Rev. Phys. Chem.* **1983**, *34*, 631.

(5) Parr, R. G.; Pearson, R. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(6) Sanderson, R. T. *Science* **1955**, *121*, 207.

(7) Sanderson, R. T. *Chemical Bonds and Bond Energy*, 2nd ed.; Academic Press: New York, 1976.

(8) Parr, R. G.; Bartolotti, L. J. *J. Am. Chem. Soc.* **1982**, *104*, 3801.

(9) Cárdenas-Jirón, G. I.; A. Toro-Labbé, *J. Mol. Struct. (THEOCHEM)* **1997**, *79*, 390.

(10) Yang, W.; Lee, C.; Ghosh, S. K. *J. Phys. Chem.* **1985**, *89*, 5412.

(11) Datta, D *J. Phys. Chem. A* **1986**, *90*, 4216. Chattaraj, P. K.; Nandi, P. K.; Sannigrahi, A. B. *Proc. Indian Acad. Sci., Chem. Sci.* **1991**, *103*, 583.

(12) Gutiérrez-Oliva, S.; Jaque, P.; Toro-Labbé, A. *J. Phys. Chem. A* **2000**, *104*, 8955.

(13) Lee, C.; Yang, W.; Parr, R. G. *J. Mol. Struct. (THEOCHEM)* **1988**, *163*, 305.

(14) Gázquez, J. L. In *Chemical Hardness (Structure and Bonding)*; Sen, K. D., Ed.; Springer-Verlag: Berlin, 1993; Vol. 80, pp 29−43.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.