Simplified Models for Hardness Kernel and Calculations of Global Hardness

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Reported in this paper are simplified models for the hardness kernel $\eta(\mathbf{r},\mathbf{r}')$ and theoretical values of the global hardness for the first 54 neutral atoms calculated using these models. It is found that a particularly simple model for the hardness kernel, $\eta(\mathbf{r},\mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'| + C$, where C is a constant, generates good results for the global hardness η. Both main-group elements and transition metal elements are considered, as are various conventional models, in approximating energy components.

Introduction

Much progress has been made in recent years in density functional theory (DFT).[1−4] It makes possible calculation of electronic properties of a molecular system with an accuracy of chemical interest at a reasonable cost. It provides simple but rigorous frameworks to handle complicated systems, and most importantly, it generates intuitive and insightful concepts for understanding chemical changes. Hardness (or its counterpart, softness) is one of these concepts.[1−3] It was first put forward by Pearson[5] from empirical considerations, and then formulated by Parr and Pearson[6] in DFT language. Early applications of hardness in DFT were to the hard and soft acids and bases (HSAB) principle[6−9] and the maximum hardness principle (MHP).[10−15] Another recent important advance is the discovery of a variational principle associated with hardness,[16] whereby molecular hardness and Fukui function[1,2] can be obtained simultaneously.

While is established how to obtain hardness from experimental ionization potential and electron affinity by finite difference approximation,[1] it is still not known how to accurately compute the hardness from theory. The reason is that the explicit form of the universal density functional $F[\rho]$ in DFT[1−4] is not known. Various attempts have been reported[15,17,18] to approximately calculate this quantity. Cedillo and Parr[17] employed a Hückel-type semiempirical approach coupled with a variational procedure to determine the global hardness. This may be regarded as the HMO (Hückel molecular orbital) version of the density functional theory. Extensions along this line should soon be seen. Another pertinent work is done by Guang H. Liu,[18] who self-consistently calculated the orbital hardness matrix, and thus hardness, in the Kohn−Sham scheme using approximate functionals for the exchange and correlation energies. The exchange approximation used was the Dirac formula,[19] and the correlation approximation was the Barth-Hedin form.[20] Very recently, we have found another pathway to compute atomic hardness.[15] It originates from the functional expansion approach,[21−24] which, up to the second order, provides relations among the total energy, chemical potential, hardness, Fukui function, etc.

In the present work, we will present a drastically simplified approach to compute atomic hardness. The basic idea comes from the consideration that the dominant contribution to the hardness kernel comes from the classical Coulomb repulsion term. Numerical data obtained therefrom confirm this observation. Extensions to combine such models as Thomas−Fermi, Dirac, Weizsäcker, Wigner, and our recently proposed local correlation form[25,26] will also be investigated. Modifications of the simple model are examined for different systems, i.e., main group elements and transition metal elements. It turns out that the modified models are capable of producing good global hardness values for these systems.

Theory

Hardness is defined as the second-order partial derivative of the total electronic energy E with respect to the total electron number N at the fixed external potential $v(\mathbf{r})$, i.e.,

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_v \tag{1}$$

Using finite difference approximation[1] one can obtain hardness from ionization potential I and electron affinity A via

$$\eta = I - A \tag{2}$$

In the past, calculated hardness values were found to be very important in the elucidation and interpretation of chemical reactivity[5] and acid−base equilibria.[27] Very recently, it was shown that such hardnesses can be calculated well by employing exact exchange density functional methods.[28]

To theoretically calculate the hardness, one may invoke the formula[16]

$$\eta = \int \int f(\mathbf{r})f(\mathbf{r}')\eta(\mathbf{r},\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' \tag{3}$$

where $f(\mathbf{r})$ is the Fukui function,[1] defined as

$$f(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_v = -\left(\frac{\delta\mu}{dv}\right)_N \tag{4}$$

Here $\rho(\mathbf{r})$ and μ are the electronic density and the chemical potential, respectively, and $\eta(\mathbf{r},\mathbf{r}')$ is the hardness kernel, defined as the second-order functional derivative of $F[\rho]$ with respect to density, i.e.,

$$\eta(\mathbf{r},\mathbf{r}') = \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \tag{5}$$

$F[\rho]$ is the Hohenberg-Kohn universal density functional. It

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comprises four elements, the kinetic energy density functional $T_s[\rho]$, the classical Coulomb repulsion functional $J[\rho]$, the exchange energy density functional $E_x[\rho]$, and the correlation energy density functional $E_c[\rho]$. That is,

$$F[\rho] = T_s[\rho] + J[\rho] + E_x[\rho] + E_c[\rho] \qquad (6)$$

in which the functional $J[\rho]$ is explicitly known as

$$J[\rho] = {}^1/_2 \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \qquad (7)$$

The three unknowns in $F[\rho]$ are thus $T_s[\rho]$, $E_x[\rho]$, and $E_c[\rho]$. Enormous efforts have been invested in recent decades to find approximations for these.[1-4] Some of their proposed approximate forms are given below.

(i). Kinetic Energy Density Functional $T_s[\rho]$. The earliest well-known formula is the Thomas−Fermi form,[29]

$$T_s^{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) \, d\mathbf{r} \qquad (8)$$

where $C_F = {}^3/_{10}(3\pi^2)^{2/3} = 2.8712$. The Thomas−Fermi form is exact for the homogeneous electron gas system and exact in the local density approximation (LDA) for nonhomogenouos systems.[24] Another well-known form for $T_s[\rho]$ is due to Weizsäcker,[30]

$$T_s^W[\rho] = {}^1/_8 \int \frac{\nabla\rho(\mathbf{r})\nabla\rho(\mathbf{r})}{\rho(\mathbf{r})} \, d\mathbf{r} \qquad (9)$$

This is exact for one- and two-electron systems. It is known[31,32] that, even for many electron systems, the kinetic energy density of Weizsäcker form accurately reproduces the exact form near nuclear cusps and at long ranges. Many authors have written $T_s[\rho]$ as[32,33]

$$T_s[\rho] = T_s^W[\rho] + T_s^R[\rho] \qquad (10)$$

where $T_s^R[\rho]$ is a remaining unknown part.

(ii). Exchange Energy Density Functional $E_x[\rho]$. The first one was proposed by Dirac 60 years ago,[19] possessing the form

$$E_x[\rho] = C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \qquad (11)$$

with $C_x = 3/4(3/\pi)^{1/3}$. It was originally obtained for the homogeneous electron gas, and later proved to be exact in LDA for nonhomogeneous systems.[24] There are several other choices available for $E_x[\rho]$, especially the forms under the gradient expansion approximation (GEA) or the general gradient approximation (GGA).[1-4]

(iii). Correlation Energy Density Functional $E_c[\rho]$. Among many empirical or semiempirical formulas for $E_c[\rho]$, the Wigner form[34] is of special interest. It takes the form

$$E_s^W[\rho] = a \int \frac{\rho(\mathbf{r})}{1 + b\rho^{-1/3}(\mathbf{r})} d\mathbf{r} \qquad (12)$$

where a and b are constants to be empirically determined. Recently, we derived another LDA formula[25-27] for $E_c[\rho]$ from the adiabatic connection formulation of DFT,

$$E_c^{LP}[\rho] = c_1 \int \rho^{3/3}(\mathbf{r}) \, d\mathbf{r} + c_2 \int \rho^{2/3}(\mathbf{r}) \, d\mathbf{r} + c_3 \int \rho^{1/3}(\mathbf{r}) \, d\mathbf{r} \qquad (13)$$

in which c_1, c_2, and c_3 are empirical constants. Related other forms have been proposed in this laboratory.[35-37]

To calculate hardness from eq 3, two quantities need to be approximated. One is the hardness kernel, whose form must be

$$\eta(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + R(\mathbf{r},\mathbf{r}') \qquad (14)$$

where the first term on the right-hand side results from the classical Coulomb repulsion term eq 7, and the second term includes contributions from the kinetic, exchange, and correlation energy functionals whose possible approximations were exhibited in foregoing paragraphs. It is anticipated that the contribution from the second term is typically small. Note for example that the Weizsäcker term contributes nothing whatever to the global hardness. On the basis of such considerations, we propose to try the approximation for the hardness kernel,

$$\eta(\mathbf{r},\mathbf{r}') \approx \frac{1}{|\mathbf{r} - \mathbf{r}'|} \qquad (15)$$

A modification is given in eq 21 below.

The other quantity required in eq 3 is the Fukui function $f(\mathbf{r})$. Among the various approximations to it,[38] the following three have been widely accepted.[1] The first is to approximate it by the HOMO (highest occupied molecular orbital) density, i.e.,

$$f(\mathbf{r}) \approx \rho_{HOMO} \qquad (16)$$

and the second is the finite difference approximation, namely,

$$f(\mathbf{r}) \approx \frac{f^+(\mathbf{r}) + f^-(\mathbf{r})}{2} \qquad (17)$$

where

$$f^-(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \qquad (18)$$

and

$$f^+(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}) \qquad (19)$$

where ρ_{N+1}, ρ_N, and ρ_{N-1} are the electron density of the $N + 1$, N, and $N - 1$ electron systems, respectively. In some systems, it is more natural to use

$$f(\mathbf{r}) \approx f^-(\mathbf{r}) \qquad (20)$$

Computational Details

To evaluate the simple form proposed for the hardness kernel and to systematically include contributions from the kinetic energy, the exchange and correlation energy density functionals in eq 5, we have performed a series of numerical calculations for global hardness. The calculations use different combinations of the approximate functionals aforementioned. The methods to approximate the hardness kernel include:

(i). the simple form proposed in eq 15, denoted by "simplest"; (ii). eq 15, plus the contribution from the kinetic energy by the Thomas−Fermi formula, denoted by TF; (iii). eq 15, plus contributions from the kinetic and exchange energies by the Thomas−Fermi and Dirac forms, denoted by TFD; (iv). eq 15, plus contributions from the kinetic, exchange, and correlation energies by the full Weizsäcker term, the Dirac term, and the Wigner term, denoted by WDW; (v). eq 15, plus contributions from the kinetic, exchange and correlation energies by the Thomas-Fermi, Dirac, and Liu−Parr formulas, denoted by TFDLP; and finally (vi). eq 15, plus contributions from the kinetic, exchange and correlation energies by the Thomas-Fermi, one-ninth Weizsäcker, Dirac, and Wigner forms, denoted by TF19WDW.
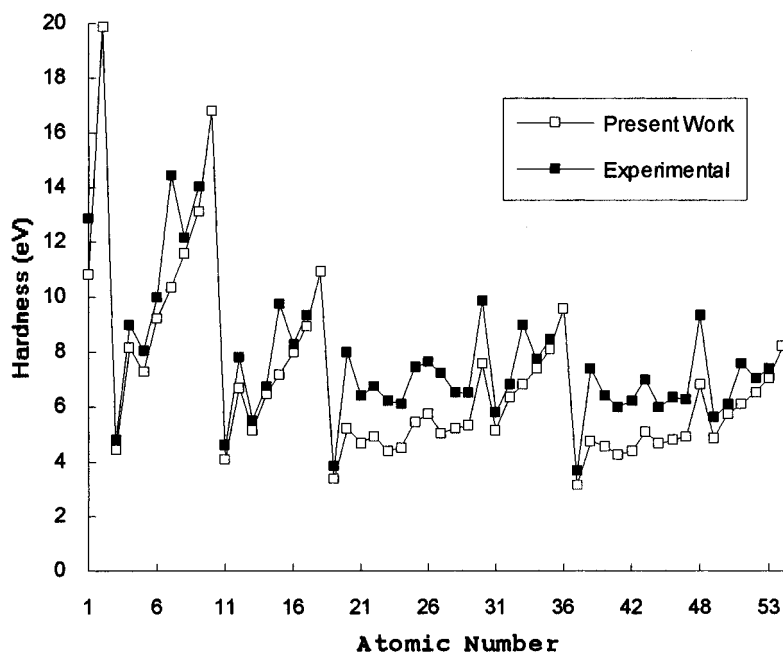
Hardness Kernel and Global Hardness

J. Phys. Chem. A, Vol. 101, No. 37, 1997 **6993**

Figure 1. Experimental and theoretical hardnesses for first 54 atoms. The calculated values are from the simplest model, eq 15, and the approximate Fukui function, eq 17. See text.

TABLE 1: Experimental and Calculated Hardness for Main Group Elements Except IIA and VA Elements Calculated Using the Approximation $f = (f^+ + f^-)/2^a$

atom	simplest	TF	TFD	WDW	TFDLP	TF19WDW	modified	exptl
3	4.428	4.961	3.514	2.893	3.508	3.426	4.927	4.78
5	7.250	8.308	7.235	6.115	7.228	7.173	7.749	8.02
6	9.225	10.772	10.004	8.418	9.992	9.964	9.724	10.00
8	11.575	13.868	13.010	10.676	12.986	12.969	12.074	12.16
9	13.123	15.885	15.032	12.231	15.002	14.993	13.622	14.02
11	4.124	4.577	3.266	2.734	3.181	3.187	4.623	4.60
13	5.165	5.759	5.071	4.437	5.008	5.031	5.664	5.54
14	6.472	7.290	6.723	5.874	6.636	6.692	6.971	6.76
16	7.984	9.106	8.526	7.375	8.410	8.496	8.483	8.28
17	8.953	10.269	9.704	8.360	9.585	9.676	9.452	9.36
19	3.371	3.672	2.673	2.310	2.645	2.612	3.870	3.84
31	5.178	5.779	5.012	4.367	4.947	4.968	5.677	5.80
32	6.322	7.107	6.553	5.738	6.473	6.523	6.821	6.80
34	7.374	8.335	7.803	6.814	7.712	7.775	7.873	7.74
35	8.087	9.168	8.661	7.554	8.569	8.635	8.586	8.44
37	3.161	3.425	2.515	2.195	2.502	2.460	3.660	3.70
49	4.885	5.418	4.821	4.254	4.777	4.787	5.384	5.60
50	5.744	6.397	5.906	5.226	5.854	5.879	6.243	6.10
52	6.514	7.270	6.807	6.027	6.751	6.783	7.013	7.04
53	7.053	7.885	7.448	6.593	7.389	7.425	7.552	7.38
STD**	0.3526	0.3980	0.3992	0.9111	0.4033	0.4131	0.1019	

^{a} Units are in electron volt (eV). Methods are described in the text. The modified data are obtained through eq 21, i.e., modified = simplest + 0.499. ^{b} STD is defined as $\sum_{i=1}^{N} (x_i - x_i^0)^2/N$, where x_i and x_i^0 are the calculated and exact hardness, respectively, and N is the data number in the Table.

In addition to the six methods to calculate the hardness kernel, we incorporate three different ways to approximate the Fukui function. Calculations of the global atomic hardness involve combination of these methods. While one might hope that as the complexity of the method increases, results would improve, the numerical data shown below do not confirm such prediction.

The electron density used is the restricted Hartree–Fock density from Koga, Tatewaki, and Thakkar.[39] The systems investigated are the first 54 neutral atoms in the periodic table.

Results

Figure 1 shows the calculated and experimental global hardness for the first 54 atoms obtained by using eq 15, the simple model, as the hardness kernel and eq 17 as the Fukui function. It is found that, except for groups IIA and VA elements,

hardness of main group elements can be fairly reproduced in this model. In Table 1, numerical results are shown for main group elements, together with the data from other approaches, such as TF, TFD, WDW, TFDLP, and TF19WDW. STD (standard deviation) data show that among the six methods proposed the simplest form produces the best result.

We have plotted the above main group element results from the simplest model in Figure 2. One finds that this model underestimates the global hardness by almost a constant amount. If an average of 0.499 eV is added to the data from the model, i.e.,

$$\eta = 27.212 \int \int \frac{f(\mathbf{r}')f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + 0.499(\text{eV}),$$

for main group elements (21)

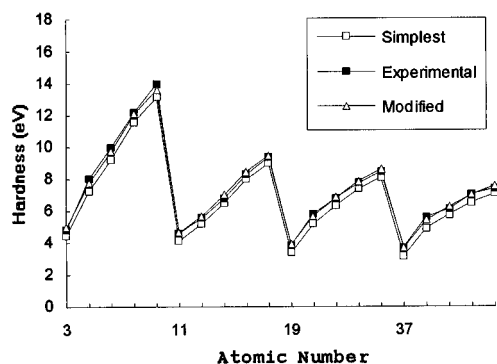**6994** *J. Phys. Chem. A, Vol. 101, No. 37, 1997*

Liu et al.

Figure 2. Experimental and theoretical atomic hardness for main group elements except for IIA and VA groups. Plotted data include the simplest model and its modified model from eq 21. The Fukui function was approximated by eq 17.

more accurate hardness values are obtained. These results imply that the simplest model for the hardness kernel might well be modified to

$$\eta(\mathbf{r},\mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'| + C \qquad (22)$$

where C is a constant. Listed in the next to last column in Table 1 and also plotted in Figure 2 are the data from this modified model. It is seen that its STD is just one-third less than the original's. Notice that we excluded Groups IIA, VA, and noble elements in our discussion. These elements are special in the sense that their shells are filled or half-filled. It is not surprising that they do not exhibit the same regularity as other main group elements.

For transition metals, it is seen in Figure 1 that the calculated results also systematically underestimate the exact hardness. Table 2 shows the calculated and exact values, together with those from the other methods mentioned, for the third- and fourth-row transition metal elements. STD data show that among the above six models the simplest produces the second best data, with Model TF giving the best. The reason that Model TF generates better results is that the simplest model always underestimates hardness, adding positive contributions from the kinetic component. Shown in Figure 3 are results from the simplest model as well as from the modified model obtained by adding an average of 1.759 eV to the model, that is,
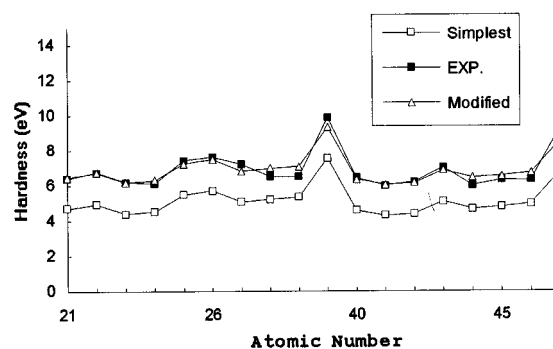

Figure 3. Experimental and theoretical atomic hardness for transition metal elements. Plotted data include the simplest model and its modified model from eq 22. The Fukui function was calculated from eq 17.

$$\eta = 27.212 \int\int \frac{f(\mathbf{r}')f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' + 1.759(\text{eV}),$$
$$\text{for transition metal elements} \quad (23)$$

It is observed in Figure 3 that significant improvement has been achieved for the modified model. The numerical data for the transition metal elements are appended in the 8th column of Table 2, giving the smallest total STD among all methods considered.

Now let us investigate other choices for the Fukui function. Figure 4 shows the experimental and calculated hardness obtained by using eqs 15 and 20, i.e., the simplest model with the Fukui function being $f^-(\mathbf{r})$. For main group elements, one again finds that Groups IIA and VA elements behave differently from the others. But for transition metal elements, there no longer is any systematic underestimation. Table 3 tabulates the results from various methods for the main group elements. It is seen from STD that WDW generates the best results, and the simplest model is again the second best. Plotted in Figure 5 are some of these data. The simplest model using $f^-(\mathbf{r})$ as the Fukui function always overestimates hardness. A modified model may be proposed as

$$\eta = 27.212 \int\int \frac{f^-(\mathbf{r}')f^-(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' + 0.022304N -$$
$$1.39766(\text{eV}), \quad \text{for main group elements} \quad (24)$$

where N is the total electron number for the system. Data

TABLE 2: Experimental and Calculated Hardness for the Third- and Forth-Row Transition Metal Elements from the Approximation $f = (f^- + f^+)/2^a$

atom	simplest	TF	TFD	WDW	TFDLP	TF19WDW	modified	exptl
21	4.704	5.114	4.127	3.657	4.115	4.067	6.464	6.40
22	4.942	5.397	3.821	3.269	3.809	3.724	6.702	6.74
23	4.410	4.884	2.995	2.405	2.955	2.879	6.170	6.20
24	4.528	5.073	3.357	2.708	3.292	3.252	6.288	6.12
25	5.481	6.033	3.925	3.243	3.906	3.795	7.241	7.44
26	5.721	6.310	4.245	3.530	4.225	4.118	7.481	7.62
27	5.062	5.662	3.429	2.692	3.367	3.292	6.822	7.20
28	5.209	5.84	3.002	2.195	2.935	2.827	6.969	6.50
29	5.334	6.044	4.992	4.220	4.881	4.930	7.094	6.50
30	7.551	8.718	8.096	6.897	7.960	8.064	9.311	9.88
40	4.585	4.949	4.268	3.864	4.256	4.228	6.345	6.42
41	4.290	4.783	3.699	3.141	3.664	3.634	6.05	6.00
42	4.383	4.891	2.743	2.102	2.703	2.611	6.143	6.2
43	5.082	5.513	4.209	3.699	4.194	4.130	6.842	7.00
44	4.675	5.232	4.143	3.521	4.089	4.078	6.435	6.00
45	4.782	5.356	4.349	3.715	4.288	4.289	6.542	6.32
47	4.947	5.548	4.594	3.936	4.520	4.537	6.707	6.28
48	6.792	7.737	7.193	6.220	7.091	7.165	8.552	9.32
STD	1.2438	0.8271	1.8445	2.3227	1.8813	1.9061	0.1901	

^{a} Units are in electron volt (eV). Methods are described in the text. The modified data are obtained through eq 22, i.e., modified = 1.759 + simplest.
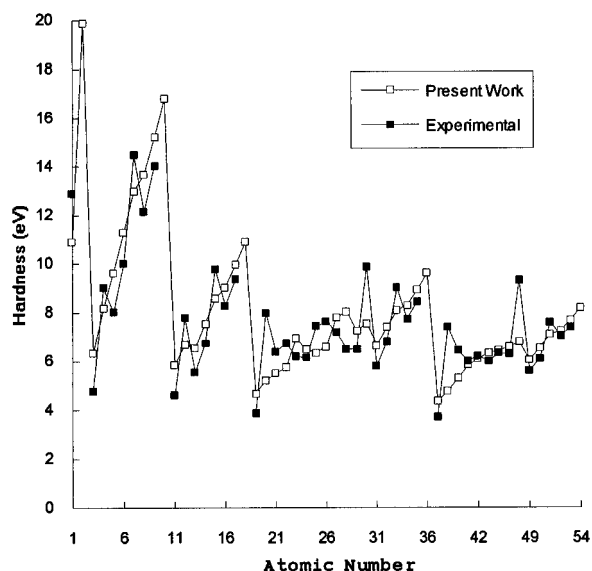
Hardness Kernel and Global Hardness

J. Phys. Chem. A, Vol. 101, No. 37, 1997 **6995**

Figure 4. Comparison of experimental and theoretical hardness for first 54 atoms. The calculated values are from the simplest model, eq 15, and the approximate Fukui function, eq 20. See text.

Figure 5. Experimental and theoretical atomic hardness for main group elements except for IIA and VA groups. Plotted data include the simplest model and its modified model from eq 23. The Fukui function was approximated by eq 20. See text.

generated from the modified model are shown in both Table 3 and Figure 5. Remarkable improvement is observed. For transition metal elements, no such tendency is found from Figure 4. Shown in Table 4 are the experimental and calculated data from six methods for these elements. One finds from STD values that the simplest model produces the best results. One also finds that, except for the simplest model, as the complexity of other methods increases, STD decreases.

Finally, we consider choice of the HOMO density as the Fukui function. Figure 6 plots the experimental results and the ones calculated from the simplest model, eq 15. It is found that hardness of main group elements is generally overestimated without a regular pattern, but that of transition element groups is fairly reproduced. Shown in Table 5 are the data of latter elements from various calculations. Compared with those in Table 4, standard deviations have been substantially reduced. It is found that the simplest model is also the best in this case, giving a STD of 0.4109. Unfortunately, no single pattern of
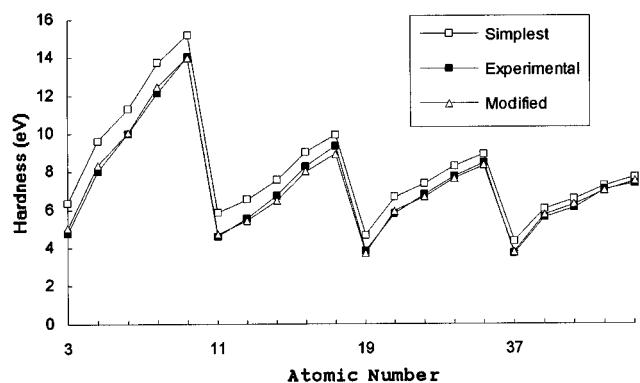
deviation from experimental values is observed so that a straightforward modification is not apparent. Notice also that as the method extends to more complicated ones, for example from TF to TFD to WDW, etc., STD becomes smaller and smaller. The only exception is the simplest model. It produces the best data.

Summary and Final Comments

Presented in this paper are models for approximating the hardness kernel and numerical results for global hardness. Numerical evidence shows that the simplest model, eq 15, generates reasonable global hardness, and it is sometimes possible to make useful modifications for various categories of systems.

On the basis of the present study, the following conclusions are in order: (i). $1/|\mathbf{r} - \mathbf{r}'|$ is the major component of the hardness kernel. Ignoring all other components, global hardness can be fairly reproduced for many systems, in particular, transition metal elements. (ii). Inclusion of the kinetic, exchange, and correlation contributions from their approximate forms does not provide significant improvements on global hardness calculations. (iii). Modified models, eqs 21, 23, and 24, are capable of generating remarkable accuracy of global hardness for main group elements or transition metal elements.

TABLE 3: Experimental and Calculated Atomic Hardness for Main Group Elements, except for IIA and VA Elements, by Using eq 20, i.e., $f = f^-$, as the Fukui Function[a]

atom	simplest	TF	TFD	WDW	TFDLP	TF19WDW	modified	exptl
3	6.366	7.461	6.543	5.397	6.518	6.493	5.035	4.78
5	9.630	11.349	10.65	8.898	10.633	10.616	8.349	8.02
6	11.292	13.453	12.737	10.542	12.716	12.704	10.028	10.00
8	13.696	16.644	15.855	12.872	15.824	15.821	12.477	12.16
9	15.200	18.646	17.848	14.369	17.814	17.815	14.003	14.02
11	5.850	6.743	5.943	5.005	5.692	5.899	4.698	4.60
13	6.543	7.424	6.855	5.944	6.747	6.824	5.435	5.54
14	7.552	8.601	8.064	6.988	7.961	8.037	6.467	6.76
16	9.039	10.389	9.850	8.474	9.745	9.824	7.998	8.28
17	9.948	11.488	10.956	9.391	10.859	10.931	8.930	9.36
19	4.680	5.247	4.625	4.022	4.529	4.589	3.706	3.84
31	6.654	7.573	6.994	6.044	6.881	6.963	5.948	5.80
32	7.364	8.373	7.849	6.813	7.752	7.822	6.680	6.80
34	8.293	9.442	8.947	7.774	8.857	8.923	7.654	7.74
35	8.919	10.172	9.695	8.419	9.611	9.672	8.302	8.44
37	4.352	4.842	4.271	3.749	4.222	4.238	3.780	3.70
49	6.026	6.788	6.267	5.477	6.189	6.239	5.721	5.60
50	6.563	7.376	6.909	6.072	6.840	6.885	6.281	6.10
52	7.232	8.118	7.687	6.780	7.624	7.666	6.994	7.04
53	7.696	8.645	8.233	7.264	8.172	8.213	7.480	7.38
STD	0.5988	1.5137	1.0896	0.1918	1.0333	1.0683	0.1168	

[a] Units are in electron volt (eV). Methods are defined in the text. The modified data are obtained through eq 21, i.e., modified = simplest + $0.022304N - 1.39766$.
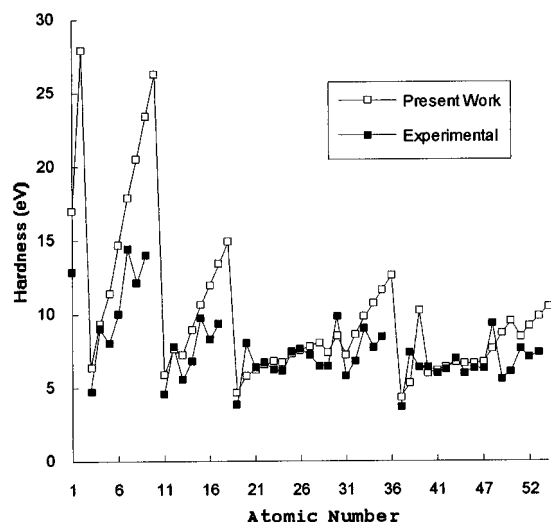
Figure 6. Comparison of experimental and theoretical hardness for first 54 atoms. The calculated values are from the simplest model, eq 15, and the approximate Fukui function, eq 16. See text.

TABLE 4: Experimental and Calculated Hardness (in eV) for Third- and Forth-Row Transition Atoms from the Approximation $f = f^+$

atom	simplest	TF	TFD	WDW	TFDLP	TF19WDW	exptl
21	5.502	6.144	5.648	4.979	5.578	5.621	6.40
22	5.741	6.434	5.921	5.200	5.842	5.893	6.74
23	6.928	9.883	8.443	5.414	8.187	8.369	6.20
24	6.482	7.620	6.868	5.690	6.689	6.827	6.12
25	6.345	7.179	6.616	5.751	6.509	6.585	7.44
26	6.609	7.513	6.937	6.002	6.823	6.907	7.62
27	7.784	11.303	9.791	6.196	9.474	9.715	7.20
28	8.046	11.763	10.221	6.426	9.891	10.144	6.50
29	7.239	8.504	7.736	6.431	7.528	7.696	6.50
30	7.551	8.718	8.096	6.897	7.960	8.064	9.88
40	5.287	5.882	5.419	4.798	5.370	5.393	6.42
41	5.828	6.794	6.136	5.134	6.031	6.101	6.00
42	6.097	7.125	6.456	5.392	6.337	6.42	6.20
43	5.817	6.518	6.015	5.287	5.946	5.988	7.00
44	6.344	7.371	6.713	5.651	6.585	6.678	6.00
45	6.439	7.466	6.807	5.745	6.673	6.772	6.32
47	6.585	7.616	6.948	5.881	6.799	6.913	6.28
48	6.792	7.737	7.193	6.220	7.091	7.165	9.32
STD	0.6356	1.0386	0.8554	0.8268	0.8083	0.8453	

TABLE 5: Experimental and Calculated Hardness (in eV) by Approximating the Fukui Function as the HOMO Density for Third- and Fourth-Row Transition Elements

atom	simplest	TF	TFD	WDW	TFDLP	TF19WDW	exptl
21	6.216	6.969	6.485	5.706	6.391	6.459	6.40
22	6.516	7.329	6.835	5.996	6.737	6.809	6.74
23	6.793	7.664	7.159	6.262	7.057	7.133	6.20
24	6.706	7.617	7.003	6.060	6.861	6.970	6.12
25	7.290	8.276	7.746	6.733	7.635	7.719	7.44
26	7.569	8.617	8.079	7.004	7.965	8.051	7.62
27	7.824	8.932	8.384	7.248	8.268	8.356	7.20
28	8.068	9.236	8.678	7.482	8.561	8.65	6.50
29	7.416	8.507	7.836	6.710	7.656	7.800	6.50
30	8.523	9.811	9.232	7.916	9.110	9.203	9.88
40	6.012	6.670	6.252	5.572	6.189	6.23	6.42
41	6.173	6.890	6.404	5.661	6.327	6.378	6.00
42	6.406	7.171	6.668	5.876	6.582	6.641	6.20
43	6.682	7.463	7.023	6.219	6.946	7.000	7.00
44	6.595	7.402	6.877	6.042	6.779	6.849	6.00
45	6.657	7.483	6.943	6.088	6.837	6.914	6.32
47	6.746	7.610	7.036	6.141	6.911	7.005	6.28
48	7.616	8.598	8.116	7.109	8.021	8.092	9.32
STD	0.4109	0.7734	0.4972	0.4322	0.4488	0.4836	

(iv). Elements of special groups, such as groups IIA and VA, merit special attention because of the special nature of their electronic structures.

These conclusions have significant implications for molecules, especially for large molecules. Extension of the present ideas to molecular systems is in process.

The ideas in the present paper, it should be observed, would be relevant for a possible semiempirical density functional theory of the electronic structure of ground states. Some time ago, Lindholm and Lundqvist[40] already observed that the Kohn–Sham implementation of density functional theory, with its single-determinantal wave function, provided an excellent framework for semiempiricization. The argument used in the present paper is analogous to the line that was used in the development of molecular orbital theory from the Hückel level to the levels in which electron–electron repulsion is taken into account.[41] Namely, effective electron repulsion in these approximate theories was represented by empirical electron–electron repulsion curves as functions of distances between orbitals, while now, in the density functional theory, we are modeling the hardness kernel $\eta(\mathbf{r},\mathbf{r}')$.

The classical argument of Pariser[42] was that to compute the energy change for

$$\dot{C} + \dot{C} \rightarrow C^+ + \ddot{C}^- \qquad (25)$$
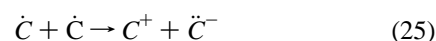
one should not use the purely theoretical repulsion between two electrons in the valence orbital but the empirical $I - A = \eta$. Now, this argument is transformed into the realization, in eqs 21 and 22 of the present text, that the hardness of C in this situation should be determined from

$$\eta = \int\int f(\mathbf{r})\frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}f(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \approx \int\int\frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \qquad (26)$$

where $f(\mathbf{r})$ is the Fukui function. Note from Figure 6 of the text that $f = \rho_{\text{HOMO}}$ yields $\eta \approx 15$ eV, but note from Table 3 that a better account of reorganization, using $f = \rho - \rho^+$, gives $\eta \approx 11$ eV. This is the Pariser result again, but this time in a context that in principle is exact.

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Hardness Kernel and Global Hardness

J. Phys. Chem. A, Vol. 101, No. 37, 1997 **6997**

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