

Electronegativities, Electron Affinities, Ionization Potentials, and Hardnesses of the Elements within Spin Polarized Density Functional Theory[†]

Juencio Robles* and Libero J. Bartolotti[‡]

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received September 23, 1983

Abstract: Spin polarized density functional theory is used to compute ionization potentials, electron affinities, electronegativities, and hardnesses of 86 elements. Two different approximations to the exchange-correlation functional are employed and compared, the Gunnarsson-Lundqvist X_{GL} and the X_{α} models. The results for the various quantities represent an improvement over previous calculations by Bartolotti, Gadre, and Parr [*J. Am. Chem. Soc.* **1980**, *102*, 2945], who employed a nonpolarized density functional theory within the X_{α} approximation to the exchange-correlation functional to compute electronegativities. They used a transition-state method for the process $N^- \rightarrow N^+$. The present calculation is spin polarized; it tests both the X_{α} and the X_{GL} approximations, and it employs a transition-state process involving the change from $N - \delta$ to $N + \delta$ electrons, with $0 \leq \delta \leq 1$. Furthermore, results are presented for 86 elements as compared with 54 in the previous work.

Density functional theory¹ provides a convenient and simple method for obtaining atomic and molecular ionization potentials,^{2,3} electronegativities,⁴⁻⁸ and electron affinities.^{4,9}

The present paper is an extension of the work done by Bartolotti, Gadre, and Parr,⁴ who introduced the first comprehensive theoretical method for the calculation of electronegativities and electron affinities within a spin nonpolarized density functional theory. Using the half-occupancy transition-state method within X_{α} theory,² Bartolotti, Gadre, and Parr⁴ obtained an expression for the electronegativity in terms of the X_{α} Lagrange multipliers. The electron affinities were obtained from the calculated electronegativities and ionization potentials with use of Mulliken's¹⁰ definition of electronegativity.

Here we improve upon the previous work in two important ways. First, we use a spin polarized density functional theory. Second, and most importantly, we use a transition-state process involving the change from $N - \delta$ to $N + \delta$ electrons.¹¹ This has the advantage that the third and higher order derivatives of the energy with respect to the occupation numbers do not contribute to the electronegativity.

We calculate electronegativities, ionization potentials, electron affinities, and hardnesses¹² for the first 86 atoms in the periodic table using the X_{α} ² and the Gunnarsson-Lundqvist¹³ approximations to the exchange-correlation energy.

Some earlier spin polarized calculations are contained in a paper by Manoli and Whitehead,¹⁴ in which also is given a detailed theoretical justification of the formulation of Bartolotti, Gadre, and Parr.⁴

Method

The negative of the chemical potential μ is the electronegativity χ .⁵

$$\chi = -\mu = -(\partial E / \partial N)_Z \quad (1)$$

where E is the ground-state energy of the chemical system, N is the total number of electrons, and Z is the nuclear charge. An estimate of $(\partial E / \partial N)_Z$ can be obtained in the following manner. A Taylor series expansion of the energy is taken about a system with $N + \delta$ electrons. The δ electrons are to be evenly distributed only among those spin orbitals whose occupancy changes in going from the N to the $N + 1$ electron system. Next, a Taylor series expansion of E is performed about the $N - \delta$ electron system. These δ electrons are to be distributed evenly among the spin orbitals involved in going from the N to the $N - 1$ electron systems. The chemical potential is now obtained from

$$\mu = \left(\frac{\partial E}{\partial N} \right)_Z = \lim_{\delta \rightarrow 0} \frac{E(N + \delta) - E(N - \delta)}{2\delta} \quad (2)$$

In other words, $(\partial E / \partial N)_Z$ is taken as the average of the left and right derivatives of E with respect to the appropriate spin orbital occupancies. In this process, we need only assume that E is a smooth function about $N + \delta$ and about $N - \delta$ electrons. For a discussion of the smoothness of E vs. N , we refer the reader to a paper by Perdew, Parr, Levy, and Balduz.¹⁵ If no limit is taken and δ is taken to be unity, eq 2 becomes identical with the equation of Bartolotti, Gadre, and Parr.⁴ Note that taking the limit makes all contributions to χ from third and higher order power derivatives identically vanish.

To use eq 2 in calculating χ , we need to evaluate the quantities $(\partial E / \partial n_{i\sigma})_{n_j, \sigma_j, \mu_i}$. These quantities can be conveniently obtained in density functional theory^{2,22} by solving the differential equation

$$-1/2 \frac{\nabla^2 \phi_{i\sigma}}{\phi_{i\sigma}} + \frac{\delta J[\rho]}{\delta \rho_{\sigma}} - \frac{\delta E_{xc}[\rho]}{\delta \rho_{\sigma}} + v_{ne} = \epsilon_{i\sigma} \quad (3)$$

where σ refers to either spin up (\uparrow or α) or spin down (\downarrow or β) electrons; $J[\rho]$ is the classical Coulomb energy:

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(1)\rho(2)}{r_{12}} d\tau_1 d\tau_2 \quad (4)$$

The quantity v_{ne} is the nuclear-electron interaction potential, $E_{xc}[\rho]$

(1) (a) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864. (b) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

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[†] Aided by research grants to the University of North Carolina from the National Science Foundation and the National Institutes of Health.

[‡] Permanent address: Department of Chemistry, University of Miami, Coral Gables, Florida 33124.

Table I. Electronegativities χ , Ionization Potentials I , Electron Affinities A , and Hardnesses η of the Elements, eV

Z	atom	χ^a		I^b		A^c		η^d	
		X_α	X_{GL}	X_α	X_{GL}	X_α	X_{GL}	X_α	X_{GL}
1	H	5.27	5.74	16.53	12.57	-5.99	-1.09	11.26	6.83
2	He	7.93	8.00	24.22	24.88	-8.35	-8.88	16.28	16.88
3	Li	1.69	2.74	5.72	5.80	-2.34	-0.32	4.03	3.06
4	Be	3.52	4.03	8.43	9.18	-1.39	-1.13	4.91	5.16
5	B	4.08	4.37	8.41	8.76	-0.25	-0.02	4.33	4.39
6	C	6.39	6.52	11.89	12.00	0.89	1.03	5.50	5.49
7	N	5.78	6.67	15.32	15.26	-3.76	-1.92	9.54	8.59
8	O	6.45	7.67	12.59	14.10	0.31	1.25	6.14	6.42
9	F	9.85	10.76	17.22	18.27	2.47	3.24	7.37	7.52
10	Ne	6.60	6.96	21.64	22.41	-8.44	-8.50	15.04	15.45
11	Na	1.67	2.73	5.25	5.63	-1.91	-0.18	3.58	2.91
12	Mg	2.56	3.22	6.92	7.85	-1.80	-1.41	4.36	4.63
13	Al	2.70	3.24	5.53	6.17	-0.14	0.30	2.83	2.94
14	Si	4.39	4.91	7.94	8.52	0.84	1.31	3.55	3.61
15	P	4.38	5.41	10.31	10.83	-1.55	-0.01	5.93	5.42
16	S	5.18	6.39	9.26	10.67	1.10	2.10	4.08	4.28
17	Cl	7.50	8.53	12.29	13.44	2.71	3.62	4.79	4.91
18	Ar	4.93	5.49	15.20	16.18	-5.34	-5.20	10.27	10.69
19	K	1.47	2.38	4.31	4.73	-1.37	0.02	2.84	2.35
20	Ca	2.48	3.24	5.43	6.32	-0.46	0.17	2.94	3.07
21	Sc	3.40	4.17	5.68	6.69	1.13	1.65	2.27	2.52
22	Ti	4.16	4.92	5.86	6.96	2.47	2.89	1.70	2.03
23	V	4.09	<i>e</i>	7.75	8.28	0.42		3.66	
24	Cr	2.30	3.69	7.25	7.75	-2.65	-0.36	4.95	4.06
25	Mn	3.38	4.70	6.28	7.57	0.48	1.82	2.90	2.88
26	Fe	4.41	5.62	6.95	8.15	1.88	3.09	2.53	2.53
27	Co	4.84	5.74	8.24	9.27	1.43	2.21	3.40	3.53
28	Ni	5.00	5.93	9.03	10.01	0.97	1.84	4.03	4.08
29	Cu	3.76	<i>e</i>	7.80	8.61	-0.28		4.04	
30	Zn	3.00	3.84	8.71	9.84	-2.72	-2.17	5.71	6.01
31	Ga	2.54	3.21	5.43	6.24	-0.34	0.18	2.89	3.03
32	Ge	4.10	4.79	7.54	8.31	0.67	1.26	3.44	3.52
33	As	4.08	5.24	9.52	10.27	-1.36	0.20	5.44	5.04
34	Se	4.79	6.09	8.55	10.05	1.04	2.14	3.76	3.95
35	Br	6.74	7.92	11.02	12.32	2.46	3.51	4.28	4.40
36	Kr	4.36	5.05	13.32	14.51	-4.60	-4.40	8.96	9.45
37	Rb	1.41	2.30	4.02	4.51	-1.20	0.09	2.61	2.21
38	Sr	1.98	2.80	4.96	5.88	-1.00	-0.29	2.98	3.08
39	Y	2.59	3.41	6.12	7.08	-0.94	-0.26	3.53	3.67
40	Zr	3.63	4.50	5.42	6.59	1.83	2.41	1.79	2.09
41	Nb	2.30	3.64	6.79	7.31	-2.18	-0.03	4.48	3.67
42	Mo	2.30	3.69	7.04	<i>e</i>	-2.43		4.74	
43	Tc	3.72	5.05	5.73	7.10	1.70	3.00	2.01	2.05
44	Ru	3.11	4.11	7.07	<i>e</i>	-0.85		3.96	
45	Rh	3.23	4.22	7.06	<i>e</i>	-0.59		3.82	
46	Pd	2.40	3.24	8.38	9.56	-3.58	-3.08	5.98	6.32
47	Ag	3.39	4.38	7.04	7.88	-0.25	0.88	3.65	3.50
48	Cd	2.80	3.66	7.89	9.01	-2.28	-1.69	5.08	5.35
49	In	2.48	3.18	5.12	5.95	-0.16	0.41	2.64	2.77
50	Sn	3.85	4.57	6.91	7.72	0.78	1.42	3.07	3.15
51	Sb	3.84	4.98	8.56	9.37	-0.88	0.59	4.72	4.39
52	Te	4.43	5.71	7.73	9.18	1.13	2.23	3.30	3.47
53	I	6.04	7.22	9.74	11.03	2.34	3.42	3.70	3.81
54	Xe	3.85	4.56	11.59	12.80	-3.89	-3.67	7.74	8.23
55	Cs	1.29	2.13	3.62	4.11	-1.04	0.15	2.33	1.98
56	Ba	2.30	3.14	4.39	5.29	0.21	0.98	2.09	2.16
57	La	2.93	3.72	5.51	6.18	0.36	1.27	2.57	2.46
58	Ce	2.97	3.77	4.81	5.56	1.13	1.97	1.84	1.80
59	Pr	3.52	4.34	4.51	5.45	2.53	3.23	0.99	1.11
60	Nd	4.00	4.80	4.55	5.49	3.44	4.10	0.55	0.70
61	Pm	4.41	5.20	4.58	5.54	4.25	4.87	0.17	0.33
62	Sm	4.79	5.56	4.62	5.58	4.96	5.54	-0.17	0.02
63	Eu	2.33	3.19	4.65	5.61	0.01	0.77	2.32	2.42
64	Gd	5.67	6.94	4.84	5.92	6.51	7.96	-0.84	-1.02
65	Tb	3.29	4.42	4.81	5.78	1.77	3.05	1.52	1.36
66	Dy	3.70	4.80	4.88	5.85	2.53	3.74	1.18	1.06
67	Ho	4.08	5.14	4.94	5.92	3.22	4.35	0.86	0.78
68	Er	4.42	5.45	5.00	5.99	3.84	4.91	0.58	0.54
69	Tm	4.73	5.73	5.06	6.05	4.41	5.41	0.32	0.32
70	Yb	1.93	2.83	5.11	6.11	-1.25	-0.44	3.18	3.27
71	Lu	2.34	3.27	5.82	6.91	-1.14	-0.38	3.48	3.64

Table I (Continued)

Z	atom	χ^a		I^b		A^c		η^d	
		X_α	X_{GL}	X_α	X_{GL}	X_α	X_{GL}	X_α	X_{GL}
72	Hf	3.71	4.60	7.51	8.54	-0.10	0.66	3.80	3.94
73	Ta	4.15	5.13	5.55	6.88	2.75	3.37	1.40	1.75
74	W	4.81	5.79	5.62	7.02	4.00	4.56	0.81	1.23
75	Re	3.60	5.00	5.68	7.13	1.52	2.88	2.08	2.13
76	Os	4.62	5.93	6.33	7.65	2.92	4.21	1.70	1.72
77	Ir	5.55	6.79	6.81	8.07	4.28	5.52	1.26	1.27
78	Pt	3.44	4.47	7.09	7.97	-0.21	0.96	3.65	3.50
79	Au	3.51	4.53	7.06	7.97	-0.04	1.09	3.55	3.44
80	Hg	2.80	3.70	7.81	8.99	-2.22	-1.59	5.02	5.29
81	Tl	2.42	3.16	4.97	5.85	-0.13	0.47	2.55	2.69
82	Pb	3.70	4.47	6.63	7.49	0.77	1.45	2.93	3.02
83	Bi	3.69	4.86	8.13	9.00	-0.74	0.71	4.44	4.14
84	Po	4.23	5.52	7.34	8.80	1.11	2.24	3.11	3.28
85	At	5.69	6.91	9.15	10.47	2.23	3.34	3.46	3.57
86	Rn	3.60	4.35	10.78	12.05	-3.58	-3.34	7.18	7.69

^a See text for detailed description of method of calculation. ^b Calculated by using Slater's transition-state method. ^c Calculated from eq 13 of text. ^d Calculated from eq 15 of text. ^e Numerical convergence was not reached for these cases. They were not included in the plots of Figures 1-4.

is the unknown exchange-correlation energy, and ρ is the electronic density:

$$\rho = \rho_\uparrow + \rho_\downarrow \quad (5)$$

where

$$\rho_\sigma = \sum_i n_{i\sigma} |\phi_{i\sigma}|^2 \quad (6)$$

The Lagrange multipliers $\epsilon_{i\sigma}$ give us our desired derivatives, namely

$$\left(\frac{\partial E}{\partial n_{i\sigma}} \right)_{\{n_{j\sigma'}\}} = \epsilon_{i\sigma} \quad (7)$$

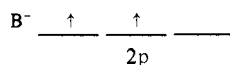
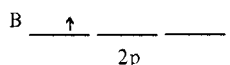
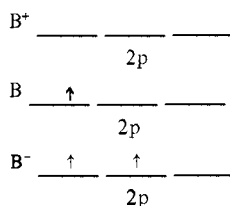
As in previous calculations of χ ,⁴⁻⁷ ionization potentials I ,³ and electron affinities A ,^{4,9} the electron configurations of the positive ion, neutral atom, and negative ion are taken from spectroscopic data.^{16,17} These are not always the same as those that would minimize the energy. For the rare earths, where most experimental anionic configurations are not yet known, we assume that the electron configuration for the anion of a given Z is the same electron configuration as the neutral $Z + 1$ atom.

When the designated electron configurations for the first 86 atoms in the periodic table are employed, either one or two spin orbital Lagrange multipliers are necessary to determine χ . Following Bartolotti, Gadre, and Parr,⁴ we denote these as cases A and B. However, in contrast to that work, both case A and case B always involve $\epsilon_{i\sigma}$ for the ground-state configuration.

Case A. One Spin Orbital Involved. In this case a single spin orbital is involved in going from the positive to the negative ion. Calling this the i th orbital, we find from eq 2 that

$$\chi = - \left(\frac{\partial E}{\partial n_{i\sigma}} \right)_{\{n_{j\sigma'}\}} = -\epsilon_{i\sigma} \quad (8)$$

As an example we consider the Boron atom:



Only the $2p\uparrow$ orbital is involved in going from $N - 1$ to $N + 1$

(16) (a) Hotop, H.; Lineberger, W. C. 1975. *J. Phys. Chem. Ref. Data, Suppl. A*, 539. (b) Moore, C. E. "Atomic Energy Levels". *Natl. Bur. Stand. (U.S.) Circ.* 1958, No. 467.

(17) "Handbook on the Physics and Chemistry of Rare Earths"; Gschneidner, Eyring, Eds.; North-Holland Publishing Co.: Amsterdam, 1978; Vol. 1.

electrons, and they are all degenerate in the present work. Thus, only one spin orbital is involved and we find

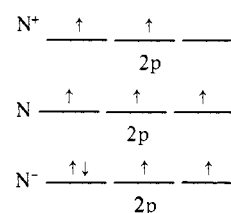
$$\chi = -\epsilon_{2p\uparrow} \quad (9)$$

Case B. Two Spin Orbitals Involved. Here there is a net change in the occupation numbers of two different spin orbitals. If the two orbitals are the i th and j th, then

$$\chi = -1/2(\epsilon_{i\sigma} + \epsilon_{j\sigma'}) \quad (10)$$

where σ' is the opposite spin of σ . Depending upon the kind of spin orbitals involved (occupied or virtual), we find three different subcases of case B.

(i) Regular Case B. Here an occupied and a virtual orbital are involved in going from $N - 1$ to $N + 1$ electrons. To illustrate this situation we consider the nitrogen atom.

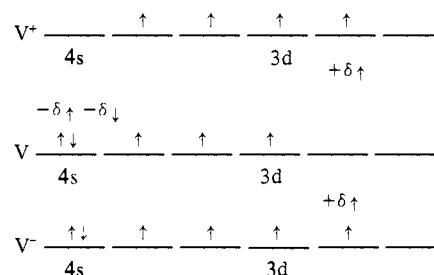


Thus, the electronegativity for nitrogen is given by

$$\chi = -1/2(\epsilon_{2p\uparrow} + \epsilon_{2p\downarrow}) \quad (11)$$

Therefore, we need to introduce a virtual spin orbital, the $2p\downarrow$, in the calculation for the ground state of atomic nitrogen.

(ii) Irregular Case B. This case involves two occupied spin orbitals in the calculation of χ . As an example we consider vanadium



We explicitly include the δ electrons added and subtracted to show clearly the cancellation of the contribution of the $3d\uparrow$ orbital. The net effect is that the electronegativity for V is given by

$$\chi = -1/2(\epsilon_{4s\uparrow} + \epsilon_{4s\downarrow}) \quad (12)$$

both spin orbitals being occupied.

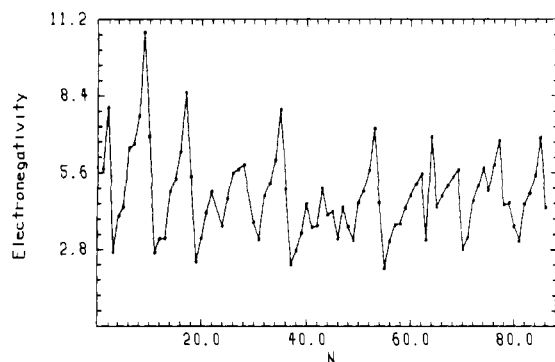
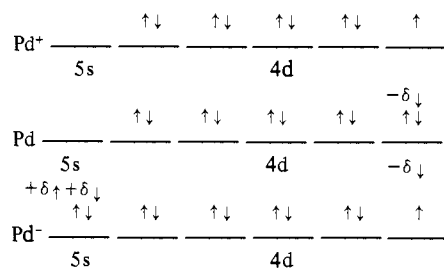


Figure 1. Plot of atomic electronegativities (in eV) as a function of the number of electrons. The exchange-correlation functional of ref 13 was used in the calculations.

(iii) **Most Irregular Case B.** This case is most unusual because two virtual orbitals are used to calculate χ . Palladium is an example of this case.



The net effect is that the electronegativity is given by

$$\chi = -1/2(\epsilon_{5s\uparrow} + \epsilon_{5s\downarrow}) \quad (13)$$

where both orbitals are unoccupied.

Ionization potentials can be easily obtained by using Slater's transition-state method.²³ Once we have values for χ and I , we can use Mulliken's¹⁰ definition of χ to get the electron affinities,⁴ namely

$$A = 2\chi - I \quad (14)$$

Since the transition-state method for obtaining A is often nonconvergent, eq 14 provides the best alternative for determining A .

The last property calculated by us is the hardness, η . The concept of hard and soft acids was first introduced by Pearson¹⁸ and has been of increasing interest within the chemical community.

A major problem in the concept of hardness has been the lack of quantification of the principle of hard and soft acids and bases. Many scales of hardness and softness have been proposed.^{12,19} However, it was only recently that Parr and Pearson²⁰ gave a theoretical justification of this principle and defined hardness as

$$\eta = 1/2(\partial^2 E / \partial N^2)_Z \quad (15)$$

The corresponding finite difference formula is

$$\eta = 1/2(I - A) \quad (16)$$

We used this equation to calculate the hardness of atoms from our calculated I and A . The Parr and Pearson derivation of the hard and soft acids and bases principle has already been commented on in these pages.²⁵

Results and Discussion

Employing the X_α^2 approximation to $E_{xc}[\rho]$ and the Gunnarsson-Lundqvist¹³ $E_{xc}[\rho]$ in eq 3, we calculated the electronegativities, ionization potentials, electron affinities, and hardnesses

(18) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) (*Science (Washington, D.C.)* **1966**, *151*, 172.

(19) (a) Ho, T. L. "Hard and Soft Acids and Bases in Organic Chemistry"; Academic Press: New York, 1977. (b) Jensen, W. B. "The Lewis Acid-Base Concept"; Wiley-Interscience: New York, 1980; Chapter 8. (c) Pearson, R. G.; Mawby, R. J. In "Halogen Chemistry"; Gutmann, V., Ed.; Academic Press: New York, 1967; Vol. 3, Chapter 2.

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

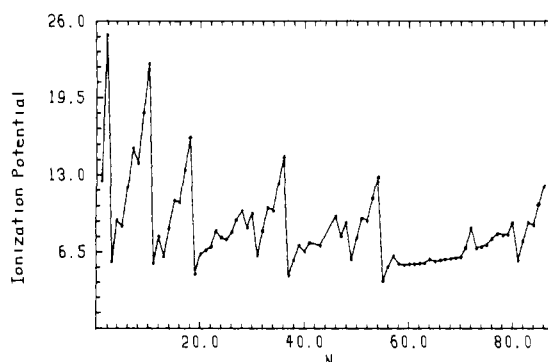


Figure 2. Plot of atomic ionization potentials (in eV) as a function of the number of electrons. The exchange-correlation functional of ref 13 was used in the calculations.

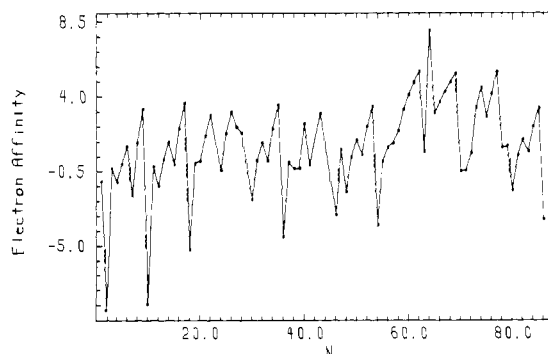


Figure 3. Plot of atomic electron affinities (in eV) as a function of the number of electrons. The exchange-correlation functional of ref 13 was used in the calculations.

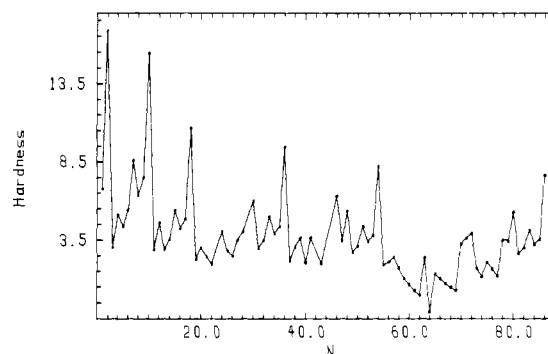


Figure 4. Plot of atomic hardnesses (in eV) as a function of the number of electrons. The exchange-correlation functional of ref 13 was used in the calculations.

for the first 86 atoms in the periodic table. The α values used in the $X_\alpha E_{xc}[\rho]$ were the virial theorem values.²¹ Figures 1-4 give plots of χ , I , A , and η determined by using the Gunnarsson-Lundqvist $E_{xc}[\rho]$.

It is clear from Table I that our results are quite satisfactory. For comparison with the available experimental values we refer the reader to the tabulations of electron affinities of Hotop and Lineberger^{16a} and of ionization potentials of Moore^{16b} and Gschneidner and Eyring,¹⁷ for the rare-earth values. Since the electronegativity and hardness scales are relative, "experimental values" for comparison can be obtained from eq 14 and 16, using the experimental A and I . The present values of χ and A are an improvement of the values of Bartolotti, Gadre, and Parr. Most expected trends in χ , A , and I are evident in Figures 1-3. We cannot compare our results for χ and A with the previous spin nonpolarized values, because the spin nonpolarized calculations

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are an average over all multiplets arising from the ground-state configuration. The spin polarized method on the other hand does, in a way, distinguish between different multiplets.

Concerning the values obtained for the hardness, we notice that indeed larger values correspond to "harder" species. Therefore, metals are soft, according to the fact that chemical softness means little resistance of the chemical potential to change in the number of electrons. It is interesting to observe that among the four atomic properties calculated, hardness was the one that turned out to be the least sensitive to the functional model used. For the other three properties, the results are in general better for the Gunnarsson-Lundqvist approximation than for the X_α model, especially for heavier atoms, as it is expected for these models. But in most cases the error is small, typically less than 1 eV.

Certainly, major inaccuracies occur within the electron affinities, where in general the computed values underestimate the experimental values, especially those of the X_α approximation. This can be explained by the fact that eq 14 does not describe accurately the relaxation effects associated with the removal of an electron from the anion, since the orbitals employed in the calculation of

χ and I are too contracted for this.

To obtain the best possible values, we should have included relativistic effects in the heavier atoms.⁷ However, we feel that the uncertainty in the results due to the approximations to $E_{xc}[\rho]$ is the dominating error in our work. The selection of a more appropriate $E_{xc}[\rho]$ such as the SIC functional²³ should greatly improve the present results. Indeed this is what Whitehead has recently done.²⁴

An exact exchange-correlation functional would give different numerical values, but most of these probably would not differ very much from the ones we have obtained. The main improvements would be expected to happen in the electron affinities values, especially in the negative ones.

Acknowledgment. We thank Professor Robert G. Parr for his encouragement and helpful comments about this work.

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Structurally Ordered Bimetallic One-Dimensional *catena-μ*-Dithiooxalato Compounds: Synthesis, Crystal and Molecular Structures, and Magnetic Properties of $AMn(S_2C_2O_2)_2(H_2O)_3 \cdot 4.5H_2O$ (A = Cu, Ni, Pd, Pt)

Alain Gleizes[†] and Michel Verdaguer^{*‡}

Contribution from the Laboratoire de Chimie de Coordination du CNRS, 31400 Toulouse, France, and from the Laboratoire de Spectrochimie des Eléments de Transition, ERA No. 672, Université de Paris-Sud, 91405 Orsay, France. Received September 27, 1983

Abstract: Bimetallic one-dimensional compounds with dithiooxalato ($S_2C_2O_2^{2-}$) bridges were synthesized. Synthesis of $AMn(S_2C_2O_2)_2(H_2O)_3 \cdot 4.5H_2O$ with A = Cu (1), Ni (2), Pd (3), Pt (4) and crystal and molecular structures of 1, 2, and 4 are reported. All these compounds are isostructural and crystallize in the monoclinic system, space group $P2_1/c$, with four formula units per cell. Cell constants are as follows: 1, $a = 11.692$ (2) Å, $b = 20.665$ (5) Å, $c = 7.360$ (2) Å, $\beta = 103.84$ (2)°; 2, $a = 11.575$ (2) Å, $b = 20.654$ (5) Å, $c = 7.323$ (2) Å, $\beta = 103.73$ (2)°; 3, $a = 11.79 \pm 0.02$ Å, $b = 20.78 \pm 0.02$ Å, $c = 7.31 \pm 0.02$ Å, $\beta = 103.5 \pm 0.5$ °; 4, $a = 11.772$ (4) Å, $b = 20.806$ (11) Å, $c = 7.266$ (3) Å, $\beta = 103.52$ (4)°. The structures consist of infinite chain molecules $\{[Mn(H_2O)_3](O_2C_2S_2)A(S_2C_2O_2)]_n\}$ crisscrossing glide planes c and therefore stacked along these planes. Each layer of stacked chains is separated from the next one by intervening water molecules. The magnetic susceptibilities of the compounds are investigated in the temperature range 4.2–300 K. Compound 1 (Cu(II)–Mn(II)) is the first ferrimagnetic one-dimensional compound: it is made of alternating Cu(II) $1/2$ spins and Mn(II) $5/2$ spins antiferromagnetically coupled. The $\chi_M T$ vs. T curve shows a minimum at 130 K and a climb from 130 to 7.5 K; then three-dimensional ordering occurs as revealed by a decrease of $\chi_M T$ with T . The theoretical $\chi_M T$ vs. $kT/|J|$ curve (J = coupling constant between nearest neighbors) exhibits a minimum in the case of antiferromagnetic interaction, as observed in experimental results. The same feature appears in a theoretical model of alternating quantum spins $1/2$ and classical spins antiferromagnetically coupled. Both theoretical approaches are compared to experimental data, and values of $J = -30.3$ cm⁻¹ and $g = 1.90$ are determined. An orbital interpretation of the interaction through dithiooxalato bridges between Cu(II) and Mn(II) ions is proposed.

Two years ago, we gave preliminary results about synthesis, structures, and magnetic data of a novel class of one-dimensional (1-D) compounds made of dithiooxalato ($S_2C_2O_2^{2-}$) bridges and pairs of Cu(II)–Mn(II) (1) and Ni(II)–Mn(II) (2) ions.¹ Synthesis and study of polynuclear complexes including 1-D systems are very active fields of inorganic chemistry and solid-state physics. Inorganic chemists try to synthesize new compounds and to predict their properties on the basis of a molecular approach to the exchange phenomenon,² whereas physicists test on 1-D materials the validity of phenomenological models using the Heisenberg–Dirac–Van Vleck Hamiltonian (HDVV).

In the last decade, both steps met noteworthy success in predicting magnetic properties or interpreting experimental data. On the one hand, useful structural magnetic correlations were established in the simplest binuclear units³ or polynuclear ones;⁴

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[†]Laboratoire de Chimie de Coordination du CNRS.

[‡]Laboratoire de Spectrochimie des Eléments de Transition.